



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

Catalytic Conversion of Low Alcohols to Olefins and their Oligomers

Submitted in fulfilment of the academic requirements for the degree of
Doctor of Engineering in the **School of Chemical and Metallurgical
Engineering**, Faculty of Engineering, and the Built Environment at the
University of the Witwatersrand

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Co-supervisor: Prof. Bilainu Obozokhai Oboirien

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Preface

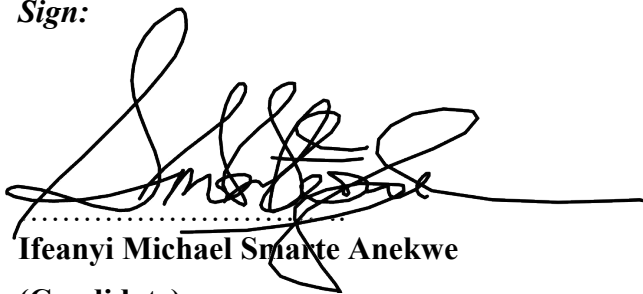
This doctoral study was conducted in the Fuel and Petrochemical Synthesis (FPS) Research Group under the School of Chemical and Metallurgical Engineering, University of Witwatersrand, South Africa. The candidate aimed to develop “a novel mesoporous ZSM-5 zeolite catalyst for effective conversion of low alcohols to hydrocarbons.” The project was led by Prof. Yusuf Makarfi Isa as the supervisor and Prof. Bilainu Oboirien as the co-supervisor, providing invaluable guidance throughout the research process. This work was financially supported by an international collaborative project (BRICS2019-040) under the BRICS STI Framework Programme with government funding organisations of South Africa NRF (BRIC190321424123), Brazil CNPq (402849/2019-1), Russia RFBR (19-58-80016), India DST (CRG/2018/004610, DST/TDT/ TDP-011/2017) and China MOST (2018YFE0183600).

Declaration

I, **Ifeanyi Michael Smarte Anekwe**, the undersigned candidate declares that

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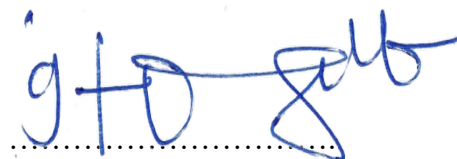


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Prof. Bilainu Obozokhai Oboirien
(Co-supervisor)

.....
Date

Dedication

This PhD thesis is especially dedicated to my wife and children, unknown to me at the time of writing, yet already deeply loved. Whenever you read these words, remember to wear that beautiful smile. Daddy loves you more than you can imagine.

It is also dedicated to my family, whose unwavering steadfastness has carried me through this journey. Your constant prayers, tremendous support, and encouragement have been my anchor.

I would also like to pass this dedication on to the next generation, reminding them that life is a journey and that with God's grace, they will reach their destination.

“Life is a journey that must be travelled no matter how bad the roads and accommodations.”

Oliver Goldsmith

Hence, “The future belongs to those who believe in the beauty of their dreams.”

Eleanor Roosevelt

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With deep reverence, I acknowledge the divine presence in my life and offer my profound thanks to God for His unending grace and guidance. To God be the glory for every achievement, every hurdle overcome, and every triumph realized. In His wisdom, I have found solace and strength to face every challenge and embrace every opportunity. As I move forward in this life journey, I do so with a heart brimming with gratitude to God and a spirit filled with hope. My journey is enriched by the love and support I have received, and I promise to carry these cherished values with me as I embrace the future with enthusiasm and determination.

Once again, I extend my sincerest appreciation to everyone who has shaped my life and contributed to my accomplishments. Thank you for being the wind beneath my wings and the light in my darkest hours. May our paths continue to intertwine with joy, love, and prosperity.

Shalom!

Warm Regards,

Ifeanyi Michael Smarte Anekwe

Summary

The global energy sector relies heavily on fossil fuels, resulting in significant greenhouse gas emissions. However, increasing concern about the environmental impact of these conventional energy sources has led to the search for alternative energy sources, such as low alcohols. Despite their potential, low alcohols, including bioethanol, face limitations as a fuel due to their inability to be used in their pure form (E100) in modern automobiles. The catalytic conversion of low alcohols (over acid zeolite catalyst) to hydrocarbons is required to overcome this limitation. While the micropores of ZSM-5 zeolite catalysts are advantageous for the mass transfer of small molecules, they are disadvantageous for the mass transfer of large molecules, as evidenced by diffusion limitations for reagents, intermediates, and products. Therefore, the novelty of this study was to synthesise a newly developed tunable ZSM-5 zeolite catalyst with mesopores to reduce the diffusion limitations of these large hydrocarbon molecules for enhanced conversion of low alcohols to olefins and their oligomers. The objectives of this study include the synthesis and promotion of a novel ZSM-5 zeolite catalyst using selected transition metals and the characterisation of as-synthesised catalysts using various techniques, the investigation of the effect of transition metal incorporation on ZSM-5 properties and catalytic performance, evaluating the effect of operating conditions and catalyst modification on product distribution and coke deposition, investigating the performance of metal-doped HZSM-5 catalyst in the conversion of low alcohols (methanol, ethanol and propanol) to fuel-range hydrocarbon, studying catalyst stability, deactivation and regeneration in bioethanol conversion, and conducting a techno-economic and environmental analysis (TEA) of the catalytic conversion process.

The ZSM-5 catalyst was hydrothermally synthesised and promoted through dry impregnation with different concentrations (0.5 - 10 wt%) of transition metals (Co, Fe and Ni). The catalytic conversion process was carried out at 350–400 °C and a weight hourly space velocity (WHSV) of 5–12 h⁻¹. The physical properties of the synthesised catalyst were investigated using X-ray diffraction (XRD), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), particle size distribution (PSD), Brunauer-Emmett-Teller (BET), Particle size distribution (PSD) and ammonia temperature programmed desorption (NH₃-TPD) analysis. Gas chromatography was used to analyse the hydrocarbon products, while thermogravimetric–differential thermal analysis (TG-DTA) was used to study the thermal stability of the material and coke deposition

on the spent catalyst. The results showed that a mesoporous ZSM-5 zeolite catalysts was successfully synthesised and modification of ZSM-5 with transition metals affected the catalyst's surface area, morphology, particle size and acidity. The as-synthesised catalysts exhibited a prismatic crystal and remarkable textural properties including a surface area of 397.5 m²/g, a pore diameter of 2.22 nm, and a total pore size of 0.706 cm³/g (0.678 and 0.029 meso- and macropores, respectively).

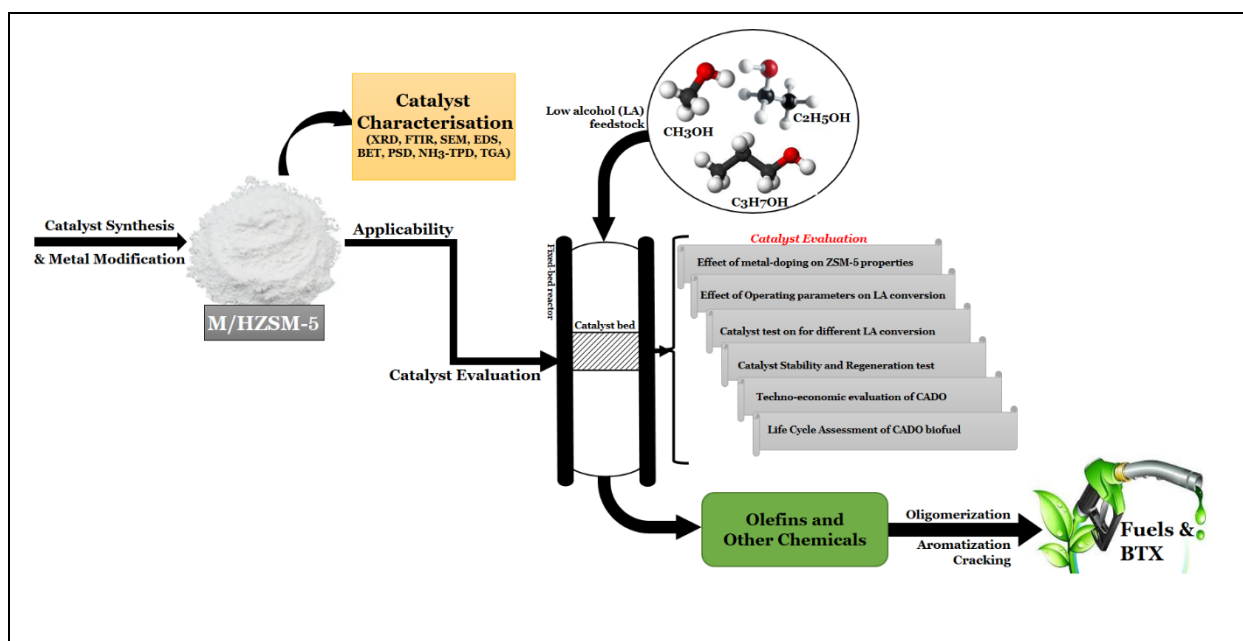
The catalytic evaluation revealed that the catalyst's performance was enhanced through metal modification during the conversion of low alcohols (methanol, ethanol, and propanol) into hydrocarbons. The effectiveness of the modification, low alcohol conversion, product selectivity and distribution were influenced by the operating conditions. The study also showed that the unmodified catalyst exhibited considerable stability compared to the metal-doped catalyst, attributed to high coke deposition on the metal-doped catalyst leading to deactivation. However, the metal-doped catalysts exhibited a broader product distribution (including gasoline and diesel fuel-range hydrocarbons) than the unmodified catalysts. The investigation of the regenerated catalysts demonstrated that the applied regeneration technique effectively maintained the catalyst's textural and morphological properties while enhancing its catalytic performance. The economic evaluation demonstrates that catalyst synthesis at baseline scale production (BSP) resulted in a net catalyst cost of \$31.4/kg. Additionally, the operating and annualized capital costs associated with converting wet ethanol into fuel blendstocks are estimated to be \$0.05/L presently, with a projected decrease to \$0.03/L in the future. The predicted minimum selling prices for fuel blendstocks produced through CADO are comparable to those of traditional gasoline fuel when oil is priced at \$100/bbl. The life cycle analysis revealed that CADO-derived fuel blendstocks achieve a reduction of >25% in greenhouse gas emissions compared to conventional gasoline derived from petroleum. The techno-economic and environmental analysis (TEA) demonstrated the economic and environmental viability of the catalytic process, making it a feasible and sustainable solution for upgrading low alcohols into fuel-range hydrocarbons.

Conclusively, understanding the behaviour of coke deposition in ZSM-5 zeolite catalysts is pivotal for optimising the catalytic process and developing strategies to mitigate coke formation and deactivation for improved catalytic performance. These results indicate that the as-synthesised catalyst is promising for industrial applications where the stability and longevity of the catalyst play a crucial role. The catalyst thus offers a potential solution to the challenges

associated with the conversion of low alcohols, providing a stable and efficient catalyst option for commercial and future use.

Keywords: Bioethanol, Catalysts, Low alcohol, Methanol, Propanol, Zeolite, ZSM-5

Graphical Summary



Research Outputs and Knowledge Dissemination

This thesis is based on the author's published papers and unpublished works under consideration for publication (Journal, Conference papers and Book chapters). The author was the corresponding author in all the papers, while the co-authors assisted in writing by making valuable comments and corrections.

I. LIST OF PUBLICATIONS

Out of the articles listed below, Papers (1-11), as referred to, were linked to the objectives of this study as supporting information to compile the Chapters of the thesis. Papers-12-14 are conference proceedings. (*corresponding author)

Publications from this work

1. **Anekwe, IMS.**, Khotseng, L., & Isa, YM*, (2021): The Place of Biofuel in Sustainable Living; Prospects and Challenges. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier. <https://doi.org/10.1016/B978-0-12-819727-1.00068-6>
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5. **Anekwe, IMS***, Isa, YM. & Oboirien, B. (2023): Synthesis and characterisation of a novel mesoporous zsm-5 zeolite catalyst for the conversion of bioethanol to aromatics and C₅+ hydrocarbons. *ICSD* 2023. <https://ic-sd.org/wp->

content/uploads/2023/10/ICSD-2023_stage-5590_question-Paper-Submission_id-566.pdf

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10. **Anekwe, IMS***, Chetty M., Khotseng L., Kiambi SL., Maharaj L., Oboirien B., Isa YM. (2024): Stability, Deactivation and Regeneration of novel HZSM-5 and Ni/HZSM-5 catalysts. *Catalysis Communications*, Elsevier. p. 106802. DOI: [10.1016/j.catcom.2023.106802](https://doi.org/10.1016/j.catcom.2023.106802)
11. **Anekwe, IMS***, Lora, E.E.S., Subramanian, K.A., Kozlov, A., Zhang, S., Oboirien, B. and Isa, Y.M., 2024. Techno-economic and life-cycle analysis of single-step catalytic conversion of bioethanol to fuel blendstocks over Ni-doped HZSM-5 zeolite catalyst. *Energy Conversion and Management: X*, 22, p.100529. [http://dx.doi.org/10.1016/j.ecmx.2024.100529](https://dx.doi.org/10.1016/j.ecmx.2024.100529)

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12. **Anekwe, IMS***, Akpasi, SO., Mkhize, MM., Zhou, H., Moyo, RT., & Gaza, L. (2024). Renewable energy investments in South Africa: Potentials and challenges for a

sustainable transition-a review. *Science Progress*, 107(2), 00368504241237347.
<http://dx.doi.org/10.1177/00368504241237347>

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14. **Anekwe, IMS***, Tetteh, E.K., Akpasi, S.O. and Isa, Y.M., 2024. Current Advances and Potentials of Nanotechnology for Biofuel Production. *Sustainable Engineering: Concepts and Practices*, pp.379-394. http://dx.doi.org/10.1007/978-3-031-47215-2_22
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16. **Anekwe, IMS***, Tetteh, E. K., Armah, E. K., & Isa, Y. M. (2023): Artificial Intelligence for the Operation of Renewable Energy Systems. In *IoT and Analytics in Renewable Energy Systems (Volume 1)* (pp. 207-242). CRC Press. DOI: [10.1201/9781003331117-16](https://doi.org/10.1201/9781003331117-16)
17. **Anekwe, IMS***, Tetteh, EK. & Armah, EK. (2023): Artificial Intelligence Applications in Solar Photovoltaic Renewable Energy Systems. Application of Artificial Intelligence in New Materials Discovery, 147, 47-86. DOI: <https://doi.org/10.21741/9781644902530-3>
18. **Anekwe, IMS***, Armah EK, & Tetteh EK, (2022): Bioenergy Production: Emerging Technologies. In S. Mohamed (Ed.), *Biomass, Biorefineries and Bioeconomy* (pp. Ch. 14). IntechOpen. <https://doi.org/10.5772/intechopen.102692>
19. Akpasi, SO*, **Anekwe, IMS.**, Adedeji, J., & Kiambi, SL. (2022). Biochar Development as a Catalyst and Its Application. Intechopen. DOI: [10.5772/intechopen.105439](https://doi.org/10.5772/intechopen.105439)

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20. **Anekwe, I MS***, Oboirien, B., & Isa, YM. (2023). Selective Production of Gasoline Fuel Blendstock from Methanol using a Metal-doped HZSM-5 Zeolite Catalyst. In *E3S* (Vol. 470, p. 01005). EDP Sciences. [10.1051/e3sconf/202347001005](https://doi.org/10.1051/e3sconf/202347001005)
21. **Anekwe, IMS**, and Isa, YM. Oboirien B. (2023). "Sustainability in Fuel and Petrochemical Production: Exploring Novel ZSM-5 Catalysts for Enhanced Clean Energy Production", *Conference Proceeding: 39th JOHANNESBURG International Conference on "Chemical, Biological and Environmental Engineering (JCBEE-23)*. Johannesburg, South Africa. (Accepted)
22. **Anekwe, IMS**, and Isa, YM. Oboirien B. (2022). "Synthesis and Application of Iron and Cobalt-Doped HZSM-5 Catalysts for Bioethanol Conversion into Hydrocarbons". *Conference Proceeding: 32nd Annual International Conference – CATSA 2022: Integration and Synergies between Homogeneous and Heterogeneous Catalysis*. Drakensberg, South Africa

II. CONFERENCES/PRESENTATION

The author was the main presenter at both the local and international conferences:

1. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2023). "Sustainability in Fuel and Petrochemical Production: Exploring Novel ZSM-5 Catalysts for Enhanced Clean Energy Production", *Presented at the 39th JOHANNESBURG International Conference on "Chemical, Biological and Environmental Engineering (JCBEE-23)*. Nov. 16-17, 2023, Birchwood Hotel & OR Tambo Conference Centre, Johannesburg, South Africa.
2. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2023). "Optimising Catalytic Conversion of Ethanol to Hydrocarbons over HZSM-5 Catalyst: Impact of Metal Content and Operating Conditions on Performance and Coke Deposition", *Presented at the 33rd Annual Conference of the Catalysis Society of South Africa (CATSA2023)*. 5-8th November 2023. Dias Hotel & Resort, Mossel Bay, Capetwon, South Africa.
3. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2023). "Synthesis and Characterisation of a Newly Developed Tunable Mesoporous ZSM-5 Zeolite Catalyst for Low alcohol

- Conversion.” *Presented at the 11th Annual International Conference on Sustainable Development (ICSD) 2023*. 18-20th September 2023. Alfred Lerner Hall on the Columbia University Campus in New York City, United State of America.
4. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2023). “Selective Production of Fuel Blendstock from Low Alcohols: A Comparative Study of Metal-Doped HZSM-5 Zeolite Catalysts”, *Presented at the International Conference ENERGY SYSTEMS RESEARCH (ESR-2023)*. September 11-15, 2023, Irkutsk, Russia.
 5. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2023). “Synthesis of Ni-doped mesoporous ZSM-5 zeolite catalyst for the conversion of methanol and ethanol into fuels and petrochemicals.” *Presented at the 2023 Young Scientists’ Conference*. 12th-13th June 2023. University of Venda in Thohoyandou, Limpopo province, South Africa.
 6. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2022). “Catalytic Conversion of Bioethanol over Transition Metal-modified HZSM-5 Zeolite Catalysts”. *Presented at the 2ND Sustainable Bioenergy and Processes Conference (SBP 2022)*. 12-14th December 2022. Cape Town International Convention Centre (CTICC 2), Cape town, South Africa.
 7. **Anekwe, IMS**, Oboirien B. and Isa, YM. (2022). “Synthesis and Application of Iron and Cobalt-Doped HZSM-5 Catalysts for Bioethanol Conversion into Hydrocarbons”. *Presented at the 32nd Annual International Conference – CATSA 2022: Integration and Synergies between Homogeneous and Heterogeneous Catalysis*. 13-16th November 2022. Champagne Sports Resort, Central Drakensberg, KwaZulu Natal, South Africa.
 8. **Anekwe, IMS**. and Isa, YM. (2022). “Synthesis and Characterization of Mesoporous HZSM-5 Zeolite Catalyst for Ethanol Conversion”. *Presented at the Post Graduate Seminar (PGS-2022): University of Witwatersrand*. 19th October 2022. City of Johannesburg, South Africa.
 9. **Anekwe, IMS**. and Isa, YM. (2022). “Effect of Promotion Technique over Ni/HZSM-5 on Product Distribution during Ethanol Conversion”. *Presented at the 2nd BRICS Workshop: Biomass Energy and Materials*. 26th March 2022. City of Johannesburg, South Africa.
 10. **Anekwe, IMS**. and Isa, YM. (2022). “Catalytic Conversion of Alcohols to Petrochemicals”. *Presented at the 1st BRICS Workshop: Biomass Energy and Materials*. 15th January 2022. Nanjing, China.

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List of Acronyms

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda Model
BSP	Baseline Scale Production
CADO	Consolidated Alcohol Dehydration and Oligomerisation
CADO-ETH	Consolidated Alcohol Dehydration and Oligomerisation, Ethanol-to-Hydrocarbon
DEE	Diethyl ether
DME	Dimethyl ether
DRH	Diesel Range Hydrocarbon
EDS	Energy Dispersive X-ray Spectroscopy
EIA	Energy Information Administration
ETG	Ethanol-to-Gasoline
ETH	Ethanol-to-Hydrocarbon
ETO	Ethanol-to-Olefin
EtOH	Ethanol
GC	Gas Chromatography
GHGs	Greenhouse Gases
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
GRH	Gasoline Range Hydrocarbon
HC(s)	Hydrocarbon(s)
HTR	Hydrothermal Reactor
ICDD	International Centre for Diffraction Data
IEA	International Energy Agency
LA	Low Alcohol

LATH	Low Alcohol-to-Hydrocarbon
LCA	Life Cycle Analysis
MTH	Methanol-to-Hydrocarbon
MTO	Methanol-to-Olefin
NH ₃ -TPD	Ammonia-Temperature Programme Desorption
NREL	National Renewable Energy Laboratory
PSD	Particle Size Distribution
PTH	Propanol-to-Hydrocarbon
SCVs	Spent Catalyst Values
SDGs	Sustainable Development Goals
SEM	Scanning Electron Microscope
TEA	Techno-economic Analysis
TGA-DTA	Thermogravimetric-Differential Thermal Analysis
USD	United State Dollar (\$)
WHSV	Weight Hourly Space Velocity
WTP	WELL-to-Pump
WTW	Well-to-Wheel
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1

INTRODUCTION:

Energy Demand and Utilization: Low Alcohols - Potentials and Limitations

1.1 Background

The rapid depletion of oil reserves due to increased energy usage and global warming are two major issues facing the world in the twenty-first century. The growing concentration of carbon dioxide in the atmosphere is widely believed to be the most significant contributor to global warming. Lately, global warming has reached the top of the social agenda, garnered international awareness and fostering a sense of unanimity that civilisation should be modified to address the primary source of CO₂ generation and pollution-related challenges, including fine dust. Moreover, the overwhelming dependence on fossil fuels as our primary energy source is primarily responsible for these issues. Petroleum is the most accessible fossil fuel for utilisation in transportation; however, at the current significant level of consumption, existing oil reserves are anticipated to be depleted within 50 years, and available natural gas reserves are likely to be exhausted within 70 years (Stambouli et al., 2012). The recognition of additional oil and natural gas sources may delay the depletion of these fossil fuels for a period. Still, substantial fuel scarcity concerns are projected in the future. The annual utilisation of petroleum and natural gas has risen more than 200-fold during the last century. Even though petroleum and natural gas contributed to just around 2 % and 1 % of energy usage, respectively, a century ago, they are now responsible for a substantial amount of total energy consumption (Newell et al., 2019). Figure 1.1 and 1.2 depicts the rising trend in global energy consumption and annual CO₂ emissions rates with projections respectively. Figure 1.1 shows that energy production will increase significantly from 2025 to 2050 due to increased energy demand.

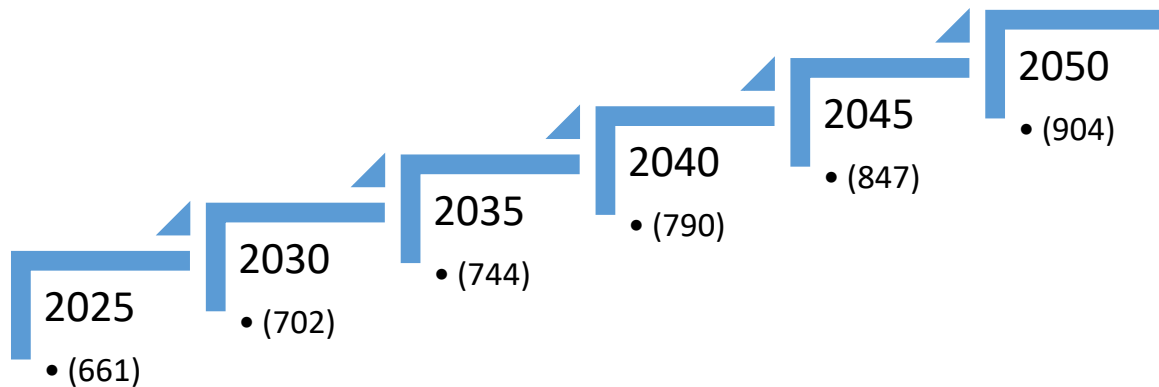


Figure 1-1. Global Energy Consumption (in quadrillion Btu), from 1990 – 2020 and Projection >2025. Source: EIA (IEA, 2020)

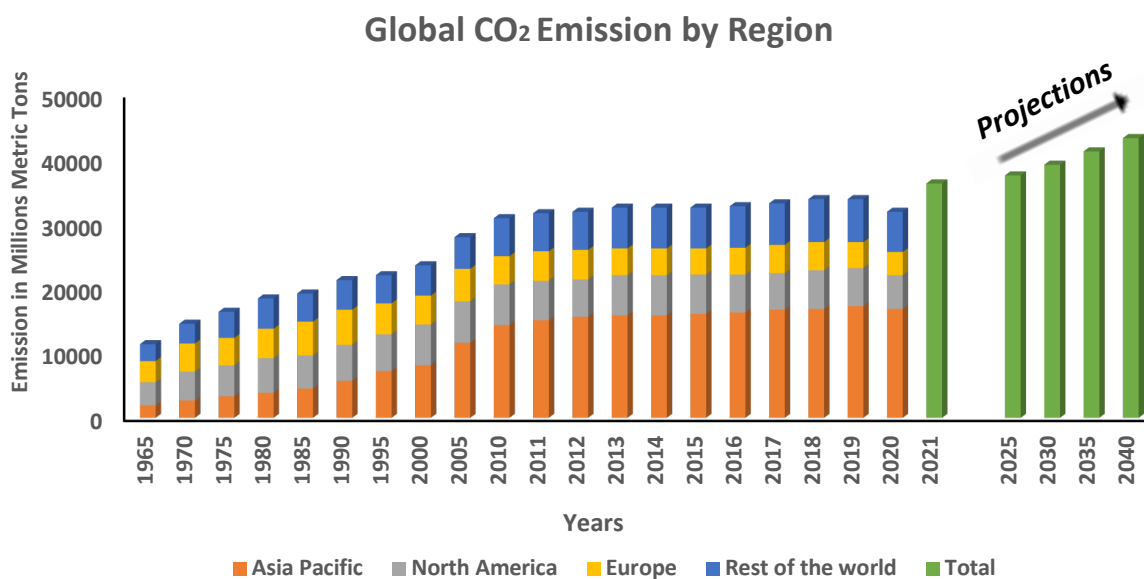


Figure 1-2. Global CO₂ Emission by Region (Sources: U.S. Energy Information Agency (EIA, 2020), [International energy outlook 2016 with projections to 2040](#) (Conti et al., 2016), International Energy Agency (IEA, 2020), Short-Term Energy Outlook (Oil, 2010))

Figure 1.2 shows that CO₂ emission rates increased during the 21st century, resulting in a rise in atmospheric CO₂ content. Additionally, it has been claimed that the Earth's surface temperature has risen by around 0.6 °C over the same period (EIA, 2020, Newell et al., 2019,

IEA, 2020). As of 2020, Asia emitted around 16.75 billion metric tonnes of carbon dioxide. This was greater than the cumulative emissions from all other areas in the world aggregated that year. China alone was responsible for approximately 60 % of CO₂ emissions in the Asia region and 31 % of world CO₂ emissions. North America was the second most polluting location in the world in 2020, with 5.3 billion metric tonnes of CO₂ released in that location. CO₂ emissions in Europe and North America decreased by approximately 12 % in 2020 as compared to levels in 2019, while no significant decrease (2.5%) was recorded in the Asia continent. The emergence of COVID-19 in 2020 prompted the imposition of tight lockdowns and limitations to reduce the transmission of the virus. As a result of the disruptions to travel and commercial activity, there was a significant drop in global emissions. Earlier in 2020, when many of the first lockdowns were implemented, some of the most dramatic decreases were observed. Worldwide energy-related CO₂ emissions decreased by more than 14 % in April 2020 compared to a similar month the preceding year. According to EIA's International Energy Outlook 2016 (IEO2016) Reference Case, worldwide energy-related carbon dioxide (CO₂) emissions are expected to raise by one-third from 2020 to 2040, primarily as a result of growing energy consumption in nations outside of the Organization for Economic Cooperation and Development (OECD). Notwithstanding a significant drop in the carbon intensity (CO₂ per unit of energy) of the global energy supply, global emissions have continued to rise in recent years (EIA 2020). During the twentieth century, increased CO₂ emission rates resulted in a rise in the atmospheric CO₂ content from around 295 ppm to 380 ppm. Additionally, it has been claimed that the Earth's surface temperature has increased by around 0.6 °C over the same period (EIA, 2020, Newell et al., 2019, IEA, 2020). The need to provide a sustainable substitute for fossil fuel becomes imperative to meet the high energy requirement for transportation and other sectors of the economy.

Most of these CO₂ emissions are caused by anthropogenic activities, including power generation, production, manufacturing, construction, transportation and domestic activities. The global emission by economic sectors and transportation emissions is presented in Figure 1.3. From the figure, the energy sector is the highest emitter of CO₂ with about 42 % emission, almost twice that of the manufacturing and construction sectors. The transportation sector is the second emitter of CO₂, including automobile, truck, aviation, marine and railway emissions. This sector depends mainly on fossil fuel-based transportation fuels presently. Providing alternative fuel sources for this sector will reduce the dependence on fossil fuels and reduce CO₂ emissions for a sustainable environment.

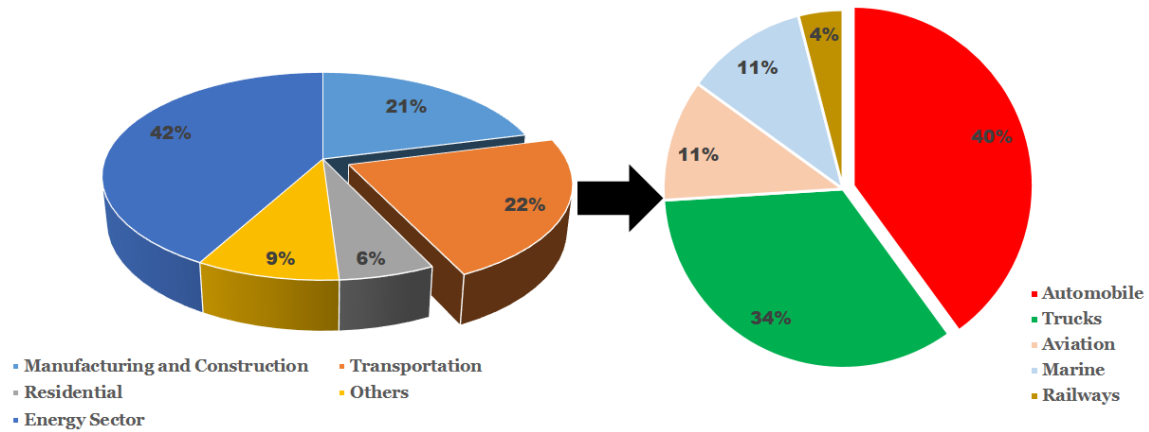


Figure 1-3. Global CO₂ Emission by Economic Sectors and Emission by the Transportation Sector (Source IEA, (IEA, 2015))

Much emphasis is given to generating energy from sustainable sources such as hydroelectricity, wind energy, and biomass. Biomass energy (bioenergy) provides a reliable prospect because of its abundance and carbon-neutral sustainable option. First-generation biofuels, including bioethanol and biodiesel, have demonstrated that biomass-derived fuels can (at least to some extent) substitute petroleum. However, the demand for transportation fuels is so enormous that biofuels can only meet a small percentage of the transportation industry's energy requirements (Lilja and Moen, 2017). Furthermore, first-generation biofuels use edible biomass as a substrate, increasing rivalry for food sources and higher production costs. Second-generation biofuels generated from lignocellulose biomass have been presented as renewable transportation sources that do not negatively influence world food security. However, the third and fourth generations focused on utilising algae and genetically engineered microbes (GEM) biomass. Biomass (consists of crops and residue, forestry waste, aquatic plants, and animal and municipal residue) (Sheldon, 2011) can be burned directly to produce heat and electricity, or it can be transformed into combustible liquids (e.g., bio-oils, methanol, and ethanol) and gases (e.g., CH₄ and H₂) through thermochemical or biochemical conversion (Zhang et al., 2010b) as shown in Figure 1.4. Low alcohols (bioethanol) can be cheaply generated from biomass feedstock, including sugarcane, sugar beet, and starch crops by fermentation, which is among the most extensively utilised biochemical transformation methods, but the biosynthesis and manufacturing of low alcohol fuels from non-food sources and agricultural leftovers are currently the primary focus of research and development. In 2021, total global bioethanol output reached 27.31 billion litres, about a 6 % increase from the previous year (Anekwe et al.,

2021a, US Energy Information Administration, 2021). Bioethanol is mainly used in motor vehicles, either as a fuel or a gasoline additive.

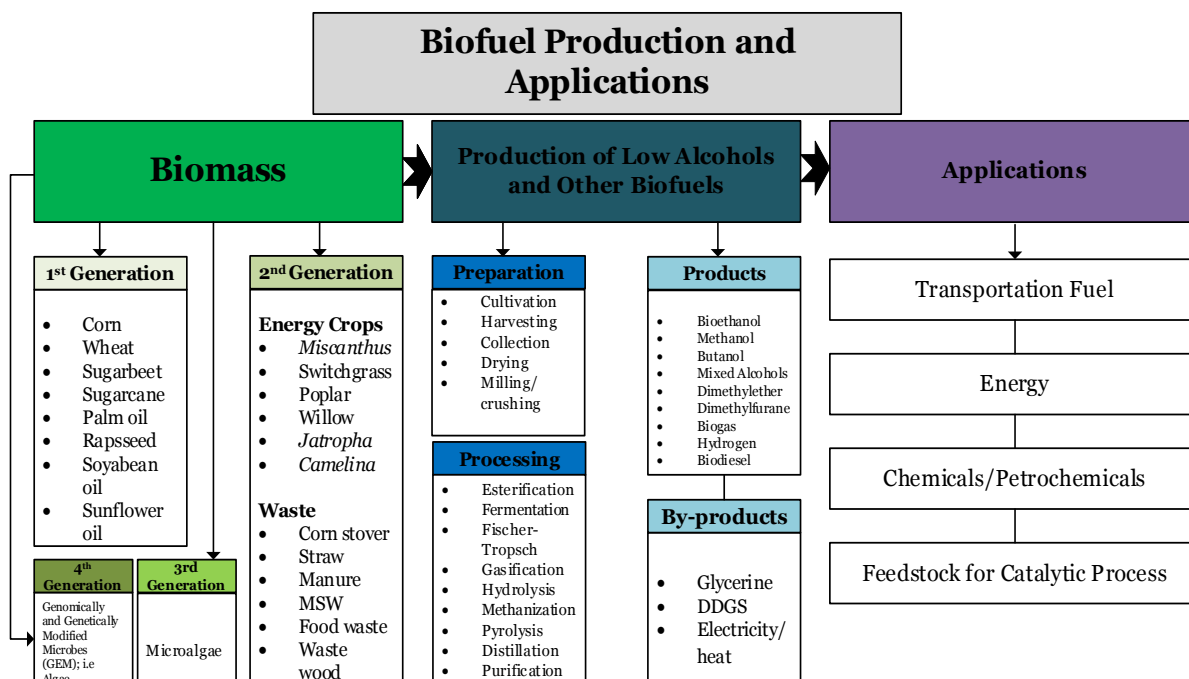


Figure 1-4. Biofuel (Low alcohol) Production from Biomass and Applications

Low alcohols, notably ethanol, have the opportunity to provide some answers to these challenges. The availability and cost-effectiveness of a diverse variety of biomass may present prospects for biotechnological bioethanol production globally. Low alcohols have gotten much industrial attention as a chemical source since they can be converted to fuels and petrochemicals. Low alcohols can be applied as a blending additive in petroleum-derived gasoline and diesel fuels, now available for purchase on the market or used as a renewable feedstock in the catalytic conversion process for fuel and petrochemical synthesis. In the petrochemical sector, crude oil is fractionated and processed to obtain several grades of liquid transportation fuel, and hydrocarbon feedstock is functionalised to generate intermediates and speciality petrochemicals. Bioalcohols, particularly low alcohols, would be comparable in scale to the petroleum refining approach, with the primary distinction being that biomass—rather than petroleum—would be exploited as a sustainable supply of carbon that can be converted into fuels and useful chemicals within a single plant. The application of biomass derivatives in the generation of heat and electricity helps to reduce greenhouse gas (GHG) emissions by utilising phases of regeneration and burning, which reduce the emissions of GHGs (Alonso et al., 2010).

1.2 Potentials and Applications of Low Alcohols as Fuel and Petrochemicals

Low alcohols can be used as a feedstock for the synthesis of olefins, including ethylene and propylene, which are employed as the primary feedstock in the production of a wide range of industrial chemicals and plastic products. In contrast, butadiene is utilised in the production of synthetic rubber. Low alcohols, including ethanol and methanol, are widely used in petrochemical, where it is used as an organic solvent to dissolve compounds with increased and mild polarity, as a required raw material in the fabrication of intermediates and synthetic hydrocarbons, such as polymers and single-cell proteins (Bozzano and Manenti, 2016). A little more than 65 % of the world's methanol is utilised to make acetic acid, methyl and vinyl acetates, methyl methacrylate, methylamines, methyl tert-butyl ether (MTBE), fuel additives, and a wide range of other compounds (Dalena et al., 2018b, Dalena et al., 2018a). Ethanol is primarily employed as a solvent in producing varnishes and perfumes, as well as a preservative for biological specimens. Propanols are commonly used as solvents but can also be used as chemical intermediates to manufacture esters and amides. Propanol can also be used as a disinfectant in the pharmaceutical business and as an anti-freezing agent. Biopropanol is a very seldom recognised biofuel.

Low-alcohol fuels have gained great interest recently, and they have begun to substitute several compounds used as octane boosters, especially in car fuels. With the prohibition of tetraethyllead as a fuel additive to raise the octane number of gasoline fuel, MTBE and alcohols have been utilised as substitute gasoline additives; however, MTBE was outlawed in the early 2000s, and alcohols have proven beneficial additives for increasing the octane number of gasoline. The low alcohols' oxygen content, octane number, and auto-ignition/flash point temperatures higher than gasoline make it a viable fuel substitute. Since the molar products to reactants ratio of alcohol combustion in internal combustion engines (ICE) is higher than that of gasoline combustion, the combustion pressures produced by alcohol combustion in ICEs are greater than those produced by gasoline. Additionally, compared to gasoline, this increases power production and thermal efficiency. Low-alcohol fuels are used in combustion engines directly or in a blend with gasoline in various ratios. The ICEs have relied on first-generation alcohols as gasoline-ethanol blends, with current energy quality laws generally permitting 5–10 % ethanol additions to the initial gasoline stream. Even though they include distinct chemical constituents, alcohol and gasoline have much in common (Göktaş et al., 2021). Unlike gasoline and diesel, alcohols contain oxygen; as a result, adding alcohol to petroleum-based

products increases the performance of fuel combustion, which ultimately leads to reduced emissions into the atmosphere (Surisetty et al., 2011). Furthermore, when it comes to employing low alcohol as a fuel, the solubility of low alcohols in water is crucial. Low alcohols (methanol, ethanol, and propanol) are all miscible in water, indicating that they will dissolve in any quantity of water added to them. Also, methanol and ethanol are easily dissolved in water, biodegradable, and do not build up in the environment (Yun, 2020).

1.3 Limitations of Low Alcohols as Fuels

Significant attention has been given to low alcohols produced from cellulosic biomass for use as a viable transportation fuel. Low alcohols, such as ethanol, can be employed as fuel in vehicle engines because of their high-octane number; nevertheless, their utilisation is fraught with difficulties. Ethanol has a calorific value of 27 MJ/kg, which is approximately 65 % that of gasoline (44 MJ/kg). As a result, ethanol fuel does not combust readily and requires significantly more fuel utilisation than pure gasoline, which has a better heating value and energy efficiency than ethanol. As a result, the low flame speed of ethanol-blend gasoline reduces engine performance and poor cold-starting capabilities, making it challenging to use during the winter periods. Consequently, the disparity between the lower calorific values of the two fuels results in a rise in the fuel utilisation of the gasoline/ethanol blend with an increase in the ethanol content in the blends, resulting in a reduction in engine fuel economy (Iodice and Cardone, 2021). When contrasted to gasoline, this feature describes why the engine will require more ethanol or methanol mixes to produce the same amount of engine power. Moreover, because no passenger automobile is designed to run on 100 % ethanol, utilising pure ethanol (E100) may damage the car engine and plastic (or rubber) fuel system elements owing to the corrosive nature of ethanol. Nonetheless, to accommodate the application of 100 % ethanol, modifications or upgrades must be made to the components and surfaces of the existing internal combustion engine chambers and any plastic parts that come into contact with fuel and the fuel injection system (Ilhak et al., 2019). This appears to be a time-consuming task with substantial cost implications.

The disadvantage of utilising pure alcohol is the cost associated with the modification of engines and the lack of dual-fuel capability. However, when the concentration of the alcohol is relatively small, the fuel alcohol may be applied with no modifications to the engine (Göktaş et al., 2021). When ethanol is blended with gasoline (in amounts <10%), there are several drawbacks to this kind of fuel. If the engine is not modified, the fuel utilisation will increase

by 5%. This results in the following setback with ethanol fuel: (1). the generation of acetic acid during the combustion operation of ethanol is highly damaging to automobile components. (2). when the ethanol concentration exceeds 15%, a preservative is required to prevent complications. (3). Due to the hygroscopic nature of ethanol, liquid phase separation may occur when the quantity of water is sufficient. Since low alcohols have considerable solubility in water, a spill or leak of a mixture of low-alcohol fuels might contaminate subsurface water. Moreover, ethanol as a fuel is more challenging to store than gasoline and more demanding to handle during the distribution and transition processes than gasoline (Liu et al., 2013a). Various studies (Gaida et al., 2016, No, 2016, Cao et al., 2016a, Wang and Chen, 2011, Jönsson et al., 2013) have shown that mixing methanol and ethanol lowers engine emissions compared to fossil fuels, particularly gasoline. The oxygen concentration of methanol and ethanol is a significant factor in engine emissions in most of these studies. Methanol has a greater oxygen concentration than ethanol (approximately 50 and 35 by weight, respectively, as shown in Figure 1.5). Hence, methanol will provide less diluting power than other oxygenates. Due to the obvious greater oxygen and carbon contents in low alcohol and ether fuels (Demirbas, 2004), their caloric value is less than that of gasoline (Osten and Sell, 1983). The greater the oxygen concentration of the fuel, the lower the heating value; on the other hand, the higher the carbon level, the higher the heating value.

It is commonly recognised that the physicochemical characteristics of low alcohols (methanol or ethanol) are significantly distinct from those of gasoline, with the heating value of methanol or ethanol being considerably lower than that of gasoline. Moreover, the octane number of ethanol and methanol is higher than that of gasoline, and the boiling point of low alcohols is typically lower than that of gasoline (da Silva Trindade and dos Santos, 2017). As a result of these challenges, finding sustainable substitute energy sources is critical. In a nutshell, low alcohols, including ethanol, has the potential as an eco-friendly transportation fuel; however, it has limitations because it does not conform to the current configuration of modern-day automobile engines. This problem requires sustainable solutions that will see ethanol as a potential alternative to fossil fuels while maintaining the design of engines, among other fuel-driven devices. Some attempts are being made to explore and develop novel techniques for producing transportation fuels using non-petroleum resources (bioethanol feedstock) to replace the conventional method. Hence, the catalytic conversion (upgrading) of low alcohols offers the opportunity to transform low alcohols into value-added chemicals and higher hydrocarbons

that can serve as petrochemicals and transportation fuels for industrial and automobile engine applications, respectively.

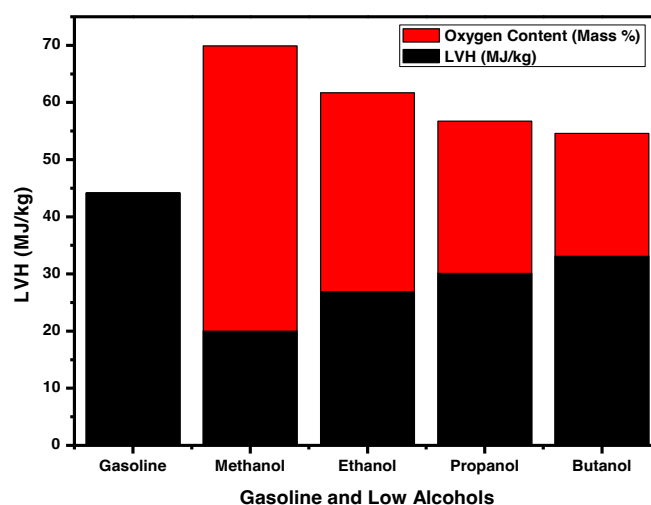


Figure 1-5. The correlation between oxygen content and heating value of gasoline and low alcohols

1.4 Rationale/Motivation for this Study: *Alignment to Sustainable Development Goals (SDGs)*

This study will potentially contribute to the actualisation of SDGs 7, 11 and 13, as discussed below:

This study focuses on the catalytic conversion of low alcohols to renewable fuel-range hydrocarbons to potentially foster the attainment of SDG 7, which guarantees access to clean, affordable, dependable, renewable, and efficient energy. At the same time, contribute to SDG 13, which is set to pursue immediate action to tackle climate change and its effects. Biomass energy can provide sustainable energy in sectors of the economy (SDG-7). In the field of power generation, bioenergy has the potential to offer flexibility, which can help stabilise the proliferation of other resources like wind and solar that are intermittent and seasonal. In the transportation sector, the utilisation of liquid and gaseous biofuels, as well as electrification and increased energy efficiency in vehicles, can assist in attaining a significant decrease in the utilisation of fossil fuels. In most cases, the use of bioenergy improves access to regional energy sources. It decreases dependency on fossil fuels responsible for greenhouse gases (GHG), reducing climate variability and its impacts on other social and environmental concerns, which aligns with SDG-13. It has the potential to revitalise both the agricultural and forestry industries

and encourage greater utilisation of renewable resources as feedstock for various industrial operations. The rationale of the study is summarised below:

- Advancement in the development of sustainable energy solutions by catalytically converting low alcohols to fuel-range hydrocarbons.
- Contribute to the achievement of SDG-7 by promoting clean, affordable, and efficient energy access.
- Support the pursuit of immediate action on climate change and its effects by contributing to reducing greenhouse gas emissions, as outlined in SDG-13.
- Promote the utilisation of renewable liquid and gaseous biofuels in the transportation sector, which can assist in achieving a significant decrease in the utilisation of fossil fuels.
- Encourage regional energy sources and decrease dependence on fossil fuels to reduce climate variability and its impacts on other social and environmental concerns.
- Revitalise the agricultural and forestry industries and promote the greater utilisation of renewable resources as feedstock for various industrial operations.
- Using renewable energy (bioenergy) sources will ensure a sustainable ecosystem while reducing environmental degradation and improving the standard of living.
- Since this project will utilise bioethanol as feedstock for biofuel production, the demand for bioethanol will increase, which will drive the conversion of more biomass waste into bioethanol to enhance effective waste management, in line with SDG 11.

In conclusion, this study holds significant promise for advancing sustainable development and offering practical solutions to the pressing energy and climate change issues confronting our world. By focusing on bioeconomy, this study presents a pathway to facilitate a successful transition towards a more sustainable and environmentally friendly future.

1.5 Research Aim and Objective:

This study aims to produce fuels and petrochemicals that meet modern-day transportation and industrial configuration from low alcohols. This aim was set to be achieved through the following outlined specific objectives:

- i. Synthesis and characterization of a newly developed tunable ZSM-5 catalyst active in low alcohol conversion

- ii. Investigate the effects of metal modification on the ZSM-5 catalyst and activities as a function of its properties
- iii. Study the effects of operating conditions on low alcohol catalytic conversion and product distributions.
- i. Evaluate the performance of transition metal doped catalysts in the conversion of low alcohols to fuel-range hydrocarbons.
- ii. Investigation of the deactivation, stability, regeneration, and reusability of the synthesised catalyst
- iii. Perform a techno-economic analysis of the catalytic conversion of low alcohols into fuel blendstocks.
- iv. Conduct an environmental analysis on the variability of catalytic upgrading and utilization of low alcohol fuels.

While the micropores of zeolite are advantageous for the mass transfer of small molecules, they are disadvantageous for the mass transfer of large molecules, as evidenced by diffusion limitations for reagents, intermediates, and products. Hence, the microporous nature of ZSM-5 zeolites may limit the diffusion of large molecules that constitute the liquid fuel-range hydrocarbons. Therefore, the novelty of this study was to synthesise a newly developed tunable ZSM-5 zeolite catalyst with mesopores to reduce the diffusion limitations of these large hydrocarbon molecules for enhanced conversion of low alcohols to olefins and their oligomers (petrochemicals and liquid fuel hydrocarbons). The catalytic conversion process was developed as a one-step method for converting low alcohols into hydrocarbons comparable to those from crude oil.

1.6 Thesis Structure and Layout

This thesis consists of 9 chapters, as shown in Figure 1.6, with a clear framework linking the study objectives to the papers (1-11) in each chapter. Each chapter begins with a brief remark (abstract) that gives the reader an overview of the content and its relevance to the thesis. The chapters are structured as follows:

Chapter 1: Introduction: This introductory chapter provides a comprehensive overview, background information, the problem statement, and the conceptualisation of the research. It justifies the need for alternative (renewable) energy sources due to the environmental impact of fossil fuels and the need to develop a tunable mesoporous catalyst for the conversion of low alcohols to fuel-range hydrocarbons.

Chapter 2: *Catalytic conversion of low alcohol to hydrocarbons: Challenges, development, prospects, and considerations for future work (papers 1-4):* This chapter provides a comprehensive literature review of various catalysts for the conversion of lower alcohols into fuels and petrochemicals. It discusses the economic implications and environmental impact of low alcohol feedstocks and provides insights into catalysis's challenges, current developments, and prospects. The literature review chapter has been published and linked to articles 1-4. Specifically, paper 1 presents a comprehensive overview of the transition to renewable energy sources, providing detailed insights into the role of biofuels in achieving sustainable living. Paper 2 explores the production and potential of low alcohol as a fuel source, examining its limitations and conducting an economic and environmental impact assessment. Paper 3 focuses on the catalytic conversion of low alcohols to fuel-range hydrocarbons and petrochemicals, reviewing various catalysts and discussing the opportunities and challenges in low alcohol catalysis. Lastly, Paper 4 investigates the mechanism of catalytic conversion of bioethanol to olefins and fuel-range hydrocarbons, highlighting the current advancements and prospects in low alcohol catalysis.

Chapter 3: *Synthesis and characterisation of a newly developed tunable and transition metal doped ZSM-5 (Si/Al = 40) zeolite catalyst (Paper 5):* This chapter presents the detailed synthesis method, modification techniques and characterisation results of the ZSM-5 catalyst. This chapter is linked to objective 1.

Chapter 4: *Effects of transition metal doping on the properties and catalytic performance of the ZSM-5 zeolite catalyst in ethanol conversion processes (papers 6-7):* This chapter discusses the effects of transition metal modification on the properties and catalytic performance of the ZSM-5 catalyst. The effects of low and high metal doping on the conversion of ethanol to hydrocarbons are investigated. This chapter corresponds to objective 2.

Chapter 5: *Ethanol Conversion to liquid hydrocarbons over transition metal-doped HZSM-5: effect of operating conditions and catalyst modifications on product distribution and coking (paper 8):* Aligned with objective 3, this chapter provides insights into the influence of operating parameters (temperature, weight hourly space velocity) and different concentrations of various transition metals (Co, Fe and Ni) on catalyst performance, product distribution and coke deposition. The chapter delves into catalyst coking and comprehensively characterises the coke formed during the ethanol conversion process. It also presented a proposed pathway for the conversion of ethanol to hydrocarbons, shedding light on the underlying processes.

Chapter 6: *Performance evaluation of transition metal-doped HZSM-5 zeolite in the single-step conversion of C1-C3 alcohols to fuel range hydrocarbons (paper 9):* Objective 4 is addressed in this chapter, which focuses on the application of the transition metal-doped catalyst in the conversion of selected low alcohols (methanol, ethanol and propanol) to hydrocarbons. The study also examines the deactivation of the catalyst and the amount of coke formed in each alcohol conversion process to enable a comparative assessment.

Chapter 7: *Stability, deactivation, and regeneration of HZSM-5 and Ni/HZSM-5 zeolite catalysts for ethanol-to-hydrocarbon conversion (paper 10):* Objective 5 examines the viability of the synthesised catalysts in terms of stability and reusability. This chapter provides insights into catalyst performance over extended time-on-stream (TOS), regeneration techniques, and regenerated catalysts' application.

Chapter 8: *Techno-economic and life-cycle analysis of single-step catalytic conversion of bioethanol to fuel blends over a Ni-doped HZSM-5 zeolite catalyst (paper 11):* Objectives 6 and 7 are addressed in this chapter, which focuses on the feasibility and economics of the one-step conversion process used in the study, also known as the Consolidated Alcohol Dehydration and Oligomerization (CADO) process and its life cycle assessment. The cost of catalysts was estimated using the Catcost model from the National Renewable Energy Laboratory (NREL), while the cost of converting biomass to ethanol and then to fuel blends was estimated according to NREL. The life cycle analysis of the conversion process and biofuel application is based on published reports by NREL.

Chapter 9: *Conclusion:* This concluding chapter summarises the study's overall findings and implications and provides recommendations for further research based on the research outcomes.

All cited articles are referenced at the end of each respective chapter.

1.7 Targeted Outputs

- Synthesis of a newly developed tunable mesoporous ZSM-5 zeolite catalyst for low alcohol conversion into fuel and petrochemicals
- Publication of research findings in reputable peer-reviewed journals
- Presentation of research findings at Conferences
- To ensure catalyst regeneration and reuse in low alcohol conversion

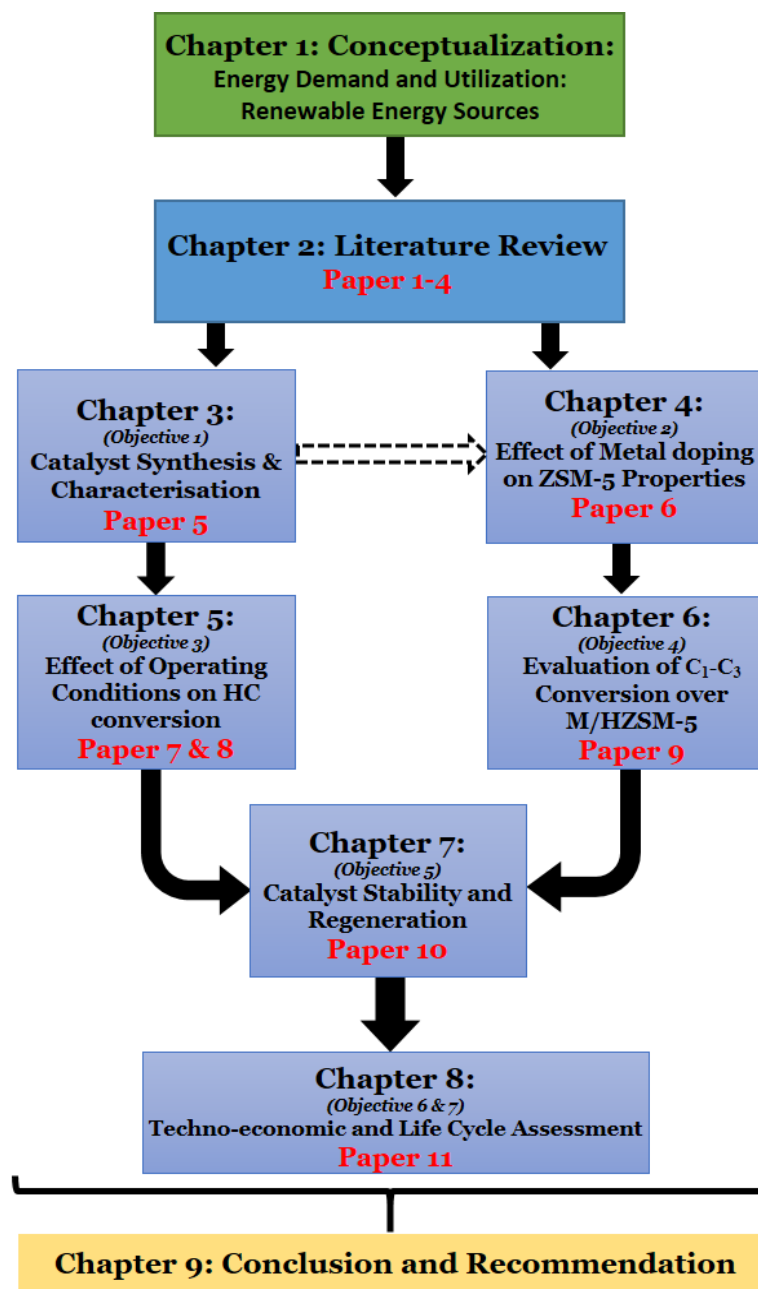


Figure 1-6. Framework of thesis layout, connecting objectives and papers to chapters

CHAPTER 2

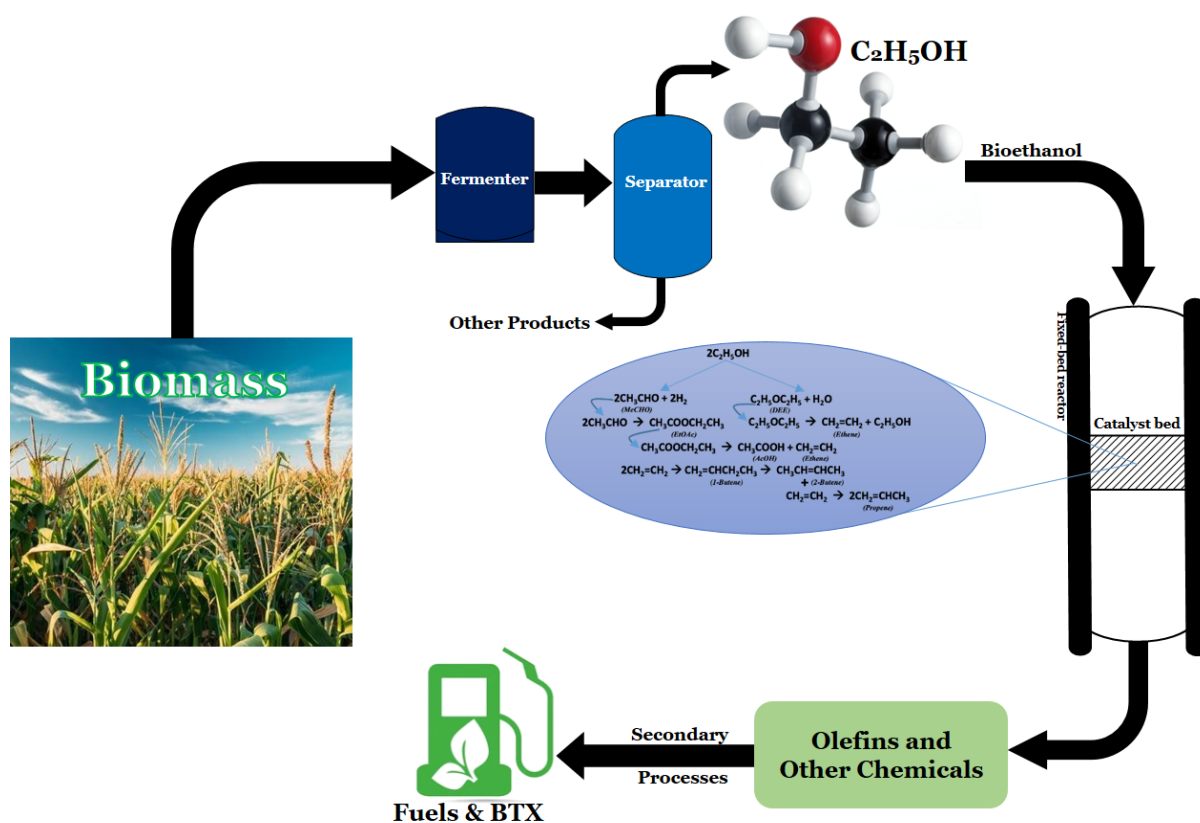
LITERATURE REVIEW

Catalytic Conversion of Low Alcohols to Fuels and Petrochemicals: Development, Challenges, Prospects and Future Work Considerations

Abstract

Recently, there has been increased interest in using low alcohols as fuel and feedstock in the petrochemical sector to produce value-added chemicals. However, several issues are associated with applying low alcohol as fuel. To this end, this insight concentrates on the catalytic conversion of low alcohol into fuels and petrochemicals. In this chapter, rather than simply summarizing the present state of our understanding of such a process, our goal was to outline and engage in critical discussion on a review of different catalysts for low alcohol conversion, current development, and viewpoints, as well as the challenges that need to be addressed and future work considerations for effective conversion of low alcohols into fuels and petrochemicals.

Graphical Abstract



2.1 Catalytic Conversion of Low Alcohols to Hydrocarbons

2.1.1 Low Alcohol Conversion to Olefins

Due to the expanding capacity of industrial production, which has been growing year after year, the need for fossil fuels in daily life and industrial processes has also increased. The non-sustainable fossil fuels will necessarily confront the issue of their reserves diminishing with time, and their depletion will be unavoidable soon. As a result, we must investigate renewable substitute energy sources. Some attempts are being made to investigate and establish novel ways for employing nonpetroleum resources such as alcohol as feedstock for the production of ethylene, which is a substitute for the typical hydrocarbon cracking method used in the ethylene production process.

One of the most significant aspects of a country's economic strength is the level of progress of its ethylene industry. The ethylene industry is also critical to the country's overall economic growth. The growth of the ethylene sector is being restricted because petroleum resources are becoming progressively scarce. The development and application of a variety of non-petroleum feedstock capable of synthesizing ethylene have piqued the interest of several nations. The procedure for converting ethanol to ethylene has vast improvement potential and is significant in fostering the economy's growth. Compared to converting petroleum into ethylene, converting ethanol into ethylene is more commercially viable. Ethylene is among the world's most essential chemical products and the significant feedstock in the petrochemical sector. Currently, ethylene is utilized to manufacture roughly 75% of all petrochemical products, including acetaldehyde, acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride, vinyl acetate, among others; it can also be utilized as a polymerization feedstock to generate a range of essential organic chemical products, including polyethylene (Li-dao, 2005). It has long been recognized that ethylene output is a valuable metric for assessing petrochemical advancement in various countries worldwide. Presently, hydrocarbon cracking is the most important technological technique for producing ethylene. This technology produces almost 99 % of the world's ethylene. (Wang and He, 2000). Hydrocarbon-cracking is a method of extracting hydrocarbons from petroleum or natural gas. Hydrocarbon components containing significant carbon atoms can be broken down into smaller hydrocarbon compounds when heated to an elevated temperature (Edwards*, 2006).

The catalytic conversion of ethanol, which takes place at an optimum temperature and under the influence of a catalyst, results in the dehydration of ethanol to ethylene. The mechanism of converting ethanol to ethylene through catalytic dehydration is the oldest process still in use in the industry (Olaf and Meng-Teck, 1976). During the conversion process, ethanol undergoes dehydration to yield ethylene, which is subsequently oligomerized to produce olefins, paraffins, naphthenes, and aromatics. Due to the use of renewable biomass in transforming ethanol to propylene, the process is deemed carbon-neutral (Duan et al., 2013). According to Harmsen et al. (2014), ethylene is utilized in synthesising plastics and rubbers, as well as ethylene glycol and vinyl chloride resin. It also makes acetic acid, styrene, and other chemicals. The synthesis of diethyl ether (DEE) from ethanol via the intermolecular dehydration process is more efficient at low temperatures. Using dehydration, DEE is turned to C₄ olefins, which are then further converted into higher hydrocarbons through oligomerization, cracking, and aromatization, among other processes. Solid acid catalysts have been shown to improve the efficiency of such processes (Inaba et al., 2006b, Robak and Balcerek, 2018, Zhao et al., 2019, Zhang et al., 2018).

Propylene is among the essential petrochemical, serving as a feedstock for the manufacture of polypropylene, polyacrylonitrile, acrolein, and acrylic acid, among other products. Propylene is now mainly generated as a by-product of petroleum refining and ethylene manufacturing through the naphtha steam-cracking mechanism rather than as a primary product. Since the availability of petroleum is tightly controlled, propylene manufacturing has received much attention recently. It is also crucial to note that propylene as a raw material in the petrochemical sector, the demand for propylene is increasing considerably more rapidly than the demand for ethylene due to the increased demand for propylene derivatives (Lin et al., 2009). As a result, much emphasis has been on developing techniques for synthesising propylene from ethanol and methanol. It is necessary to develop innovative and sustainable procedures to produce a high propylene yield due to the increasing demand for chemicals and the anticipated scarcity of petroleum resources.

Since methanol can be readily conventionally produced from fossil fuel, the ethanol/methanol-to-olefins (E/M-TO), methanol-to-propylene (MTP) and ethanol-to-propylene (ETP) processes are viable alternatives to the petroleum-based pathway for the synthesis of propylene. As a result, these new routes have received a great deal of interest (Chen et al., 2005). Compared to the standard MTO approach, in which ethylene is the primary product, the significant propylene

to ethylene (P/E) ratio of the MTP process is the most distinctive feature, as it allows for an increased propylene yield in the recirculation system. Extensive research has been focused on the MTO technique involving zeolite catalysts (Chen et al., 2005, Barger et al., 2003, Stöcker, 1999, Zhang et al., 2010c). So yet, there have only been a handful of reports on the MTP process (Zhao et al., 2006a). The one-pass specificity to propylene and the P/E ratio in the latest studies on the MTP process is still low, but a high P/E ratio is required to produce propylene from methanol using recycling techniques (Zhao et al., 2006a). The P/E ratio can be increased under low methanol partial pressure conditions caused by the introduction of substantial carrier gas or a high water-to-methanol ratio in the feed stream. However, from a technical perspective, having a methanol partial pressure that is too low is economically unviable. It was discovered by Mei et al. (2008) that reducing the Brønsted acidity of HZSM-5 zeolite might increase its specificity for propylene during the MTO process. During the catalytic transformation of methanol to hydrocarbons, Prinz and Riekert (1988) reported that the preference for the formation of ethylene and propylene, including the P/E ratio, improved with a reduction in HZSM-5 crystal size, implying that shortening the diffusion route in HZSM-5 zeolite may enhance the P/E ratio (Mei et al., 2008).

The process of the methanol-to-olefin (MTO) reaction has been widely contested. The intricacy of reaction pathways has been described, specifically in the synthesis of propylene (Stöcker, 1999, Bjørgen et al., 2007b, Bjørgen et al., 2007a). The chemical procedure for ethanol-to-olefin conversion over ZSM-5 is currently unknown. Ethanol was believed to be transformed into diethyl ether before turning into ethylene. The generation of ethylene from ethanol is different from that of methanol. In the case of ethanol transformation, ethylene may be easily generated by dehydration. However, in the case of methanol transformation, a carbon-carbon bond between C₁ reactants must first be created before ethylene can be synthesised. The further conversion of ethylene to higher hydrocarbons, such as propylene, was thought to occur by an oligomerization cracking mechanism. Intermediate hydrocarbons like ethylene are converted into higher hydrocarbons (C₃+ aliphatic and aromatic) by a catalyst with an increased surface acid density and strong acidity. The secondary process was enhanced by increasing the process contact time; as a result, ethylene production declined while the yield of higher hydrocarbons improved. A rise in temperature at low temperatures favours the primary dehydration of ethanol to ethylene, but a secondary process occurs on the catalyst at high temperatures. As a result, the higher hydrocarbons generated during the transformation of ethanol (C₃+ aliphatics and aromatics) are more prone to breakage at higher temperatures, giving more of the light olefins,

ethylene, and propylene. To look at it another way, thermodynamic equilibrium constraints product distribution. These catalytic conversion processes will enhance the reduction of petroleum reliance and carbon dioxide emissions (Song et al., 2009).

2.1.2 Ethanol-to-Ethylene (ETE) and -Propylene (ETP) Reaction Mechanism

The usual description of the ETE process, which includes the steps of electron transfer, is shown in Figure 2.1. The coordinated (direct) method of ethanol dehydration to ethylene is called path A. The stepwise (indirect) dehydration approach is illustrated by pathways B and C (Rossetti et al., 2017, Galadima and Muraza, 2015), which involve the conversion of ethanol to diethyl ether (DEE, a process intermediate) and then the transformation of DEE to ethylene. The endothermic nature of path A implies a closed system that absorbs heat energy from its environment, resulting in heat exchange with the system. The pathway B, conversely, is exothermic, hence, heat is released during the process (the net standard enthalpy change H is negative). As a result, path A is favoured at moderately elevated temperatures, and path B leads the process at mild temperatures. Within the stepwise method, two ethanol molecules combine by intermolecular dehydration to form DEE (pathway B), which is then dehydrated to ethylene (pathway C). Zhang and Yu (2013) briefly explained the ethanol dehydration process and proposed a process temperature range for the synthesis of DEE that is below 240 °C. It has been noted that both the concerted (path A) and stepwise (path B and C) mechanisms often coexist during the process (Roca et al., 1969) and that the presence of water can hinder both processes (DeWilde et al., 2013). The formation of coke deposits is caused by ethylene going through the following reactions in the system, including oligomerization, cyclization, and aromatization, which result in higher hydrocarbons (Galadima and Muraza, 2015).

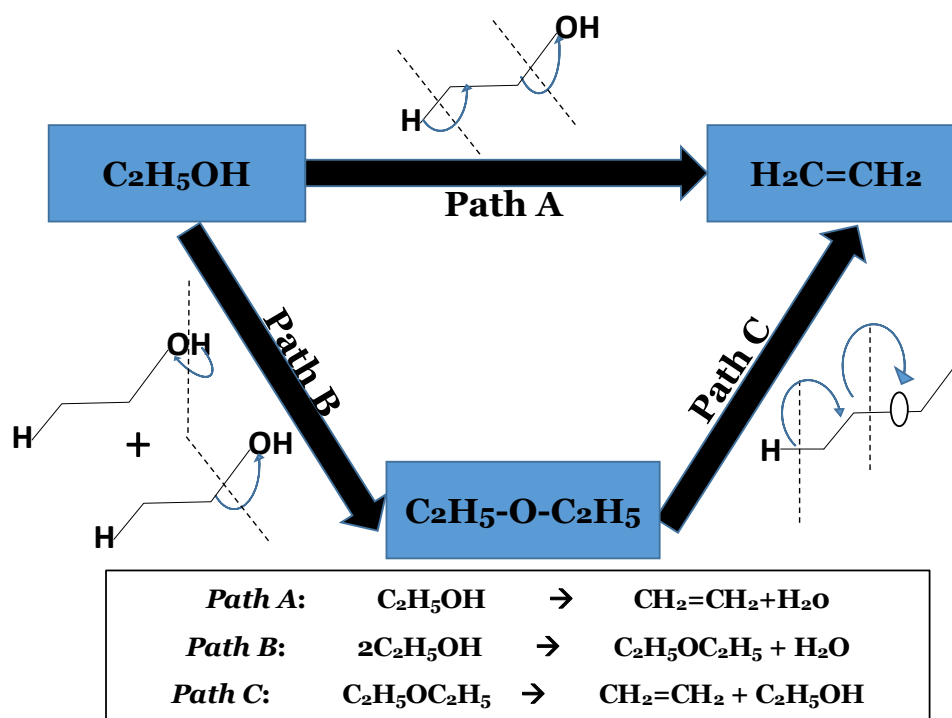


Figure 2-1. Reaction pathway for ETE conversion (Xiang et al., 2022)

The types of catalysts used considerably affect the ETP and ETE processes. Mesoporous materials (Iwamoto, 2015), metal oxides (Iwamoto, 2015, Iwamoto et al., 2013), and zeolites (Xia et al., 2010b, Takahashi et al., 2013, Li et al., 2016) are the three major types of catalysts employed in the ETP/ETE process. According to the suggested reaction mechanism for the H-ZSM-5 catalyst in Figure 2.2, ethanol is dehydrated to ethylene before being simultaneously transformed into propylene and butylene (Li et al., 2016). The oligomerization of ethylene, propylene, and butylene also aids the synthesis of paraffins and higher hydrocarbons. Iwamoto (2015) did, however, identify two parallel paths (routes A & B as illustrated in Figure 2.3) of the ETP over the Ni-doped MCM-41 catalyst. Pathway A involves first dehydrating ethanol to make diethyl ether, which is then transformed into ethylene. After that, ethene is converted to butene (excluding isobutylene), and 2-butene combines with ethene to form propene. From route B, acetaldehyde and ethyl acetate are produced as intermediates rather than DEE. Dehydrogenation of ethanol initially produces acetaldehyde, which is then transformed into ethyl acetate, and later converted into butenes (except isobutylene), and finally, 2-butene combines with ethene to form propene. However, Eqs. 2.1-2.3 shows the formation of propylene via a secondary reaction that occurs concurrently with the acetone synthesis from acetaldehyde. This reaction pathway was discovered by Iwamoto (2015) and Iwamoto et al. (2013)

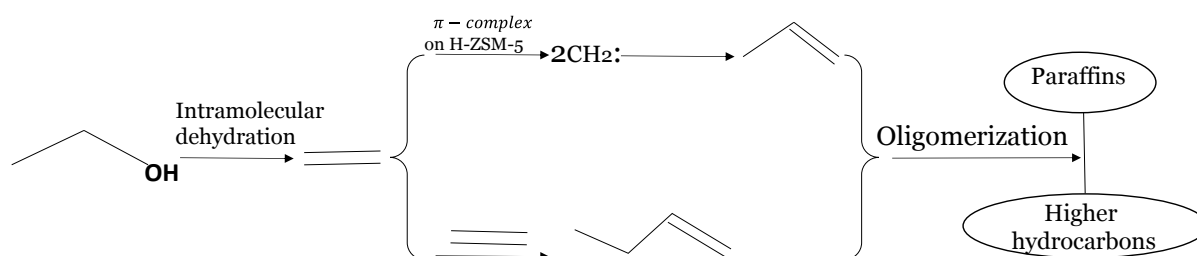
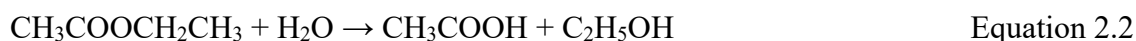
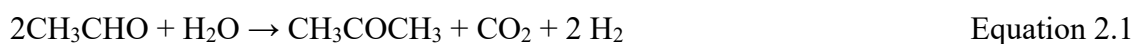


Figure 2-2. ETP reaction route on H-ZSM-5 (Xia et al., 2010a, Takahashi et al., 2013, Li et al., 2016)

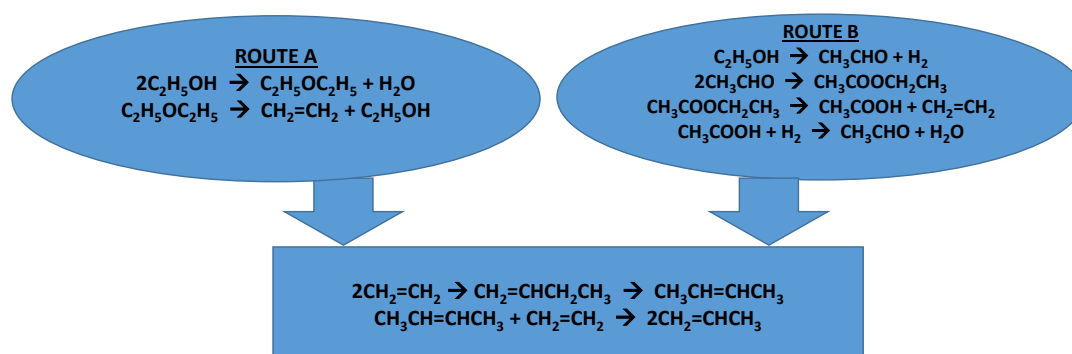


Figure 2-3 Process mechanism for ETP on Ni-doped MCM-41 (Iwamoto, 2015)

2.1.3 Oligomerization of Olefins to Oligomers (C_5+)

In several acid-catalysed conversions of olefins, olefin oligomerization is a deactivation or undesirable reaction process, but it can also be a beneficial approach to carbon-carbon bond creation when the correct catalyst and parameters are used (Parvulescu et al., 2010). For over 80 years, light olefins (C_2 - C_5) have been oligomerized over acidic catalysts to form fuels, primarily gasoline, but more lately to distillates and other products. The market potential is difficult to determine because the fuels obtained through oligomerization are not always reported differently from those obtained through other refinery processes. However, around 60 oligomerization facilities exist, predominantly transforming propene, butene, or mixtures thereof, with a rated output of over 67.5 million barrels of feed per year. According to the

worldwide refining survey, there are around 650 oil refineries worldwide, with oligomerization used by 9 % of those refineries (Stell, 2002).

As has been vividly demonstrated, homogeneous catalysis has made enormous strides in recent decades, and new, more viable and preferential methods for the oligomerization of olefins are continually being discovered. Numerous catalysts for the selective manufacture of linear and branched higher olefins have been developed and put into commercial production, with applications in fuel and chemicals. However, given significant research work and the ease with which heterogeneous catalysts are handled in refineries and petrochemical facilities, only a few global oligomerisation facilities are equipped to work with heterogeneous systems. None of them has anything to do with the conversion of ethylene. The oligomerization of propylene and butene by solid acids occurs through unspecific cationic pathways (Muraza, 2015), resulting in high-branching-indices oligomers that are mostly used in the production of gasoline and diesel (Marcilly, 2003, Corma and Iborra, 2006, Bellussi et al., 2012). Only butenes are selectively converted into low-branching octenes for use in petrochemistry on a commercial scale using nickel-based heterogeneous catalysts, which are used in contrast to homogeneous techniques. With the help of nickel, olefins may be oligomerized under mild circumstances than raw solid acids, allowing specificity to be oriented in a coordinated manner, resulting in more linear products with a selectivity comparable to their homogeneous counterparts. Available heterogeneous catalysts do not give adequate stability, selectivity, efficiency, or atom economy toward the required products to contend with homogeneous processes in the Ni-species catalysed oligomerization of ethylene and propylene. The conversion pathway for the transformation of ethanol into hydrocarbons is presented in Figure 2.4.

On an industrial scale, oligomerization operations are commonly utilized to convert lower olefin streams from various hydrocarbon generating techniques (steam cracking, FCC, Fischer—Tropsch) into heavier olefins with uses in energy or petrochemicals. This process is catalyzed by multiple methods, including heterogeneous acid-catalysis, which is used to produce fuels, and homogeneously catalysed techniques, which are mostly used to produce high-value chemicals (Forestière et al., 2009). In the last decade, a few novel commercial homogeneous-catalyzed procedures have evolved. The oligomerization of short-chain alkenes is essential in homogeneous catalysis, primarily for producing second-generation intermediates (or feedstocks) for the petrochemical industries. Ethylene oligomerisation dominates the industry for homogeneous-catalyzed oligomerization to linear alpha olefins (LAOs), which are

even-carbon-numbered olefins with carbon atoms (C_4 to C_{30}). LAOs are primarily employed as co-monomers in synthesising polyethylene, as oxo-alcohols in detergents and plasticizers, and to create poly-alpha-olefins for the artificial lubricant pool. In 2012, the entire global output of LAOs was 3.5 Mt, with an overall capacity of 4.3 Mt/y (except for 1-butene synthesis from refinery streams). The worldwide yearly average growth rate for LAOs was more than 3.3% in 2012, however, this varies significantly by area, with more robust growth in emerging nations. Globally, the utilization of co-monomer grade LAO (C_4 - C_8) is the highest and most commonly used, mainly for the manufacturing of linear low-density polyethylene resins (LLDPE) (Breuil et al., 2015).

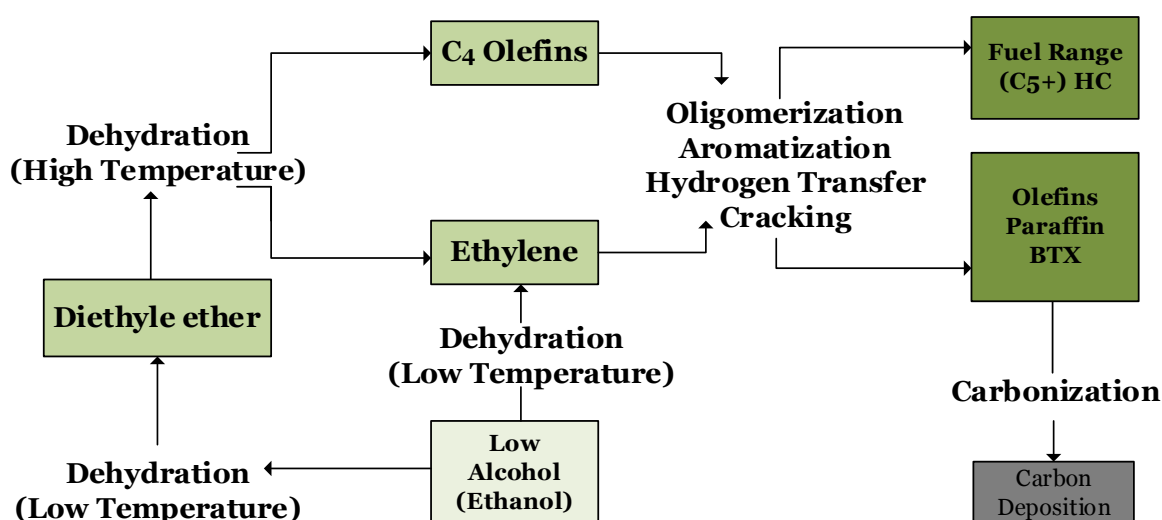


Figure 2-4. Reaction Pathway for the catalytic conversion of ethanol to Hydrocarbon (HC)
(adapted from (Inaba et al., 2006a) with modifications)

2.1.3.1 Mechanism of the Catalytic Reaction for Ethanol-to-Gasoline (ETG) Conversion

The ETG by catalysis reaction is a complicated process (Figure 2.5). The ETG procedure is comprised primarily of three stages (Sun and Wang, 2014, Krzywonos et al., 2017): the ETE through dehydration, the oligomerization of ethylene through secondary processes, and the synthesis of aromatics and paraffin via hydrogen transfer (HT). The distribution of HC products in ETG is comparable to that in the methanol-to-gasoline (MTG) (Aguayo et al., 2002a, Johansson et al., 2009, Aguayo et al., 2002b), except for durene, which does not take place in the products of the ETG procedure because it is an undesirable by-product of the MTG technique (Costa et al., 1985). To convert ethanol into hydrocarbons, acid catalysts such as zeolites (Madeira et al., 2009) and hydroxyapatites (Tsuchida et al., 2008) are essential. For the ETG process, Brønsted acid sites are typically considered active sites (Chaudhuri et al.,

1990). When Brønsted acid sites are inactivated by carbon deposition, the radicals formed in this process are recognised as another type of active site in the oligomerization of ethylene to C_3+ hydrocarbons (Madeira et al., 2012, Madeira et al., 2010)

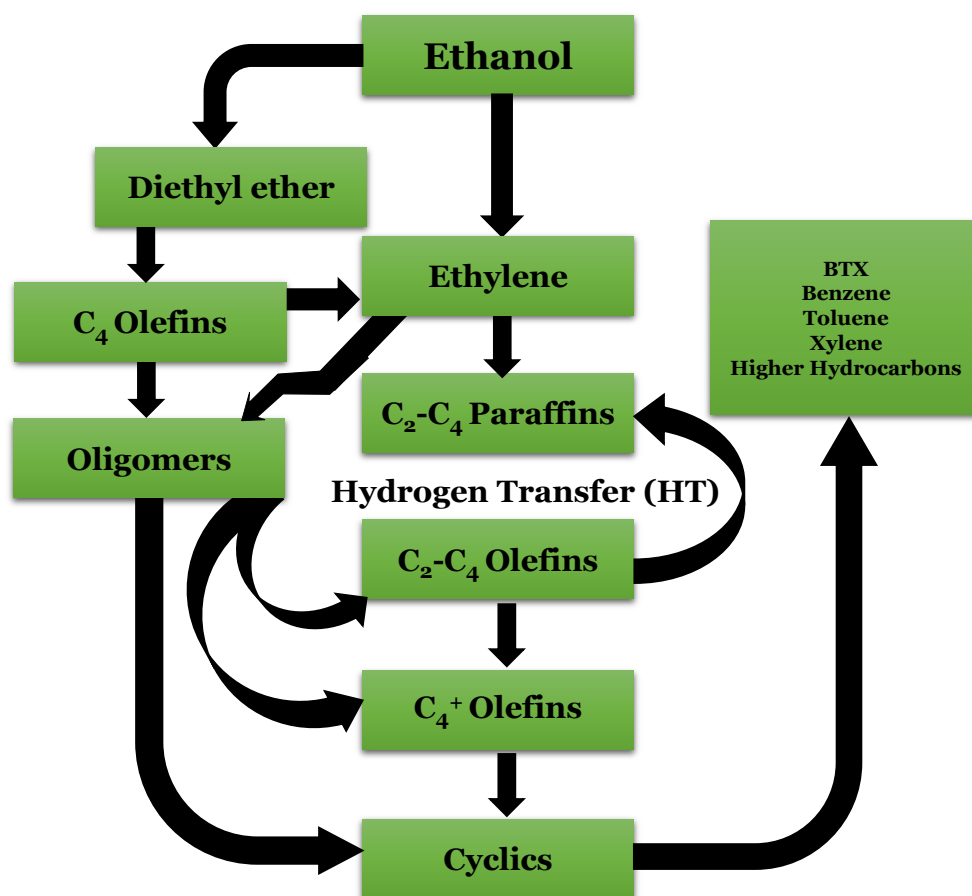
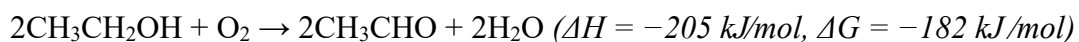


Figure 2-5. Process pathway for ETG mechanism (Viswanadham et al., 2012).

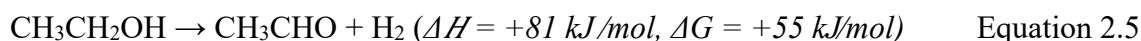
2.1.4 Conversion of Low Alcohol (Bioethanol) to Other Value-added Chemicals

Bioethanol can be preferentially transformed into other chemical compounds (acetaldehyde (MeCHO), diethyl ether (DEE), acetic acid (AcOH), acetone (ACE), and ethyl acetate (ETAC)). In most cases, the synthesis of the required chemical can be attained and improved by manipulating key operational parameters and the catalyst employed. Producing acetic acid AcOH, 1-butanol, ETAC, and crotonaldehyde require MeCHO as an essential feedstock. Compared to the conventional technique of synthesizing acetaldehyde, the transformation of bioethanol to acetaldehyde is an environmentally friendly approach. This transformation can be accomplished through partial oxidation (Eq. 2.4) and non-oxidative direct dehydrogenation (Eq. 2.5) (Boldog et al., 2018, Hanukovich et al., 2019, Raynes and Taylor, 2021). Owing to the application of supported rare metals like gold, the process of ethanol partial oxidation,

which is an exothermic rxn that results in the generation of water as a byproduct, is often carried out at mild temperatures of ~473 K. Contrary to partial oxidation, the direct dehydrogenation of ethanol is an endothermic reaction normally occurs at T= 473 – 573 K.

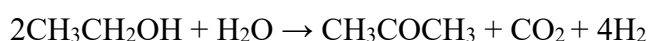


Equation 2.4



Equation 2.5

Diethyl ether (DEE) is a common solvent. The process of ethylene to bioethanol vapour-phase hydration produces DEE as a by-product. Conversely, DEE is also produced commercially via acid ether synthesis. In this procedure, ethanol is mixed with a strong acid, such as sulfuric acid, and heated to the appropriate temperature (less than 150 °C to prevent ethylene generation). On the other hand, the method can be quite corrosive if it involves the application of strong acid catalysts. As a result, the production of DEE has a high potential during ethanol dehydration over supported catalysts like Cu-Fe/ZSM-5 (99.99% DEE specificity) (de Oliveira et al., 2018) and Ru/HBeta (99% DEE specificity) (Kamsuwan et al., 2017). Acetone (ACE) is utilised in numerous industries as a solvent, including the manufacturing of methyl methacrylate and bisphenol A (Silva-Calpa et al., 2017). The cumene technique, which is presently utilised in the production of acetone, not only uses the raw material derived from fossils but also produces low yields and requires a lot of energy (Niwa et al., 2002). As a result, a one-step procedure that is beneficial to the environment and uses bioethanol as the feedstock starting has been proffered (Eq. 2.6). The synthesis of acetic acid via steam reforming of ethanol over a CuO/CeO₂ catalyst at 653 K also produced ACE as a by-product (Nishiguchi et al., 2005). At a temperature of 400 °C, Nakajima et al. (1987) discovered that a ZnO-CaO catalyst (molar ratio = 9:1) had a significant catalytic performance for manufacturing ACE from ethanol. This catalyst demonstrated a 100% ethanol transformation and a 91% acetone specificity (Nakajima et al., 1987). Employing bioethanol as the feedstock in their subsequent trial, the researchers found that a Fe-Zn mixed metal oxide catalyst achieved 99.99% ethanol transformation and 94% ACE specificity at 713 K; however, the output of acetone declined by 34% after 24 hours (Nakajima et al., 1994). Similarly, the research conducted by Murthy et al. (1988) found that ZnO-promoted catalysts had a higher acetone specificity than MnO- and CaO-promoted catalysts, which deactivated more quickly.



Equation 2.6

It is also feasible to generate ethyl acetate (ETAC) directly from ethanol via the dehydrogenative and oxidative pathways (Gaspar et al., 2010). Both pathways involve a comparable process mechanism, where ethanol is initially transformed to acetaldehyde (MeCHO) by either non-oxidative direct dehydrogenation or partial oxidation. The resulting MeCHO then reacts with an additional ethanol or ethoxide species to produce a hemiacetal, which is dehydrogenated to form ETAC. Compared with esterification, the first procedure, which has already seen widespread use in industry, offers superior efficiency in terms of cost. Cu-based catalysts, including Cu/ZnO/ZrO₂/Al₂O₃ (Inui et al., 2002b, Inui et al., 2002a, Inui et al., 2004), Cu/m-ZrO₂ (Sato et al., 2013), Cu/Cr₂O₃ (Colley et al., 2005), and a physical combination of Cu/ZnO/Al₂O₃/ZrO₂ (Gaspar et al., 2010), are employed extensively in this process. With Cu/ZnO/ZrO₂/Al₂O₃ catalyst, a significant ETAC specificity of 93.0% was achieved (Inui et al., 2002a). On the other hand, the CuCrAl catalyst demonstrated an ethanol transformation and ethyl acetate specificity of approximately 60–65% and 98.8%, respectively (Carotenuto et al., 2013).

2.2 Reactors for Low Alcohol Conversion

The dehydration of ethanol to ethylene is an endothermic mechanism, and as a result, it needs a greater heat and reaction temperature; nonetheless, the reaction temperature significantly impacts the specificity of the desired product, ethylene. Moreover, ethylene, as a major product, is produced at a temperature greater than 300 °C, while the primary product, ether, is generated at a lower temperature (<300 °C). It is vital to choose and build a reactor suitable for ethanol dehydration to ethylene (de Moraes et al., 2011). Two types of reactors are primarily used for ethanol dehydration to ethylene production: the fixed bed and the fluidized bed reactor.

Fixed bed reactors are used for ethanol dehydration to ethylene production. In today's world, the fixed-bed reactor is mainly employed in industrial manufacturing (de Rezende Pinho et al., 2017). The fixed bed reactor is the most common type of reactor for a gas-solid catalytic process, and it is found in a broad range of applications in the chemical process industries (Andrigo et al., 1999, Jafari et al., 2008). Overall, there are two types of fixed bed reactors for the dehydration of ethanol to ethylene: the isothermal tubular and the adiabatic reactor. Historically, the isothermal column tube fixed bed reactor was employed in the operation of ethanol dehydration to ethylene, and it continues to be utilized in the majority of ethanol dehydration to ethylene production facilities currently in operation throughout the world. A disadvantage of the tubular fixed bed reactor is that it has weak temperature regulation

capabilities, and the restoration and substitution of the catalyst are also more complicated. Furthermore, the reactor is extremely sensitive to even the slightest alterations in the reaction process. For instance, even minor variations in the temperature of the raw materials are likely to cause reactors to become uncontrollable. This phenomenon is referred to as "parametric sensitivity" by researchers (Henning and Perez, 1986, Nargessi and Karimzadeh, 2021, Anastasov, 2002). From the 1950s until the 1980s, many studies investigated the tube-fixed bed reactor, but they could not completely resolve the issues in the reactor (Zhang and Yu, 2013). Based on their research, the adiabatic fixed bed reactor is assumed to be the most fundamental type of fixed bed reactor (Worstell, 2014, Durham et al., 2013). The feedstock and heat carrier should be introduced into the reactor at the same time, and the reaction should proceed in stages; that is, a multi-adiabatic fixed-bed reactor should be utilized to heat the reactants between the two reactors to make sure that both reactors achieve the process temperature, and that the reaction can proceed smoothly. Using a multi-parallel or a parallel series of adiabatic fixed bed reactor, Barrocas and de Assis (1980) were able to achieve increased temperature ethanol catalytic dehydration to ethylene conversion, with the heat needed for the process being supplied by steam that was introduced into the reactor along with feedstock. The research findings demonstrate that the reactor significantly increased ethanol transformation efficiency and ethylene production.

The fluidized bed reactor has only been in existence for a while. It can be employed in a multiphase chemical process and has several benefits, including an increased heat and mass transfer rate, a more homogeneous bed temperature, and a comparably steady operation. It is notably well-suited for commercial synthesis with a high thermal effect, and it has been successfully used in manufacturing facilities for a wide range of chemical products (Zhang et al., 2009). A Si–Al-oxide catalyst was used in a fluidized bed reactor, and the method was designed by Ladisch et al. (1979) to produce ethylene from ethanol catalytic dehydration. The one-way ethanol transformation rate was more than 99.5 %, and the ethylene production was higher than 99 % before distillation. Both were constantly greater than the values obtained using the tube-fixed bed process. A viable improvement potential exists for the fluidized bed reactor used to dehydrate ethanol to ethylene, but there are also critical issues to resolve. For example, there is a high likelihood that the catalyst (Si–Al–oxide) will be worn out due to friction and collision between catalyst particles, as well as collisions between catalyst particles and the reactor surfaces. The wear resilience of the catalyst requires enhancement.

2.3 Catalyst Synthesis Methods

It is possible to synthesise any finely divided systems, such as most solid catalysts, using one of two primary techniques: condensation or dispersion. Condensation is involved in developing a heterogeneous system from a homogeneous one due to combining molecules, atoms, or ions into aggregates. Dispersed solids can be formed by condensing either a liquid or a gaseous phase to form dispersed solids. This is called dispersion when macroscopic layers are crushed or powdered to microsizes (or colloidal sizes). It is essential to mention that all recognized conventional and novel catalyst synthesis techniques depend on these two concepts. However, the synthesis of catalysts, from the preparation of starter chemicals to the fabrication of an industrial product with a specific form and size, is a multiphase process that involves several steps. The name "catalyst preparation technique" comes from the critical phase that defines, to a significant extent, the primary properties of the final catalyst. Ordinarily, conventional techniques are described as those that have gained widespread acceptance (such as an industrial application). Conventional means of catalyst synthesis involve but are not limited to the techniques described below.

2.3.1 Precipitation and Co-precipitation

Precipitation from solutions (or co-precipitation from a multi-component process) involves the development of a gel or precipitate, accompanied by washing, drying, and heat treatment. These procedures should be seen as a subset of the condensation approaches used to produce powders and suspensions. Co-precipitation is preparing supported catalysts through metal co-precipitation with the support ions. This process typically results in thoroughly combining the catalysts and the support. Some researchers used this procedure (Sharma et al., 2017, Sun et al., 2012, Lewis, 2010, Mohammadi et al., 2021, Peng et al., 2021) in their studies, and they discovered that it was the most effective process for synthesising catalysts.

2.3.2 Sol-gel Technique

In the sol-gel procedure, particles are suspended in a liquid solution (a sol), which is then aged and dehydrated to produce a semi-solid suspension of particles in a liquid (a gel), which is then calcified to produce a mesoporous solid or powder (a mesoporous solid or powder). The sol-gel process consists of four independent steps (Teranishi et al., 1999): (i) the production of the gel; (ii) ageing to facilitate fine-tuning of the gel characteristics; (iii) dehydration to eliminate the solvent from the gel; and (iv) calcination to alter the physicochemical characteristics of the solid completely. By manipulating factors such as time, temperature, heating rate, and the

content of the pore liquid, the ageing and calcination processes precisely regulate pore size distribution and volume. A plethora of techniques can be used to introduce metallic nanocatalysts into the mesoporous framework. Two methods for incorporating nanoparticles into mesoporous materials are by introducing prefabricated nanoparticles to a sol-gel combination or by including the microemulsion, which generates the nanoparticles, into a premade mesoporous framework. Conversely, metal salts can be introduced during the gelation phase or after the creation of the mesoporous framework (Bronstein, 2003). An example of the former is the fabrication of Wox and Wox/Pt films, which were produced by synthesising ($\text{W}(\text{OC}_2\text{H}_5)_6$ and H_2PtCl_6) sol-gel solutions, accompanied by ageing and calcination (McLeod and Birss, 2005). One major limitation of this approach is that the catalytic nanoparticles may be buried within the framework instead of close to the pores. The particles must be placed close to the pores because otherwise, they will not be available to reactants or serve as effective catalysts (Bock et al., 2008, Ezinkwo et al., 2014).

2.3.3 Incipient Wetness Impregnation (IWI) and Wet Impregnation (WI)

The IWI, or capillary or dry impregnation, is a prevalent technique for fabricating heterogeneous catalysts by dissolving the active metal precursor in an aqueous or organic solution. It is then added to catalyst support that has the same pore volume as the metal-containing solution that was previously added. Capillary force is responsible for drawing the solution into the pores. When a solution is added in large amounts of the support pore volume, the solution transport changes from a capillary action to a diffusion phase, which is much more sluggish. To expel the volatile constituents within the solution and deposit metal on the catalyst surface, it is necessary to dry and heat the catalyst for a while (Ezinkwo et al., 2014). The solubility of the precursor in the solution plays a role in determining the highest loading. It depends on the mass transfer parameters within the pores during impregnation and drying to determine the concentration of the impregnated substance. Some of the authors referenced above have used this method. Their comparative study with other catalyst synthesis techniques showed that the impregnation approach is viable. Unlike the dry impregnation approach, which entails filling the pores of the adsorbent with a specific amount of solvent, the *wet impregnation* technique includes introducing an excess amount of solvent, more than the pore volume, accompanied by drying (Patel et al., 2016, Singh et al., 2016, Singh et al., 2018).

2.3.4 Microwave-assisted Hydrothermal Method of Catalyst Synthesis

The hydrothermal method simulates crystal development during the mineralization procedure in nature, in which the process is carried out in a closed environment using water as the solvent at a specific temperature and pressure. The characteristics of water, including its vapour pressure, density, surface tension, viscosity, and ionic product, will be significantly altered under hydrothermal circumstances. The hydrothermal crystallisation technique was employed as early as 1882 to generate crystals. It can substantially lower the process temperature of systems and synthesise high crystalline products with a narrow size distribution, increased purity, and reduced cluster. It is challenging to monitor the growth phase of materials in a closed environment since the reaction occurs there (Meng et al., 2016). A notable application of the conventional hydrothermal technique is the fabrication of $\text{Al}_2\text{O}_3/\text{Al}$, $\text{MO}_x/\text{Al}_2\text{O}_3/\text{Al}$, and $\text{M}^1/\text{M}^2\text{O}_x/\text{Al}_2\text{O}_3/\text{Al}$ cermets (where M^1 and M^2 are cations of catalytically active metals), a novel class of materials (Pakhomov and Buyanov, 2005). The synthesis of these materials depends on the partial oxidation of aluminium powder with water in a confined area, followed by the hydrothermal process with water or steam. Exchange activities at particle interaction sites and a rise in solid-phase volume result in a fine powder's aggregation into a structurally robust composite with a macroporous framework. The thermal degradation of the hydroxo compounds in air results in a composite in which metal particles are distributed equally throughout the alumina matrix, forming a microporous framework. Such composites hold great promise for fabricating a wide range of supports and catalysts that are both effective and efficient. However, the hydrothermal approach has several drawbacks, including considerable facility demand, a long process time, and high energy utilization (Ezinkwo et al., 2014, Pakhomov and Buyanov, 2005).

2.3.5 Vapour Deposition Techniques

These techniques rely on incorporating a starter material (a precursor of the active constituent) into a porous support, followed by the deposition of the active component on the surface of the support. These processes are also referred to as condensation approaches. This method can be classified into Chemical Vapour Deposition (CVD) and Physical Vapour Deposition (PVD).

2.3.5.1 Chemical Vapour Deposition (CVD)

The CVD method begins with vaporising the precursor, an inorganic constituent comprising the required metal (s) (Bock et al., 2008). The substrate is situated in a process chamber where the vaporised precursor is injected with a carrier gas and other gaseous reactants. The

precursors disperse or are transported to the surface of the substrate and adsorb there, where they break down thermally, forming a metallic coating. The precursor's purpose is to guarantee that any process by-products are gaseous and desorb into the gas phase during the process. CVD procedures depend on the pyrolysis of organic and inorganic volatiles with or without oxidizing reagents. Examples include the production of carbon black, technical carbon, and carbon-comprising composite supports of the Sibunit family of hydrocarbons (Teranishi et al., 1999). To synthesise dispersed powders of SiO_2 , TiO_2 , and other oxides, the vapour-phase hydrolysis or oxidation of the volatile chloride MeCl_4 is employed. The breakdown of metal carbonyls, such as nickel tetracarbonyl, allows for the production of metal particles with a size smaller than 4 nm (Bock et al., 2008).

2.3.5.2 *Physical Vapour Deposition (PVD)*

Mechanical processes, including cathodic sputtering and thermal procedures like evaporation, are classified under PVD designation (Antolini et al., 2007). For a PVD experiment to be successful, it must have the following four components: (i) it must take place in a vacuum, (ii) it must have a source of material to deliver to the target, (iii) it must have a substrate on which the film will be incorporated, and (iv) it must have an energy source to transfer the material from the source to the substrate. The techniques by which energy is delivered to the particles and how the energised particles are transferred to the substrate differ among the different forms of PVD. Evaporation PVD happens when the substance to be deposited is heated to a high temperature. The thermal formation of a molecular beam of the catalyst material occurs in a vacuum under controlled conditions (Harsha, 2005). A molecular beam is made up of atoms and molecules that are moving in a specific path without clashing. Molecular beam epitaxial (MBE) deposition is feasible when the environment is devoid of oil, and the substrate is atomically clean before applying the laser beam. Depositing alloys using evaporation PVD is problematic because the different elements' vapour pressures can vary. As a result, the incorporated film becomes more affluent in the less volatile species (Harsha, 2005).

2.3.6 *Mechanical Mixing (MM)*

In this method, the catalyst is synthesised by mechanically combining the compounds, followed by a paste and extrusion into shapes, and subsequently drying and heating process. Methodologies related to the mechanical mixing of constituents are utilized as a substitute for co-precipitation and deposition. Their benefit is that they generate little to no wastewater or emissions. The even distribution and homogenization of the beginning components,

accompanied by drying or calcination, are the most critical stages of the method. The fact that MM is fulfilled by little advantageous solid-phase production parameters than co-precipitation or calcination of heteronuclear complexes is a distinguishing characteristic of this category of techniques (Ezinkwo et al., 2014, Pakhomov and Buyanov, 2005).

It is imperative to note that this grouping of catalyst preparation techniques is just preliminary, even though it is quite useful in enabling the concepts of catalyst synthesis to be studied within the context of a single approach. This is because several sequential processes produce the end product (the catalyst), each proceeding via its procedures and obeying its guidelines. This categorization does not include catalyst shape, the most significant operation in fabricating a commercial catalyst (Ezinkwo et al., 2014). Moreover, when developing an industrial catalyst technology, it is necessary to employ a variety of several preparation procedures to achieve the best results. Based on the findings made by various researchers, it is possible to conclude that the effects of the catalyst synthesis approach cannot be ignored. Although other elements affect catalyst behaviour and efficiency, a more systematic study is needed to reduce the criticism in the literature on the subject. It is also necessary to pay more attention to the subject of the preferred technique for catalyst fabrication to achieve the highest possible output with enhanced catalytic performance.

In the present study, we used the hydrothermal synthesis method to fabricate the newly developed mesoporous HZSM-5 catalyst. This technique was selected because it facilitates the development of mesoporous materials with specific properties ideal for our study's requirements. The hydrothermal synthesis method allows for precise control over the catalyst's structure, porosity and other physicochemical properties ensuring its effectiveness and relevance for the intended applications.

2.4 Review of Catalysts for Low Alcohol Conversion into Fuels and Petrochemicals

Numerous catalysts have been applied in the conversion of low alcohols, and they are often classified based on their reaction phase. That is, systems in which the reactants and the catalyst are of the same phase are known as homogeneous (Zhao et al., 2021), whereas systems in which the reactant phase differs from that of the catalyst are known as heterogeneous (García-Serna et al., 2022). Irrespective of the reaction phase, catalysts have significantly contributed to the production of chemicals in industry, and this has invoked interest in researchers to synthesise novel catalysts through various methods such as metal doping, complex composites, and

catalyst supports (Kaninski et al., 2021). Interestingly, heterogeneous catalysts produce 85% of industrial chemicals, whereas homogeneous catalysts account for almost 15% (García-Serna et al., 2022). As such, optimisation of these catalysts has proved beneficial in the catalytic conversion of safe, renewable and readily available materials such as low alcohols (methanol, ethanol and propanol).

2.4.1 Homogeneous Catalyst and Classifications

Biorefining of low alcohols has sparked interest in recent years due to their application as fuel blends for diesel engines, where blends can consist of alcohols as high as 30% (Cesari et al., 2022). The application of these low alcohols as blends has drawn criticism due to their low lubricating properties, which negatively affect the durability of internal combustion (IC) engines. Proposed solutions to overcome this bottleneck involve the catalytic conversion of low alcohols, such as bio-ethanol, into higher alcohols or hydrocarbons that are both linear and branched (Cesari et al., 2022).

Homogeneous catalysts with high catalytic activity and selectively have been applied to upgrade ethanol into advanced biofuels. Amongst these, ruthenium, iridium and manganese are the commonly used homogeneous catalysts to better control yields and selectivity (Cesari et al., 2022). These homogeneous catalysts use the Guerbet reaction to convert low alcohols into biofuels and can be applied to a variety of alcohols, this reaction is also known as the *borrowed-hydrogen chemistry*. An interesting study by Black et al. (2006) used the Guerbet reaction to catalytically convert an alcohol substrate through the carbon-to-carbon bond formation to produce longer-chain alkanes. Although the Guerbet process has shown potential in the conversion of alcohols, the conversion of ethanol through homogeneous catalysts has faced challenges due to two drawbacks: 1) low alcohols (ethanol) tend to resist the dehydrogenation step, however, Carlini et al. (2003) has recommended creating alcohol mixtures (methanol/ethanol and methanol/ethanol/n-propanol) to alleviate this problem. 2) controlling the based-catalysed aldol condensation of acetaldehyde is challenging, which leads to the formation of oligomeric and polymeric species (Pang et al., 2016). A review of the homogenous catalysts used to convert ethanol into *n*-butanol is summarised in **Error! Reference source not found..** It should be noted that these homogeneous catalysts require mild reaction conditions compared to the heterogeneous catalyst, they achieved higher control on selectivity and yield towards advanced biofuels (Cesari et al., 2022).

Table 2-1. Comparative performance between homogeneous catalysts for the upgrading of ethanol to Guerbet products reported in the literature

Catalyst	Base	Conversion (%)	Yield (%)	Selectivity (%)	TON ^[b]	Ref.
Ir(acac)(cod)	NaOEt	41.0	21.0	51.0	1220	(Koda et al., 2009)
Ru-1	NaOEt	22.1	20.1	93.6	221	(Dowson et al., 2013)
Ru-2	NaOEt	31.4	28.1	92.7	314	(Dowson et al., 2013)
Ir	[Ni(Tp')(μ-OH)] ₂	37.0	34.0	99.0	185	(Chakraborty et al., 2015)
Ir (0.2) ^[a]	KOH	31.0	26.0	83.0	155	(Chakraborty et al., 2015)
Ir (0.1) ^[a]	KOH	34.0	28.0	80.0	340	(Chakraborty et al., 2015)
[{RuCl ₂ (η ⁶ - <i>p</i> -cymene)} ₂]	-	10.2	7.80	88.0	102	(Dowson et al., 2013)
[RuCl(η ⁶ - <i>p</i> -cymene)]Cl	-	11.0	9.30	90.7	110	(Dowson et al., 2013)
acac: acetylacetonate cod: 1,5-cyclooctadiene [Ru-1]: [RuCl(η ⁶ - <i>p</i> -cymene)[{bis(diphenylphosphanyl)methane}]Cl [Ru-2]: [{RuCl ₂ (η ⁶ - <i>p</i> -cymene)} ₂], additive: 2-(diphenylphosphino)ethylamine Tp': tris(3,5-dimethylpyrazolyl)borate [a] mol concentration of iridium [b] is the turnover number that is calculated based on moles of alcohol converted to Guerbet products per mol of iridium or ruthenium						

Several researchers have shown the potential of using homogeneous systems to catalytically upgrade low alcohols due to their high selectivity and activity. The complex catalysts used in these processes contain a precious metal (Ir, Ru) which is coupled with a strong inorganic base (KOH, NaOEt) (Wu et al., 2017). These systems proceed through the Guerbet reaction scheme. Through the use of palladium coupled with a sodium butoxide homogenous catalyst, Carlini et al. (2004) achieved the conversion of *n*-butanol to 2-ethyl-1-hexanol, where reaction conditions such as concentration of the strong base (sodium butoxide) and metal loading (palladium) were investigated. It was reported that the dehydrogenation of *n*-butanol was promoted by the presence of the precious metal (palladium), whereas the strong base facilitated the aldol coupling step. The intermediate product further reacted through the aldol condensation and rehydrogenation reactions to yield high-carbon alcohol (2-ethyl-1-hexanol). For comparative reasons, Carlini et al. (2003) extended the study to investigate a heterogeneous palladium catalyst coupled with sodium butoxide. The heterogeneous catalyst showed good activity during the conversion of *n*-butanol, however, excessive metal leaching occurred, and this

phenomenon was confirmed through recycling experiments which were similar to that of Carlini et al. (2003). The leaching out of the metal resulted in reduced catalytic activity.

2.4.2 Heterogeneous Catalyst and Classifications

The use of heterogeneous catalytic reactions in catalysis has enabled researchers to effectively and economically convert low alcohols into valuable chemicals and biofuels without any negative environmental impacts. Due to their traditional usage in the chemical industry, these heterogeneous catalytic reactions have shown potential in the application of biotechnology, nanotechnology and green chemistry. Furthermore, compared to homogeneous catalysts, heterogeneous catalysts are responsible for producing most chemicals and over 20% of all industrial products (Wang et al., 2022). Heterogeneous catalysts are water-insoluble, environmentally friendly, non-corrosive to equipment and reusable; thus, they are considered a green sustainable alternative due to their ability to avoid using harmful substrates and producing toxic wastes. The most commonly used heterogeneous catalysts include transition metal oxides, rare earth metals, supported metal catalysts, hydroxyapatites (HAP) and zeolites (Sun and Wang, 2014, van Deelen et al., 2019). The choice of catalyst used depends on the targeted products since each heterogeneous catalyst will have a specific reaction pathway to produce the targeted product. Various studies have been conducted to upgrade low alcohols into other useful chemicals catalytically. The subsequent sub-sections intend to review the common heterogeneous catalysts used to upgrade low alcohols.

2.4.3 Classifications of Heterogeneous Catalyst for Low Alcohol and Olefin Conversion to Hydrocarbons – Catalyst Review

2.4.3.1 Transition Metals and Metal Oxides Catalysts

Given the commercial significance of the synthesis of linear alpha olefins (LAO), a process that is frequently conducted utilizing homogeneous catalysts, researchers have "navigated the periodic table looking for potential transition metal and lanthanide-inclined olefin polymerization systems" (Small, 2015). Metal-based catalysts for catalysis, including olefin oligomerization, commonly employ a Cossee-Arlman 1,2-insertion technique (Arlman and Cossee, 1964) to catalyze the reaction. According to the synergy, the olefin fits into the metal-hydride or metal-alkyl bond with the least replaced carbon linked to the metal. A vinylidene-replaced product is produced due to this process, which is typically followed by β -hydride removal. Since tremendous steric relationships with the alkyl chain on the incoming olefin prevent olefin coordination before insertion, several catalysts can only oligomerize ethylene or

1-olefins. Since metals often exhibit substantially greater reactivity towards ethene than exchanged olefins, most of the research has concentrated on ethene oligomerisation, with some investigations also employing propylene (Svejda and Brookhart, 1999, Olivier-Bourbigou et al., 2020).

2.4.3.1.1 Nickel-based Catalysts

Various metals have been used as catalysts for olefin oligomerization, although nickel is the most used metal, as well as the homogeneous catalysts employed in the well-known Shell High Olefins Process (SHOP) (Turner et al., 1990). Nickel catalyst has been widely recognized as applicable in oligomerization since the early exploration of the Aufbau reaction (Finiels et al., 2014). Several complexes have been studied and lately examined due to the potential to precisely tune the structure-characteristics connections in the SHOP kind Ni complexes by making modest adjustments to the ligands (Kuhn et al., 2007, Speiser et al., 2005). Nickel-catalyzed olefin oligomerization has a long track record. The finding of the “nickel effect” by Wilke (2003) was the commencement of the substantial milestone by Ziegler, who demonstrated that nickel salts could adjust the result of an AlR_3 -catalyzed “growth reaction”. Nickel has been a critical component of recent transition metal catalysis for olefin oligomerization and polymerization since its emergence in the 1960s, and it is among the most investigated metals in this research area by academia and industrial laboratories (Gao et al., 2013). The emphasis has primarily been on ligand development. Phosphorus, nitrogen, and/or oxygen heteroelements have all been described as multifunctional ligand support. Many nickel(II) pre-catalysts have been reported, revealing surprisingly diverse interaction chemistry. Neutral and cationic nickel catalysts are the two primary groups of active nickel species identified hitherto and categorized based on the type of ligand bonding within the nickel metal. Cationic nickel active species (type A) are highly electrophilic and electronically unsaturated. They are nickel (II)-based, contain a donor ligand, and have a square planar shape. Due to their high reactivity, they are not easy to separate (Olivier-Bourbigou et al., 2020). Wilke et al. (1966), however, isolate cationic π -allyl nickel complexes, which can be used as a prototype for this active species. It should be noted that the neutral π -allyl nickel halide complexes are not olefin-active. They are active homogeneous catalysts for the dimerization of ethylene and propylene and the polymerization of butadiene when paired with Lewis acids such as aluminium halides. The development of an electrophilic cationic metal center and a free linkage location on the nickel where the olefin can integrate occurs when the halide is

transferred from nickel to aluminium. The electrophilicity of neutral nickel catalysts (type B) is lower than that of cationic nickel catalysts (Olivier-Bourbigou et al., 2020).

Light olefin oligomerization is a practical approach for producing a variety of essential intermediates for fuel, petrochemistry, and fine chemistry. Nickel's extensive and unusual reactivity with unsaturated chemicals has made it a breakthrough in olefin oligomerization in homogeneous and heterogeneous catalysis, research, and commercial perspectives. Nickel, unlike other prevalent metals in oligomerization, including titanium and chromium, can oligomerize not just ethylene but also propylene and butenes, two traditionally complex alkenes with respect to catalytic oligomerization. Because of their versatility, nickel-based catalysis can convert light olefins into specialized high products. The most challenging aspect of Ni-catalyzed oligomerization of short olefins is specificity. However, the distribution pattern of longer olefins, linearity and the double bond placement are all crucial in terms of the product's characteristics and applications. When ethylene is to be oligomerized, the strong reactivity of Ni with propylene and butenes has the unintended consequence of weaker specificity regulation. Over the years, many studies have strategically developed ligands and solid supports for homogeneous and heterogeneous catalysis to optimally regulate oligomerization processes and selectivities, particularly with ethylene. However, determining these framework/activity/specificity correlations and recognizing and developing Ni active sites and pathways to select the best nickel conditions and process parameters for optimal application has proven highly difficult and time-consuming. While preferential propylene oligomerization was the primary purpose for fuel synthesis in the past decades, market shifts have created new hurdles for nickel in the years ahead, as consumption for critical petrochemical products, including short linear alpha-olefins, 1-butene, 1-hexene, and 1-octene grows. As a result, their preferential and on-purpose ethylene synthesis represents an attractive study field for the coming years. Moreover, Ni-catalysed olefin oligomerization offers an opportunity to identify the differences between homogeneous and heterogeneous catalysis: active site and process discrepancies, outlining correlation and discrepancies, can subsequently contribute to the development of effective, specialized, and reliable catalysts for future commercial growth (Olivier-Bourbigou et al., 2020).

The commercial demand for linear low-density polyethylene (LDPE) and high-density polyethylene (HDPE) is determined by the need for short-chain LAOs in the C₄-C₈ range (1-butene, 1-hexene, and 1-octene). These three Linear Alpha Olefins (LAOs) are the ethylene

co-monomers used to make specialized polyethylene. As a result, one of the primary obstacles for Ni-catalysed ethylene oligomerization is achieving their specific synthesis from ethylene beyond the typical Schulz-Flory distribution produced from SHOP-type processes. Homogeneous and heterogeneous catalysis are the two basic approaches to these setbacks. The homogenous technique has benefited from the diversity provided by the ligand environment, contributing to the breakthrough of the oligomerization of ethylene, propylene, and butene. Nickel-based heterogeneous catalytic systems, on the other hand, are solely used to produce octenes from butene dimerization. Thus, from a heterogeneous standpoint, developing specific and reliable heterogeneous mechanisms for the catalytic oligomerization of the shortest olefins, particularly ethylene, is a serious concern. The historical background of nickel in olefin oligomerization demonstrates the significance of the synergy between scientific knowledge and advancements reported in the patents, followed mainly by equivalent commercial growth. It is also clear that although Ni-catalyzed olefin oligomerization is a study area that began more than 50 years ago, it is still in progress, with many unanswered issues and concerns (Lutz et al., 2021, Olivier-Bourbigou et al., 2020).

Ethylene oligomerization over Ni-based catalysts has been studied in static, slurry, and dynamic reactors across various temperatures (from 20 to 360 °C) and pressures (from 0.4 to 40 bar). The process parameters strongly influence the activity/productivity, oligomer dispersion, and catalyst characteristics. NiO on supports is a weak catalyst for ethylene oligomerisation: yield was less than 3.5 g.g⁻¹ h⁻¹, and TOF values ranged from 5 to 33 h⁻¹. Improved outcomes were achieved with Ni-exchanged alumina: productivity of up to 11.5 g.g⁻¹ h⁻¹ and TOF of up to 1500h⁻¹. Ni-zeolites (Ni-Y, Ni-Beta, Ni-MCM-22) with just micropores had reasonable reactivity, whereas solids containing both micropores and mesopores, such as Ni-Y (Si/Al = 30) and Ni-MCM-36, had an outstanding performance with TOF=10,500 h⁻¹ and 16,000h⁻¹, respectively. Ni-exchanged mesoporous materials with MCM-41 and MCM-48 topologies were the most effective catalysts. Ethylene yields of 110 to 158 g.g⁻¹ h⁻¹ and TOFs of 15,700 to 47,380h⁻¹ were recorded in a batch process at 150°C and 35 bar (Lallemand et al., 2007, Lacarriere et al., 2012). The catalyst and the reaction mechanism and conditions influenced the oligomer's form. Based on these indicators, ethylene oligomerization can be guided to dimers (C₄) (Pae et al., 2006, Sohn et al., 2007, Sohn and Park, 2002), intermediate olefins (C₆–C₁₀) ((Hulea and Fajula, 2004, Lallemand et al., 2006, Lallemand et al., 2008a, Lallemand et al., 2008b, Scurrrell, 2001) or diesel range

products (Martínez et al., 2013, Lavrenov et al., 2015). Table 2.2 shows a review of nickel-based catalysts for olefin oligomerization.

Table 2-2. Review of Ni-based Catalysts for Olefin Oligomerization

Feedstock	Operating Conditions	Catalyst Type	Products	Inference	Ref.
Ethylene	10-30bar, 2hr, 20g of catalyst, 2°C min ⁻¹ heating rate, 5-60°C	<i>Ni-based (meso-CTF and micro-CTF), imine-linked porous organic network (IL-PON)</i>	C ₆ ⁺ olefins (C ₆ -C ₂₀)	The textural characteristics of the support are an essential factor in product composition, with meso-CTF and IL-PON showing a strong preference for long-chain olefins and a higher amount of deactivation build-up on the catalyst under process parameters.	(Rozhko et al., 2017)
Ethylene	5g NiAlKIT-6, 1-20bar, 250 – 350°C, 0.28 – 1.12h ⁻¹ WHSV	NiAlKIT-6 catalyst	C ₈ ⁺ hydrocarbons	Improved ethylene transformation (>95%) and C ₈ ⁺ specificity (55%) were achieved with higher Si:Al ratios and Ni loadings, although increased alumination altered the pore structure and hence lowered catalytic performance.	(Panpian et al., 2021)
Ethylene	200 °C, 1-15 h, N ₂ flow at ATM, 1000rpm	Ni-MCM-41 and H-MCM-41 catalysts	C ₄ -C ₁₀ ⁺	With simultaneous co-oligomerization with a combination of Ni-MCM-41 and H-MCM-41 catalysts at a prolonged reaction period (15 hours), ethylene transformation yielded a significant amount of product (58%) with long chains up to c18 and a Poisson-type distribution.	(Lacariere et al., 2012)
Ethylene and 1-hexene	Feedstock supplied at 0.025 mL min ⁻¹ , 0.5 g (2.0 h ⁻¹ WHSV) of catalyst at 35 bar and 200°C at 200 – 1000 mins	NiH- and H-forms of ZSM-5 and beta zeolite catalyst	C ₁₀ ⁺	Results show that the zeolite catalyst's small crystal size and mesoporosity are essential to enhance diffusion restriction during light-olefin oligomerization. Main oligomeric product specificity shifted to C ₁₀ ⁺ hydrocarbons in connection with this development.	(Moon et al., 2018)
Ethylene	80 – 360°C, 3.5 MPa and 2h ⁻¹ of WHSV	Ni-supported Silica Alumina	C ₁₀ ⁺	Significant ageing temperature, low Si/Al ratio and high activation temperature benefited an increased preference for C ₁₀ ⁺ hydrocarbons.	(Chen et al., 2020)

2.4.3.1.2 Zirconia-based Catalysts

Li et al. (2004) describes ZrO_2 as a distinct mesoporous metal oxide with certain chemical characteristics (acid, base, and redox features) (Setoyama, 2006). The function of acid sites is to dehydrate ethanol, which then results in the synthesis of ethene while the basic sites dehydrogenate ethanol, forming acetaldehyde and subsequent hydrogenation to produce propylene. As a result, ZrO_2 with both sites (acidic and basic) can facilitate ethanol conversion into various compounds (Xia et al., 2017a). Zirconia has demonstrated excellent performance in ethanol dehydration and has attracted much attention. Sato et al. (Sato et al., 2012) studied the effect of different catalysts (Cu/SiO_2 , $\text{Cu/Cu}_2\text{O/SiO}_2$, and Cu/ZrO_2) on ethanol conversion into petrochemicals. All processes were carried out in a fixed bed reactor at $T=473\text{--}548\text{ }^\circ\text{C}$, $P=1\text{--}10\text{ bar}$, and $\text{WHSV}=29.1\text{ g}_{\text{cat}}\text{h/mol}_{\text{EtOH}}$. It was found that the highest ethylene and acetaldehyde selectivities of 17% and 54%, respectively, with the highest conversion of ethanol (57%) recorded at $498\text{ }^\circ\text{C}$ over Cu-modified zirconia. Acetaldehyde was the most abundant product generated in this experiment. When heated to $523\text{ }^\circ\text{C}$, the $\text{Cu}_2\text{O/SiO}_2$ catalyst yielded acetaldehyde with complete selectivity and just 15% ethanol conversion (Sato et al., 2012). Moreover, Phung et al. (2015a) studied the catalytic performance of some catalysts in ethanol conversion, including $\text{MgO-Al}_2\text{O}_3$, SiO_2 , ZrO_2 , TiO_2 , Al_2O_3 , $\text{WO}_3/\text{MgO-Al}_2\text{O}_3$, WO_3/SiO_2 , WO_3/ZrO_2 , and WO_3/TiO_2 . The catalytic process was conducted with 0.5 g of catalyst at $P=1\text{ bar}$ and $T=150\text{--}500\text{ }^\circ\text{C}$. It was observed that ethylene production improved to 99 % with the WO_3/ZrO_2 catalyst at $350\text{ }^\circ\text{C}$ while the commercial WO_3/TiO_2 catalyst demonstrated a 93 % ethylene production at $250\text{ }^\circ\text{C}$. The generation of DEE plateaued at $150\text{ }^\circ\text{C}$ and then began to decline with a subsequent increase in temperature. Ethanol conversion on metal oxides occurred in the following order: $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{ZrO}_2 > \text{MgO-Al}_2\text{O}_3 > \text{SiO}_2$. In the study, 100% ethanol conversion was obtained using a variety of catalysts; however, only the commercial WO_3/TiO_2 catalyst demonstrated 100 % transformation at $250\text{ }^\circ\text{C}$, which was the lowest temperature tested. Compared to the study of Sato et al. (Sato et al., 2012), Phung et al. (2015a) recorded considerable ethylene production due to the promotion of ZrO_2 with WO_3 . Furthermore, the findings from Phung et al. (2015a) show that the introduction of WO_3 to ZrO_2 and TiO_2 leads to a substantial increase in Brønsted acid sites and a decrease in the generation of by-products, including acetaldehyde and higher hydrocarbons, which in turn promotes ethylene yield. It can be deduced that W-doped zirconium catalysts exhibit improved catalytic performance.

Xia et al. (2017b) employed a co-precipitation approach to prepare a yttrium-modified zirconia catalyst. The operating parameters for ethanol conversion in a fluidized bed reactor were $T=550\text{ }^{\circ}\text{C}$, $P=11.1\text{ bar}$, $W/F=0.05\text{ g.min/mL}$, and employing 0.7 g catalyst. When Y doping was increased from 0 to 3 wt.%, the ethanol transformation initially improved from 91 to 98 %, then reduced to 95 % when Y doping increased from 4 to 5 wt.%. In the presence of 2 wt % Y, the ethylene production increased from 33 to 35 % and then declined to 30.7 % in the presence of 2 to 5wt % Y. Propylene production rose above 40 % with an increment in yttrium doping (0 to 3 wt.%) and subsequently declined to 39 % with a rise in Y loading (4 to 5 wt.%). Moreover, Y-doped zirconia has outstanding textural qualities, which favour catalytic performance, as demonstrated by the study (Xia et al., 2017b). Wang et al. (2018a) synthesised a Y-doped zirconia catalyst for ethanol to transform propylene by co-precipitation with varied Y contents. This experiment was performed in a fluidized bed reactor with operating conditions similar to Xia et al. (2017b). When using parent ZrO_2 , ethylene and propylene yields were 44% and 33%, respectively. However, with 0.01% Y/ ZrO_2 , the yields were 35% and 42%, while 0.03% Y/ ZrO_2 recorded 33% and 44%, respectively. Conclusively, it is evident that varying Y concentration affects the catalytic activity and product yield. Increasing Y doping over ZrO_2 leads to a decline in ethylene yield with increased propylene synthesis (Wang et al., 2018a).

The isomorphous incorporation of Zr or other transition metals (Ni, Co, Fe, and Mn) into the zeolite structure is crucial in altering the physicochemical properties of supported catalysts such as SAPO-34 (Ali Zeinali et al., 2020, Varzaneh et al., 2016, Varzaneh et al., 2015). As a result of this modification, the SAPO-34 samples incorporated with metal often showed improved catalytic activity and longer lifetimes (Varzaneh et al., 2016). The combined effect of the catalytic abilities of these metal-active phases with the acidic sites of SAPO-34 causes the formation of bifunctional catalysts with interestingly high catalytic performance. To investigate the effects of hierarchical Zr/SAPO-34 and ZrAPSO-34, the MTO reaction was carried out at $430\text{ }^{\circ}\text{C}$ and atmospheric pressure by Ali Zeinali et al. (2020). The initial methanol conversion over the tested Zr-doped catalysts was the same and corresponded to about 100%. On the other hand, it was observed that the lifetime of the different catalysts in the MTO process was very different. The steady methanol conversion for SAPO-34 was 140 min, while it increased for ZrAPSO-34 (201 min) and decreased for Zr/SAPO -34 (125 min). This indicates that adding Zr to SAPO-34 through the process of isomorphous substitution can extend the catalytic lifetime of SAPO-34 in the MTO process. The weight losses due to coke combustion in SAPO-34, ZrAPSO-34 and Zr/SAPO-34 were about 15.91, 13.66 and 12.82%, respectively

(Ali Zeinali et al., 2020). According to these results, the amount of coke formed on the Zr-doped SAPO-34 catalysts was lower than that on the unmodified SAPO-34 catalysts. A decrease in the amount and strength of acid sites may be responsible for the increased lifetime of ZrAPSO-34 during the MTO reaction. The rate of chemical reactions and coke formation may be slowed down by decreasing the strength of acid sites. On the other hand, the acid sites become more distant from each other as the population decreases. This results in fewer successive chemical processes along the path taken by the intermediates during diffusion, which slows down the rate of coke formation (Hu et al., 2019). The review of zirconia-based catalyst for low alcohol conversion at varying process conditions is shown in Table 2.3.

Table 2-3. Review of Zirconia-based catalyst for low alcohol conversion

Catalyst	Process	Catalyst Synthesis Methods	Operational Conditions	Results (%)			Inference	Ref.
				X	S	Y		
Zr _{0.05} APSO-34	MTO (E+P)	HTM	T=400 °C, GHSV = 10,500 cm ³ /g _{cat} h, M _c =0.4 g	100	61+27	-	Increasing the reaction temperature leads to an increase in ethylene and a decrease in propylene selectivity.	(Aghaei et al., 2016)
Sulfated Zr (S-Zr)	MTO (E+P)	PIM	T=160 °C, M _c =2 g	41	94+0	-	Formation of C ₃ H ₆ requires the participation of a third carbon atom (*-CH _x), which is not offered by S-Zr catalyst. (* = surface site)	(Hussain et al., 2006)
Si-doped S/Zr	MTO (E+P)	PIM	T=160 °C, M _c =2 g	52	86+10	-	Compared to the unmodified catalyst, Si-doped S-Zr was more stable and less susceptible to sulfate leaching.	
Sr-ZrO ₂	ETE	CPM	T =450 °C, P =11 bar, M _c =0.7 g, W/F =0.05 g·min mL ⁻¹	99	43	42	The addition of alkaline earth metals resulted in a rise in ethylene synthesis, ascribed to the increased presence of strong acid sites.	(Xia et al., 2018a)
La-ZrO ₂	ETP	CPM	T =450 °C, P =11 bar, M _c =0.7 g, W/F =0.05 g·min mL ⁻¹	94	45	42	The considerable increase in process efficiency observed with La/ZrO ₂ catalysts can be attributed to the coordination of redox and acid-base characteristics.	(Xia et al., 2020)
ZrO ₂	ETP	PM	T =450 °C, P =11.1 bar, M _c =0.7 g, W/F =0.01-0.08 g·min mL ⁻¹	98	36	35	ZrO ₂ improved the efficiency of ETP conversion.	(Xia et al., 2017a)

Y-ZrO ₂	ETP	CPM	T=450 °C, P =11.1 bar, M _c =0.7 g, W/F =0.05 g·min mL ⁻¹	98	45	44	The efficiency of Y/ZrO ₂ with either a tetragonal framework or a higher surface area was significantly improved.	(Xia et al., 2017b)
Y-ZrO ₂	ETP	CPM	T =450 °C, P =11 bar, M _c =0.7 g, W/F =0.05 g·min mL ⁻¹	-	-	44	The substantial enhancement in process activity over Y-doped ZrO ₂ catalysts is due to the coordination of acid-base characteristics.	(Wang et al., 2018a)
WO ₃ -ZrO ₂	ETE	IM	T =500 °C, P =1 bar, M _c =0.7 g	100	100	100	The introduction of WO ₃ to ZrO ₂ creates strong Brønsted acid sites, acts as the active sites in the process and suppresses the creation of byproducts, acetaldehyde and long-chain HC.	(Phung et al., 2015b)
Cu ₂ O-ZrO ₂	ETE	IM	T =200-275 °C, P =1 bar, W/F =29 g·min mL ⁻¹	57	30	17	The behaviour of the catalyst indicates that very strong and mildly acidic (+ highly basic) sites were critical for ethanol dehydration and dehydrogenation, respectively.	(Sato et al., 2012)
HPW-Ce _{0.8} Zr _{0.2} O ₂	ETE	IM	T =300 °C, WHSV=17h ⁻¹	100	100	100	Catalysts have been shown to produce less coke deposit and have a longer lifespan.	(Clemente et al., 2019)
MoO ₃ -ZrO ₂	ETE	IM	T =380 °C	98	69	100	An increase in % loading (up to 15 wt.%) of MoO ₃ improved the surface area, with further addition of MoO ₃ resulting in a reduction in N ₂ -S _{BET} .	(El-Sharkawy et al., 2007)
SiO ₂ -ZrO ₂	ETE	IM	T =380 °C, P =11.1 bar	100	96	96	Incorporating Si leads to a considerable increase in the surface area and the total number of acidic sites.	(Xia et al., 2018b)

Processes: ETE – Ethanol to Ethylene; ETP – Ethanol to Propylene, MTO (E+P) – Methanol to olefin (Ethylene and Propylene)
Catalyst Synthesis Methods: CPM – Co-precipitation method; PM – Precipitation Method; IM – Impregnation Method; HTM – Hydrothermal Method;
PIM - Precipitation-Impregnation Method
Results: X, S, Y – Conversion, Selectivity, and Yield, respectively
W/F & WHSV – Space velocity; M_c – Catalyst weight

2.4.3.1.3 Aluminium

For the first time in 65 years, Ziegler's invention of the Aufbau process provided the initial evidence that metals might be used to accelerate the creation of CC bonds from olefins (Ziegler, 1952). Introducing ethene into an aluminium alkyl results in a pseudo-Poisson distribution of even-numbered carbon olefins, which is utilized as the principal technique of synthesizing linear alpha olefins (LAO) (Lutz et al., 2021). Both the Gulfene (now Chevron Phillips AlphaPlus®) and the Ethyl (now Ineos) technologies use solution-based procedures with trialkyl aluminium as the primary promoting species (Nicholas, 2017). According to current findings, heterogeneous catalysts with surface Al-H moieties can also be used for ethene incorporation and chain elongation in addition to these improved solution-phase reactions (Mazoyer, 2010, Werghi et al., 2018).

2.4.3.1.4 *Titanium and Hafnium*

The group metals IV (titanium, zirconium and hafnium) have been employed in the oligomerization process. Another most often used metal is zirconium, which is widely recognized for its catalytic role in olefin polymerization (Makio and Fujita, 2009). To manufacture oligomers instead of polymers, chain transfer reagents such as trialkyl aluminium or impediments, including thiophene or aryl ethers, are used to regulate the molecular weight of the final product. This basic principle is used by several commercialized LAO processes, such as those from Idemitsu (Tanaka et al., 2003), the Alpha-Sablin process from Sabic/Linde (Meiswinkel et al., 2011), and the Alphaselect method from IFP-Axens (Forestière et al., 2009). They can operate at mild pressures of 20–40 bar and relatively reduced temperatures of 298–100 °C. A detailed investigation into the nature of the reaction has revealed that rather than β -hydride removal, chain transfer to monomer can be used to promote the narrow carbon number distributions of olefin oligomers (Hessen and van der Heijden, 1996). The insertion of ethene into the Hf complex is 40 times more sluggish than the insertion of ethene into the Zr complex, as demonstrated by Hessen and van der Heijden (1996), resulting in low total efficiency. With the use of a $[\text{Cp}^*\text{2M}(\text{CH}_3)_2(\text{tetrahydrothiophene})][\text{BPh}_4]$ catalyst system, it was observed that propene inserted into Hf-CH₃ more slowly than it did into Zr-CH₃ (Eshuis et al., 1992). Moreover, the Zr catalyst yielded a broad spectrum of oligomers ranging from C₆ to C₂₄, whereas the Hf catalyst formed only one isomer of the C₆ and C₉ carbon atoms. It has been demonstrated that heterogeneous zirconium catalysts may be used in oligomerization operations in addition to homogeneous processes. Zr-H systems generated by combining organometallic precursors with hydroxyls of silica-alumina support, accompanied by H₂ treatment to hydrogenolyze residual Zr-C bonds, dimerize 2-butene to produce mono- or di-branched octenes with high efficiency (Szeto et al., 2015).

Until the Zr/Hf-based catalysts were established, titanium was an essential metal for oligomerization. Ziegler described one of the earliest catalytic methods for dimerization of ethene to one-butene, employing Ti(OBu)₄ and trialkyl aluminium (Ziegler et al., 1960). Titanium alkoxides are the catalytic precursors still used today, in conjunction with aluminium alkyls, to manufacture linear butenes on a commercial scale, such as in the AlphaButol process, to generate linear butenes (Forestière et al., 2009).

2.4.3.1.5 *Vanadium and Tantalum*

The homogenous vanadium complexes (of group V) chelated with nitrogen-based ligands have demonstrated significant (>90%) specificity for 1-butene or 1-hexene in ethylene oligomerization (Lang et al., 2010, Schmidt et al., 2004). V and V(III) complexes have been found to work in tandem for the ethene oligomerisation to Schultz-Flory distributions of olefins. The size of imido substituents in V(V) complexes is crucial in determining oligomerization, with smaller substituents resulting in polyethylene rather than oligomers (Zhang and Nomura, 2010). When examined with ethylene and a larger olefin, one of the few studies found that V(III) complexes reacted much less with propylene than ethylene (Lang et al., 2010). The steric bulk of the ligands also influences the 1,2- versus 2,1-insertion of the second propylene, demonstrating once more that steric contacts, both between the ligands and the entering olefin, contribute substantially to the specificity of oligomers in both group IV and group V catalysts. However, to enhance oligomerization, all vanadium compounds are activated with methyl aluminoxane (MAO) (Negureanu et al., 2006), a process that has a complex and time-consuming effect on oligomerization operation and efficiency (Schmidt et al., 2004). During this activation stage, V-alkyl and/or -hydride species are generated, which are thought to be responsible for the appreciable catalytic activity (Nomura and Hou, 2017). As observed earlier, assisting these complexes with supports triggers a substantial improvement in the molecular weight of the final yield (Romero-Fernández et al., 2010).

Tantalum has also been used, with the Ta-H process synthesised in the same manner as Zr-H systems demonstrating a combination of dimerization and metathesis activity at 423 K, similar to Zr-H systems (Szeto et al., 2015). Moreover, metathesis is more favourable at elevated temperatures, but oligomerization is more favourable at reduced temperatures (Mazoyer et al., 2010). A species was created by grafting $\text{Ta}(\text{CH}_3)_3\text{Cl}_2$ onto partly dehydroxylated silica that, when exposed to ethene, decreases to a Ta^{III} intermediate that contains two chloride ligands as well as one siloxy bridge to the surface (Chen et al., 2012). It is trigonal bipyramidal in shape and specificity to 1-hexene during ethylene polymerization. Heat treatment of the silica-supported Ta-H catalyst mentioned above forms a silica-supported Ta^{III} species that polymerizes ethylene, a phenomenon attributable to a square pyramidal coordination system (Chen et al., 2013).

2.4.3.1.6 Cobalt- and iron-based catalysts

Cobalt oxides (CoO) supported on carbon base were used to dimerize 1-butene into straight octenes to manufacture linear oligomers from 1-olefins. The researchers successfully produced linear oligomers from 1-olefins with up to 80% specificity for linear octenes (Xu and Yoshikai, 2016). Linear octenes might be generated from 1-butene by 1,2-insertion followed by 2,1-insertion or by collapsing a 1,4-disubstituted metallacycle. Cobaltocyclopentanes were recommended as the catalytic intermediary because the mixed oxidation state oxide Co_3O_4 was the most active precatalyst (Xu and Yoshikai, 2016). The same catalysts had earlier been used in a series of studies to dimerize various compounds, with a Co-H species serving as the crucial intermediate in each case (Nicholas, 2017). While the exact pathway of the reaction and the existence of catalytically active species is still questionable, it was evident that these CoO-on-carbon catalysts exhibit more specificity for linear products than most other oligomerization catalysts.

While Fe complexes are well recognized as viable olefin polymerization catalysts, various Fe complexes, frequently collaborating with chain exchange agents, have demonstrated potential as oligomerization catalysts (Small, 2015). The dimerization selectivity of several bis(imino)pyridine (PDI) ligands for a 1-butene feed at reduced temperature is exceptional, with the ligands producing either iron or copper complexes. In this case, the Cossee-Arlman process is assumed, with a 1,2-insertion into the metal hydride and a 2,1-insertion to generate a linear dimer, which is subsequently accompanied by a β -H removal (Small, 2015). In addition to 1,10-phenanthroline, several other versions of this ligand have been produced, with some of the 1,10-phenanthroline derivatives exhibiting some intriguing selectivity trends towards monomers in ethene oligomerization (Zhang et al., 2013). Cariou and Shabaker (2015) lately demonstrated that iron-bipyridyl complexes, in conjunction with ZnEt_2 and the Fe-PDI catalyst, can regenerate the ZnEt_2 chain transfer agent and provide a single-pot ethylene oligomerization process. Moreover, increased concentrations of ZnEt_2 result in greater specificity for oligomerization, but at the expense of product α -olefin purity (Cariou and Shabaker, 2015).

The Fe and Co precatalysts containing tridentate ligands are favourable for ethene oligomerization owing to their benefits, such as increased performance and specificity for linear olefins, whereas the polyethene formed during the polymerization process supplied distinctive materials with long-chain vinyl-type linearity. In addition to bis(imino)pyridyl iron

and cobalt procatalysts, there are a variety of other procatalyst models that exhibit excellent activity and selectivity, such as alumina. Most notably, some catalyst models demonstrated great activity and selectivity for ethylene oligomerization while being very selective for α -olefins. However, despite small quantities of polyolefin waxes, the reaction involving such catalysts appears viable due to waxes with low molecular fractions. Generalized polyolefins with a high molecular weight, such as polyolefins, have the potential to clog up the pipelines of the ethene oligomerization operation. Moreover, the ease with which Fe and Co procatalysts may be synthesised, their relative stability, and their decreased toxic effects are all significant realistic major benefits.

2.4.3.2 *Alumina and Silica-alumina Catalysts*

The elevated internal surface area of $50\text{--}300\text{m}^2\text{g}^{-1}$ of alumina catalyst and its excellent stability to thermal processing at $600\text{ }^\circ\text{C}$ make alumina catalyst a commercially essential catalyst (Chorkendorff and Niemantsverdriet, 2017, Cesteros et al., 1999). Unimolecular and bimolecular approaches to lower olefins are available for the dehydration of alcohols, including ethanol over an Al_2O_3 catalyst (Knözinger, 1968), although both methods produced water as a by-product. As a result, this catalyst is employed for alcohol conversion irrespective of a catalytic site or occurrence of molecular process. Alumina-platinum catalyst (AP24) was utilized for reductive ethanol dehydration in a study by Yandieva et al. (2010a). The transformation of ethanol was conducted in a fixed bed catalytic reactor at $350\text{ }^\circ\text{C}$ and $P=5\text{ MPa}$ under controlled conditions. It was found that the introduction of γ -alumina recorded 60% ethanol to ethylene conversion, with 4.5 and 30 wt.% DEE and ethylene selectivity, respectively. However, the selectivity of ethylene and DEE reduced to 14.1% and 1.3% when using Pt/alumina and the yield of ethylene increases with the production of $\text{C}_4\text{--C}_{10}$ alkanes, as reported by Yandieva et al. (2010a). Furthermore, contrary to Yandieva et al. (2010a), DeWilde et al. (2013) demonstrated that ethanol dehydrates when it reacts with alumina at lower temperatures and pressure. The reaction performed at $T=215\text{ }^\circ\text{C}$ in a quartz tube-packed bed reactor recorded 59% and 34% ethylene and DEE, respectively. The study also noted that ethylene and DEE synthesis was slowed down by the inhibition of H_2O produced during the process at $215\text{ }^\circ\text{C}$. Interestingly, ethylene production efficiency was unaffected by ethanol pressure (0.01–0.07 bar), but it reduced with a rise in the H_2O pressure (0.004–0.02 bar) during the study (DeWilde et al., 2013). It can be deduced that Pt/alumina catalyst was ineffective at high temperatures for ethanol conversion compared to γ -alumina, which recovered appreciable

olefin yield. Moreover, at low temperature, alumina catalyst was effective in ethanol conversion, however, water production poses a challenge during the process. Moreover, the study by Wannaborworn et al. (2015b) recorded an ethanol conversion of 75.2 % and ethylene selectivity of 45.6 % while using Fe-modified alumina catalyst (Fe/Al-SV) at 523 K and 1 bar. The study revealed that Fe/Al-SV catalyst increased the specificity of acetaldehyde due to the ethanol dehydration in the presence of Fe species (Wannaborworn et al., 2015b).

In the oligomerisation process, amorphous silica-aluminas (ASA) have been used as acidic solid catalysts for decades. This is primarily because, at elevated temperatures, these substances are more stable than acid resins or SPA and can be regenerated using carbon burn (de Klerk, 2008, de Klerk, 2006). The chemistry of silica and alumina depends on the amount of Brønsted acid present at the site, although these sites also coke quite quickly. Consequently, after the initial period of operation, the relatively strong acid sites are responsible for the oligomerisation process (Misono and Yoneda, 1967). However, operating in the liquid phase at considerable temperatures (150 to 250 °C), achieving long run times of many months is possible before renewal is required. De Klerk (2008) explains that oxygenates in the feed generate a greater coking level because carbonyls are rapidly transformed into coke precursors. Also of note is that, despite the shorter run lengths, amorphous silica-alumina (ASA-based) catalysts can convert feedstock in the existence of substantial amounts of toxins, including CO, thiophene, NH₃, and H₂S (Nicholas et al., 2014, Van Grieken et al., 2008). The synthesis of silica-alumina is quite affordable, and a single run of the distillation process with these materials can give a specificity of up to 70% for light olefins. On the other hand, they exhibit significant hydrogen transfer rates and generate distillates with a low cetane rating (between 20 and 30) (de Klerk, 2008, de Klerk, 2007). The blended octane values of olefins obtained by these procedures are exceptionally high (Golombok and de Bruijn, 2000, Golombok and de Bruijn, 2001), and the research octane number (RON) of olefins achieved by these methods is usually in the range of 92–94 (de Klerk, 2006). It should be noted that with a higher octane number, the knock resistance of the gasoline mixture also increases. The application of higher octane fuels in automobile engines allows for increased compression ratios, turbocharging and downsizing at the same engine speed, which contributes to improved engine performance and efficiency.

It has been demonstrated that combining alumina (as a binder) with ZSM-5 zeolite can increase the amount of DME produced from methanol (Kim et al., 2006). The production of light olefins requires three steps: (a) dehydration of methanol to produce DME, (b) dehydration of DME to

obtain olefins, and (c) conversion of olefins to aromatics and alkanes (Hajimirzaee et al., 2015). DME is the main medium for the production of light olefins. It should be noted that the first stage of dehydration is very rapid, reversible, and very close to reaching equilibrium (Jiang et al., 2004). Since γ -alumina contains a more significant number of sites with strong and moderate acidity, this material can be used as a binder to regulate the acidity of the catalyst so that a compound can be preferentially produced. In contrast, using zeolite on alumina decreased the micropore area and surface area of BET compared to pure ZSM-5 (Hajimirzaee et al., 2015). Although Al_2O_3 has considerable activity for the formation of DME from methanol, due to its hydrophilic nature, it tends to adsorb water on its surface and loses effectiveness when water is present. In this case, water prevents methanol from being consumed by the catalyst because its adsorption on the catalyst's surface competes with that of methanol (Jun et al., 2003). The effects of using ZSM-5 zeolite and γ -alumina as binders on DME synthesis in the MTO process were studied by Kim et al. (2006). According to their results, zeolite modified with Na containing 70% alumina is very stable to coke formation and water for 15 days at 270 °C, achieving about 80% of DME output. Although ZSM-5, with its medium pore size, had greater specificity for propene, boehmite (γ -alumina) was responsible for giving the catalyst considerable strength and a suitable shape. Comparing the results of the catalyst without a binder (ZSM-5 (100)) and the catalyst with 25% zeolite on alumina (ZSM-5 (25)), it can be concluded that the catalyst with alumina as binder can increase the selectivity for light olefins (such as ethene or propene) while producing less by-products (such as paraffins or heavy hydrocarbons). However, when the zeolite was combined with different amounts of γ -alumina, a larger amount of alumina resulted in a higher coke weight (2.2 to 2.9 wt%), which was due to a larger number of strong acid sites (Kim et al., 2006). The review of alumina-based catalysts for low alcohol conversion at varying process parameters is presented in Table 2.4.

Table 2-4. Review of Alumina catalyst for low alcohol conversion to hydrocarbons

Catalyst	Process	Operational Condition	Results (%)			Inference	Ref.
			X	S	Y		
γ - χ $\text{Al}_2\text{O}_3/\text{B}$ (M-Al-B)	ETE	T =400 °C, P =1 bar, M _c =0.05 g,	100	92	92	Increasing temperatures, from 200 to 400 °C., led to a surge in ethanol transformation.	(Chaichana et al., 2019)
CS2/AMA	ETE	T =400 °C, P =1 bar	94	93	88	The catalyst boosts the catalytic performance, increasing the amount of ethylene produced.	(Banzaraktsaeva et al., 2019)
ZAl (Alumina-based ZSM-5)	MTH	T =350 °C, TOS=10 h,	100	73	-	P in the binder for increased specificity of C ₂ -C ₄ olefins, especially C ₃ H ₆ . HC yield	(Lee et al., 2010)

		WSHV =2.55 h ⁻¹				improved to a P/Al value of 0.8 and then decreased to 1.2.	
ZAPO (P/Al=0.4)	MTH		100	77	-		
ZAPO (P/Al=0.6)	MTH		100	83	-		
ZAPO (P/Al=0.8)	MTH		100	85	-		
ZAPO (P/Al=1.0)	MTH		100	83	-		
ZAPO (P/Al=1.2)	MTH		98	74	-		
PTH	ETE	T =500 °C, P =1 bar, M _c =0.5 g, WHSV=12 h ⁻¹	100	98	98	Ethylene forms the primary product at increased temperatures, with a significant output at >350 °C; however, this is inhibited by the formation of the little quantities of higher HC.	(Garbarino et al., 2018)
γ-Al ₂ O ₃	ETE	T =215 °C, P =0.02 bar	-	59	-	Bimolecular surface species account for the majority of the inhibition of ethylene and DEE synthesis, which agrees with the findings of the study	(DeWilde et al., 2013)
H-USY ZEOLITE	ETE	T =350 °C, P =1 bar, M _c =0.5 g, WSHV =1.43 h ⁻¹	100	100	100	H-USY achieved significant ethylene at >300 °C with stability at 6.75 hours TOS	(Phung et al., 2015c)
Pt/γ-Al ₂ O ₃	ETE	T =250 °C, P =8 bar,	60	50	30	Ethylene may go through oligomerization at acid sites, eventually leading to the predominance of the synthesis of normal alkanes.	(Yandieva et al., 2010b)
Al-SV	ETE	T =350 °C, P =1 bar, WHSV=8.4 h ⁻¹	100	100	100	The solvothermal method of alumina synthesis resulted in the product with the greatest performance. This is due to the increased surface area and amount of acid sites, particularly the weak-to-strong acid strength ratio.	(Wannaborworn et al., 2015a)
Al ₂ O ₃	ETE	T =450 °C, P =1 bar	99	90	89	With increased temperature, ethylene specificity improved for all the evaluated catalysts.	(Ramasamy et al., 2016)
γ-Al ₂ O ₃	ETE	T =450 °C, P=0.005	100	97	97	At T=350–450 °C., the catalyst effectively converted the specific ethanol to ethylene.	(García et al., 2018)

Processes: *ETE* – Ethanol to Ethylene; *ETP* – Ethanol to Propylene; *MTH* – Methanol to Hydrocarbons
Results: *X*, *S*, *Y* – Conversion, Selectivity, and Yield respectively
W/F & *WHSV* – Space velocity; *M_c* – Catalyst weight

2.4.3.3 Silicoaluminophosphate (SAPO)-based Catalyst

Aluminophosphate (AlPO) materials are similar to zeolites and are widely used in catalysis, sorption, ion exchange, etc. The benefit of AlPOs over zeolites is their structural flexibility and the ability to incorporate various metal ions into their framework. As a result, their acidity can

be adjusted or changed. The introduction of silica to the AlPO framework leads to the formation of silicoaluminophosphate (SAPO); the exchange of Si^{4+} ions with P^{5+} ions leads to the formation of acidic sites in the catalyst (Yadav and Singh, 2021). Metal aluminophosphates (MeAPO) are produced when metal ions are isomorphously substituted in AlPO_4 structures. On the other hand, metal silicoaluminophosphates are produced when metal ions are isomorphously substituted in SAPOs (MeAPSOs). Their characteristics are comparable to those of the molecular sieves from which they originated. Compared to the thermal and hydrothermal stability of the AlPO_4 and SAPO molecular sieves, the MeAPSO molecular sieves are somewhat inferior (Fechete et al., 2012). Different types of pore openings, ranging from small, medium to large diameters, and their multidimensional openings make them unique for catalysis in refineries, petrochemicals and organic conversion. Among the most researched SAPO materials for fuel production are SAPO-11, SAPO-34, SAPO-5 and SAPO-31 (Yadav and Singh, 2021). Even the extreme silicon SAPOs have lower catalytic performance than zeolites such as USY, as reported by Martens (Martens et al., 1988).

The study of ethanol transformation performed on SAPO-based catalysts (SAPO-34) at 500 °C recorded almost 100% conversion on all catalysts, as Duan et al. (2011) reported. Under the process parameters, SAPO-34 only produced C_2H_4 as a product. On HZSM-5, ZS-MM (HZSM-5/SAPO-34 prepared by mechanical mixing), and ZS-HS (HZSM-5/SAPO-34 prepared by hydrothermal synthesis), the following products were identified: C_1 – C_4 alkanes, C_2H_4 , C_3H_6 , C_4H_8 and C_5+ . As a result, various processes took place on these catalysts, including dehydration, cracking, hydrogen transfer, and aromatization. On HZSM-5, the primary products were C_3H_8 and C_4H_{10} , even though a yield of 16% and 10% was obtained for C_3H_6 and C_2H_4 , respectively. ZS-MM yielded 88% and 7% for C_2H_4 , and C_3H_6 , respectively (Duan et al., 2011). It appears that SAPO-34 improved the transformation of ethanol to olefins because both ZS-HS and ZS-MM displayed a greater olefin yield than HZSM-5. It was discovered that ZS-HS demonstrated a much-improved C_3H_6 yield compared to the other tested catalysts. Therefore, the interactions of SAPO-34 and HZSM-5 took place in ZS-HS, which supported the formation of propylene during ethanol transformation. The ZS-HS catalyst recorded an increase in ethylene yield with an increase in temperature. However, the yield of C_3H_6 initially increased with reaction temperature, peaking at 30% at 550 °C, and then began to decrease. The higher the reaction temperature, the more likely the cracking of hydrocarbons to C_2H_4 ; therefore, the yield of C_2H_4 increases with increasing temperature (Goto et al., 2010a, Song et al., 2009, Inoue et al., 2010). Compared to ZS-MM, the ZS-HS demonstrated

significantly higher propylene yield and catalytic stability in ethanol transformation. It can be concluded that the synthesis technique altered the consistency and acidity of the HZSM-5/SAPO-34 composites, which in turn influenced the catalytic performance of the materials. In the case of ZS-HS, SAPO-34 may partially overlap with HZSM-5, and an interfacial contact between HZSM-5 and SAPO-34 may have occurred (Duan et al., 2011).

The study by Wu et al. (2011) on the effects of the SAPO-11 synthesis technique on ethanol dehydration to ethylene noted that the catalyst synthesised by adding Al before H_3PO_4 , SAPO-11-4 (Si/Al = 50), was the most effective technique. Synthetic SAPO-11-4 demonstrated a 17% higher ethanol transformation than commercial SAPO-11 at 280°C with 99% and 96% ethylene specificity, respectively (Wu et al., 2011). According to the investigation's findings, the artificially produced SAPO-11 can compete favourably with the commercial type (Wu et al., 2011). Similarly, the results of a study by Li et al. (2018c) showed the efficacy of the SAPO-based catalyst, SAPO-34, which recorded 9% higher ethanol conversion than ZSM-5 after 10 hours TOS. Furthermore, Potter et al. (2014) reported that SAPO-5 and SAPO-34 frameworks could all convert ethanol to a significant extent, however, only the SAPO-34 catalysts efficiently catalyse ethylene production. This is due to the strong acid sites in the SAPO-34 catalyst, which are widely available and capable of successfully promoting ethylene synthesis while enhancing overall ethylene production at temperatures as low as 250 °C (Potter et al., 2014). Compared to the SAPO-5 catalyst, which has larger pores, the SAPO-34 is more effective due to its smaller pores. As a result, SAPO-34 has proven to be an excellent catalyst for the sustainable synthesis of ethylene from ethanol and becomes a viable candidate for potential industrial application (Lefenfeld et al., 2014).

Due to its smaller crystal size, the zeolite SAPO -34 proved to be more efficient in terms of specificity than ZSM-5 zeolite. Smaller crystal size resulted in less coke deposition during the Methanol-to-olefin (MTO) process (Nishiyama et al., 2009). Based on the fact that SAPO-34 performs significantly better than amorphous Al_2O_3 in terms of both specificity and ethene-to-propene ratio (Chang, 1984), it can be inferred that the shape specificity of SAPO-34 significantly impacts the MTO process. This high activity level of SAPOs can be attributed to the strong bonding between the internal channels, which prevents the passage of aromatic molecules and branched hydrocarbons (Chen et al., 1999, Bos et al., 1995). Using a SAPO-34 catalyst with a small crystallite size can improve the accessibility of methanol into the SAPO-34 cages, which in turn leads to an increase in catalytic performance (Lee et al., 2009). Using

SAPO-34 and SAPO-5 catalysts with variable crystallite size, Hajfarajollah et al. (2014) investigated the effect of crystallite size on several parameters, including conversion, lifetime and selectivity for the MTO process. SAPO-34 and SAPO-5 were prepared in a size range from 0.45 to 8 micrometres. Not surprisingly, the SAPO-5 samples have lower methanol conversion activity than the SAPO-34. Catalysts with smaller crystal sizes were found to have longer lifetimes, better methanol conversion rates, and specificity for light olefins (> 50%) compared to catalysts with larger crystal sizes. Overall, it was found that the specificity and total conversion of the MTO process depend significantly on the catalyst size and phase (SAPO-34 or SAPO-5) (Hajfarajollah et al., 2014). In addition, the hydrothermal synthesis conditions were found to significantly affect the shape, particle size, purity, and textural characteristics of the SAPO catalysts. For example, in the MTO process, the catalysts prepared at a temperature of 300 °C and a reaction time of 3 hours showed a significant improvement in the lifetime as well as the specificity of the olefins. In 3 hours of reaction time, a specificity for light olefins of 90% and a conversion of methanol of 94% were achieved. It can be inferred that the catalyst preparation technique affects the structure of the catalyst SAPO, which affects the product selectivity and output in the MTH process (Aghaei and Haghighi, 2015). In another study, Najafabadi et al. (2012) investigated the effect of temperature on SAPO-34 catalyst in the temperature range of 300-500 °C using kinetic models for the MTO process. According to the results, an optimum temperature of 400 °C is more favourable for converting MeOH to ethylene and propylene. Meanwhile, the rate at which undesirable compounds are formed due to side reactions is also remarkable (Ahmad et al., 2021). The review of SAPO-based catalysts for low alcohol conversion at varying process conditions is shown in Table 2.5.

Table 2-5. Review of SAPO-based catalyst for low alcohol conversion

Catalyst	Process	Catalyst Synthesis Methods	Operational Conditions	Results (%)			Inference	Ref.
				X	S	Y		
SA (SAPO-34)	MTO (E+P)	DGC	T=450 °C, P=0.169 bar, Mc=0.05 g, W/F=5 ghmol ⁻¹ , TOS=40 mins	100	39+41	-	Coke formation led to the degradation of SAPO-34 catalyst	(Fujimoto et al., 2021)

SA-UZ (ZrO ₂ /SAPO-34)	MTO (E+P)	STM		100	36+ 40	-	ZrO ₂ -modified SAPO-34 showed reduced coke formation and improved catalytic performance	
SA-Z (Zr/SAPO-34)	MTO (E+P)	STM		-	32+ 30	-	Increased acidity and basicity in Zr species (>ZrO ₂) affect the reaction mechanism and HC yield	
SA-MZ (15% ZrO ₂ & 85% SAPO-34)	MTO (E+P)	MM		100	39+ 40	-	The lack of acidity on the external surface of the treated SAPO-34 catalyst inhibited coke deposition	
NiAPSO-34	MTE	RCM	T=450°C; GHSV=1000 h ⁻¹ , Mc=0.325g, TOS=1 hr	97	72		Compared to the other catalysts, the Ni-doped SAPO-34 showed the highest ethylene selectivity @450°C	(Kang, 2000)
CoAPSO-34	MTE	RCM		99	61	-	Increase in coke formation and coke combustion temperatures	
FeAPSO-34	MTE	RCM		98	60	-	Coke combustion temperature was lower, attributed to a decrease in the amount of acid site and particle size	
SAPO-34	MTE	RCM		100	59	-	Ethylene selectivity decreased with an increase in TOS	
SAPO-34	ETE	HTM	T=400 °C, WHSV=3.5 h ⁻¹ , Mc=0.5 g, TOS=600 min	92	52	-	Lower conversion and selectivity than the modified catalyst	
Cr/SAPO-34	ETE	IM		98	99	-	Improved ethylene selectivity compared to unmodified SAPO-34 catalyst	
Co-Cr/SAPO-34	ETE	IM		100	100	-	Co-Cr loading provides suitable pore structure and moderate acid-base properties, increasing catalytic performance.	
SAPO-11	ETE	HTM	T=340 °C, WHSV=2 h ⁻¹	95	91	-	The incorporation of Mn ²⁺ and Zn ²⁺ into SAPO-11 was unfavourable for the ETE process compared to unmodified SAPO-11	(Chen et al., 2010)
Mn/SAPO-11	ETE	HTM & IM		92	77	-		
Zn/SAPO-11	ETE	HTM & IM		87	69			
HZSM-5/SAPO-34 (Si/Al:25:1 wt)	ETO (E+P)	HTM & MM	T=400 °C, P =1 bar, Mc=0.5 g	100	-	88+ 7	Synergistic catalysis of HZSM-5 and SAPO-35 occurred in HZSM-5/SAPO-35 catalyst. However, the synthesis method and composition of HZSM-5/SAPO-35 affected performance and olefin yield.	(Duan et al., 2013)
HZSM-5/SAPO-34 (Si/Al:25:4 wt.)	ETO (E+P)	HTM & MM		100	-	24+ 35		

HZSM-	ETO	HTM	100	-	26+
5/SAPO-34	(E+P)	& MM			34
(Si/Al.38:4 wt)					

Processes: *ETE* – Ethanol to Ethylene; *ETP* – Ethanol to Propylene; *MTO (E+P)* – Methanol to olefin (Ethylene and Propylene)
Catalyst Synthesis Methods: *IM* – Impregnation Methods; *RCM* – Rapid Crystallization Method; *STM* – Solvothermal Method; *MM* – Mechanical Mixing; *DGC* – Dry Gel Conversion; *HTM* – Hydrothermal Method
Results: *X*, *S*, *Y* – Conversion, Selectivity, and Yield respectively
GHSV & *WHSV* – Gas & Weight Hourly Space Velocity; *W/F* – catalyst weight/flowrate; *M_c* – Catalyst weight

2.4.4 Introduction to Zeolite Materials

The International Zeolite Association (IZA) Structure Commission has identified over 230 distinct structure kinds, each of which has been assigned a three-letter designation by the organization. Zeolites are allocated appropriate names when they are synthesised under different circumstances, for instance, UZM-9 (Park et al., 2014) or ZK-4 (Kerr, 1966), however, they are classed by structure type, which in the case of these two materials is LTA. Classifying the structure types according to pore size and connectivity is possible. For example, 8-membered ring (8MR), 10-membered ring (10MR) and 12-membered ring (12MR) delimited pore channels are all commonly experienced with standard size openings of 4.0, 5.5, and 7 Å respectively. Recently, the field of molecular sieves (micro-porous materials) has advanced to become a fantastic category of inorganic-hybrid materials with a wide range of commercial potential, primarily in catalysis. Molecular sieves are generally comprised of zeolites/zeotypes (Cundy and Cox, 2003), mesoporous materials (Kresge et al., 2004, Martín-Aranda and Čejka, 2010), and metal-organic frameworks (MOFs) (Salles et al., 2008, Dhakshinamoorthy et al., 2010, Gascon et al., 2014, Xamena et al., 2008, Pérez-Mayoral and Čejka, 2011). Many molecular sieves have remarkable features in adsorption (Areán et al., 2009), catalysis (Bejblová et al., 2009), sensing (Zhou and Ahmad, 2008, Zhou et al., 2008), fuel cells (Yeung and Han, 2014), medicine or optical applications (Serati-Nouri et al., 2020, Hoffmann and Marlow, 2003), and other uses, resulting in a wide range of porous materials of significant interest (Corma et al., 2010, Ríos R et al., 2012, Martínez and Corma, 2011, Čejka et al., 2012). The computational developments in this sector, together with characterisation and testing, have offered a surprisingly thorough insight into the design of molecular sieves (Nachtigallova et al., 2004, Garrone et al., 2006). Despite these significant advancements, the number of different varieties of zeolites currently used in the industry is still limited to less than 20.

2.4.4.1 Zeolite Structural and Textural Properties

The zeolites are organized in a crystalline structure made of a tetrahedron of TO₄ (T is Si or Al in a native zeolite and can be other elements, including Ga, Ge, Fe, B, P, Ti in a synthesised

material) joined by oxygen atoms (Zhang and Ostraat, 2016). Molecular access to the zeolite structure is provided through channels and cavities with diameters of roughly one nanometer (Serrano et al., 2013), which are available for various molecules. The mixture of silicon and oxygen in tetrahedra produces a solid with no charge (SiO_2). When Al is introduced into a silica structure, the structure is negatively charged due to the Al. This occurs due to the Al_{3+} Si_{4+} substitution and necessitates compensatory cations to maintain the overall framework's neutrality. ZSM-5 (MFI zeolite) has a morphology comprising unit cells with 10 rings of 5 T-atoms, which are linked together by oxygen atoms to an identical chain, forming a channel (Figure 2.6). The channels of ZSM-5 zeolite work together to generate a three-dimensional framework. ZSM-5 also has a significant Si/Al ratio ($\text{Si/Al} > 11$), which is beneficial. Interestingly, this ratio significantly impacts the ion exchange capacity, with the concentration of Al in the framework increasing in direct proportion to the amount of charge-compensating cation present (Wang et al., 2016b). Zeolite materials have unique characteristics, including a wide surface area, good thermal stability, increased ion exchange capacity, the existence of acid sites, and shape specificity (Feliczak-Guzik, 2017). While the morphological micropores of zeolite are advantageous for the mass transfer of small molecules, they are detrimental to the mass transfer of large molecules, as evidenced by diffusion restrictions for reagents, intermediates, and products (Fang et al., 2008). Many investigations have been conducted recently to produce zeolites with mesopores and reduce the diffusional constraints of these materials (Kustova et al., 2007b).

ZSM-5 zeolites are microporous aluminosilicates with a crystalline framework formed by interconnected AlO_4 and SiO_4 tetrahedra. These zeolite types have various industrial applications in petroleum refining, chemical processes, and other operations due to their unique properties, such as wide surface area, thermal stability, high ion exchange capacity, presence of acid sites, and shape selectivity. Zeolite materials have unique characteristics, including a wide surface area, good thermal stability, high ion exchange capacity, the existence of acid sites, and shape selectivity (Vasconcelos et al., 2023). While the morphological micropores of zeolite are advantageous for the mass transfer of small molecules, they are detrimental to the mass transfer of large molecules, as evidenced by diffusion restrictions for reagents, intermediates, and products (Liu et al., 2022b). Recently, efforts have been made to overcome these diffusion constraints by producing zeolites with mesopores to reduce the diffusional constraints of these materials. Metal-organic frameworks (MOFs) offer an alternative approach, combining inorganic and organic species to create a three-dimensional crystalline

channel system. MOFs provide regulated porosity and offer more flexibility in terms of pore design and chemical variation. Although not extensively used on an industrial scale, MOFs have shown promising breakthroughs for more efficient and environmentally friendly processes (Zhang et al., 2022).

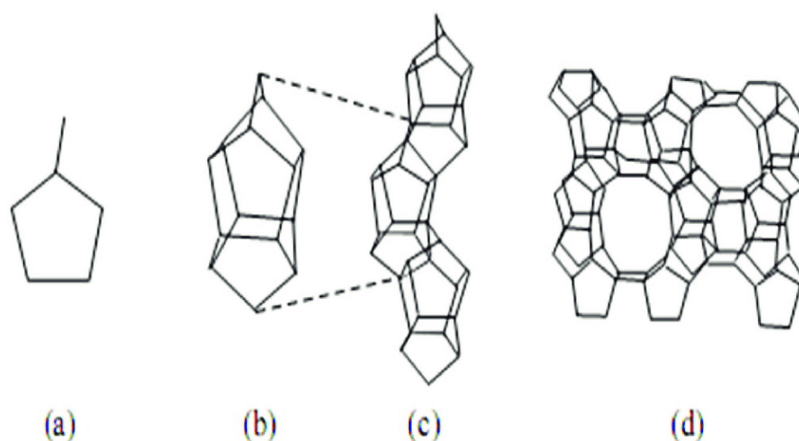


Figure 2-6. Tetrahedrons Structure of ZSM-5 zeolite (Adapted from (Lounis and Belarbi, 2018))

2.4.4.2 Factors Affecting the Synthesis of ZSM-5 Zeolite Catalysts

Several factors influence the synthesis of ZSM-5 zeolite catalyst for application in hydrocarbon reaction. The choice of precursors and the catalyst preparation method play a crucial role in determining the activity and selectivity of the products. Catalyst preparation is affected by ageing, temperature, pressure, batch composition, water content, and the seeding process. The composition of the synthesis gel, including pH, Si/Al ratio, silica and aluminium source and ratio, type of template, template concentration, and ionic strength, also impacts catalyst synthesis (Koekkoek et al., 2011). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (Si/Al) is a vital parameter in the hydrothermal synthesis of zeolites. Different zeolite types are associated with low or high Si/Al ratios. Low Si/Al ratio zeolites, such as type A, X, and hydroxysodalite, are synthesised from reaction mixtures with strong alkalinity and a low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. High Si/Al ratio zeolites, such as beta, ZSM-5, and ZSM-11, are made from gels with a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and weak alkalinity or neutral F- medium. The Si/Al ratio in the initial reaction mixture does not directly correlate with the final product (Zimmermann et al., 2019). Secondly, the Organic Structure Directing Agents (OSDAs) are crucial in controlling the development of channels and pores in zeolite synthesis. OSDAs influence gel chemistry and lead to the formation of specific zeolite frameworks. Parameters such as size, rigidity, shape, and hydrophobicity of

OSDAs impact the structure of the resulting zeolite (Moliner et al., 2013). Thirdly, the water concentration in the synthesis process of zeolite catalysts is important. In the synthesis process, water acts as a solvent, accelerator, space filler, and hydrolyzer. Its non-solvent effects influence crystal growth and nucleation. Higher H₂O/Si levels increase synthesis yield and ease mass transfer in large-scale zeolite synthesis. The water concentration also affects the structure-directing ability of the template. Finally, the crystallization temperature and time are critical factors in synthesizing specific zeolite types. Different zeolite phases have distinct temperature ranges for synthesis. Temperature affects crystal growth and nucleation rates, with higher temperatures leading to faster rates. Crystallinity generally increases with longer crystallization times. Ostwald's rule of successive phase transformation states that metastable products form initially, which may convert into more stable but less desired products over time. The choice of crystallization conditions can impact the final catalyst formed (Widayat and Annisa, 2017). These factors should be carefully considered and optimized to achieve the desired properties and performance in zeolite synthesis and catalytic conversion processes.

2.4.4.3 ZSM-5 Zeolite Catalysts in Low Alcohol Conversion

2.4.4.3.1 Application in Low Alcohol Dehydration

Zeolite catalysts, such as HZSM-5, have been extensively utilized in several catalytic operations due to their numerous characteristics, which include a precise porous framework, increased thermal and mechanical strength, better acidity, and reactivity (Xia et al., 2010b, Tret'yakov et al., 2010, Makarfi et al., 2009b, Makarfi et al., 2009a). Some catalyst fabrication techniques, including wet impregnation or ion-exchange procedures for metal or phosphorous doping, NaOH treatment, and steaming at specified temperatures, are applied after the catalyst preparation to improve its catalytic activity. According to Rahimi and Karimzadeh (2011a), all of these post-modifications can give excellent stability to thermal treatment, a reduction in catalyst deactivation, or an increase in the activity/ selectivity of a specific product. Much research has been done in ethanol dehydration employing zeolite, some of which are discussed in a broader context (Isa et al., 2022). Zhang et al. (2008b) synthesised ethylene from ethanol dehydration using the HZSM-5 catalyst (Si/Al=25) and evaluated the activity and stability of the zeolite employed in the reaction. The dehydration processes were conducted in a fixed bed reactor at temperatures ranging from 250 to 450 °C, with an LHSV of 3 h⁻¹ and a pressure of 0.07 MPa. Since the ethanol dehydration was insufficient at reduced temperatures, the transformation was also low. Increasing the temperature resulted in an improvement in the rate

of conversion of the ethanol. At a temperature of 325 °C, the maximum conversion of ethanol was 97.3 %. The highest selectivity of ethylene was 98.5 % at a temperature of 300 °C. When operated at a reduced temperature, the HZSM-5 exhibited the most significant ethylene specificity. When the HZSM-5 catalyst was tested after 60 hours, it was discovered that it had substantial initial efficiency of 93.1 %, reached after only 10 hours of process run time (Zhang et al., 2008b). The study showed that the HZSM-5 catalyst was efficient but deactivated with a more prolonged process time, reducing catalytic performance and efficiency. Figure 2.7 shows the operating condition's effect on ethanol conversion to olefin and BTEX.

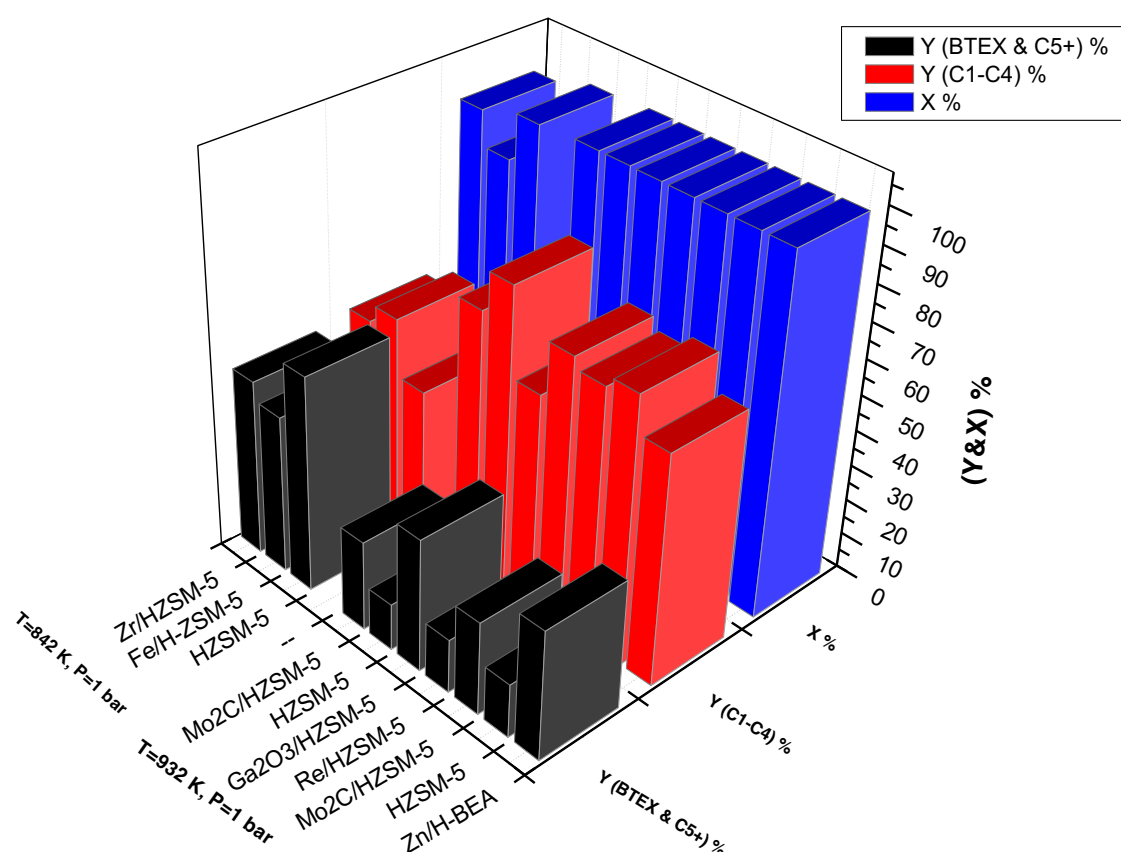


Figure 2-7. Conversion Efficiency (X) and Selectivity (Y) of C₁-C₄, BTEX and fuel (C₅+) range hydrocarbons in Catalytic conversion of bioethanol over different zeolite catalysts (adapted from (Galadima and Muraza, 2015))

The Figure above shows the catalytic performance of different zeolite catalysts at P=1 bar, T=842 and 932 K, and catalyst weight of 0.15-0.3 g. It can be deduced that although all the catalytic conversion processes at operating conditions, T=932, P=1 bar, recorded 100% conversion, the C₅ and BTEX yield was low (13-36%), with an appreciable yield of C₁-C₄ range hydrocarbon (59-74%). However, at T=842 K and P=1 bar with ethanol conversion rate

below 100% (86.3-99.2%), more C₅+ and BTEX hydrocarbons were produced (44-68%) with 40-56% yield of C₁-C₄ hydrocarbon. This showed that the operating condition, T=842 K, P=1 bar favours the production of fuel range (C₅+) hydrocarbons than T=932 K, P=1 bar.

In addition to performance and specificity, catalyst stability is another critical consideration for the catalytic process in commercial applications. When exposed to elevated temperatures, HZSM-5 is rendered inactive for ethanol transformation, attributed to the poisoning of the surface by coke deposition (reversible deactivation) and dealumination with water (irreversible deactivation). It is possible to restore catalytic activity to a catalyst that has been deactivated by coke deposition by calcining it at elevated temperatures in the air. Unfortunately, in the case of dealumination, the framework of the catalyst was broken, and it is challenging to restore the catalytic activity of the catalyst. At temperatures above 450 °C, irreversible deactivation is crucial due to dealumination caused by water production in the process media (Aguayo et al., 2002b).

Xia et al. (2010b) studied the conversion of ethanol to propylene on the MFI zeolite catalyst. They observed that the MFI zeolite catalyst was efficient in the transformation of ethanol to propylene. In this study, Na-type zeolite and H-type zeolite was synthesised hydrothermally, and the reactions were carried out using 0.1–0.8 g of catalyst at P=0.1 MPa in a fixed bed reactor with a temperature range of 400-600 °C. The ethylene and propylene yields were 38 % and 28 %, respectively, when the Si/Al ratio was 97, and the W/F ratio was 0.0125 g min mL⁻¹; 40.7 % and 25 %, respectively, with the Si/Al ratio of 128 and the W/F ratio of 0.03; 35.6 % and 25.5 %, respectively, when the Si/Al ratio was 176, and the W/F ratio was 0.05; 31.6 % and 28.6 %, respectively when the Si/Al ratio was 207 and the W/F ratio was 0.05. From the result, it can be established that a reduced W/F ratio promotes the highest possible ethylene production, with the product distribution being completely independent of the Si/Al ratio. (Xia et al., 2010b). Ferreira Madeira et al. (2012) investigated the HZSM-5 catalyst with Si/Al ratio lower (Si/Al=16) than that explored by Xia et al. (2010b) for ethanol conversion to hydrocarbons and discovered that it is more stable than other catalysts. Moreover, an investigation of the catalytic conversion process by (Madeira et al., 2010) was conducted using HZSM-5 (Si/Al=16), 0.3 g of catalyst in a fixed bed reactor with temperatures of 350 °C and pressures of 3 MPa. The results revealed that at a temperature of 350 °C and a reaction time of 25 hours, complete ethanol conversion into hydrocarbons and a yield of 35 % ethylene were obtained. After 25 hours of catalytic operation, no deactivation of the HZSM-5 catalyst was

discovered. Paraffin and aromatics were shown to have high selectivity of 58% and 38% at TOS (time on stream) are 0.9 h, respectively. At TOS=13 h, the specificity of paraffin and aromatics were 52 % and 31 %, respectively. Paraffin and aromatics were preferred at TOS=25 h with specificity values of 45 % and 25%, respectively. There is no significant difference with ethylene yield recorded by Xia et al. (2010b) and Madeira et al. (2010) using different Si/Al ratio. However, this may be attributed to the process parameters employed for the studies.

Song et al. (2009) studied the influence of metal doping on the catalytic activity of ZSM-5. To improve the catalytic transformation of ethanol to propylene, the ZSM-5(80) zeolites were modified by adding a range of metal ions to the material's surface. An ion-exchange technique was employed to incorporate the ions; Mg, Ca, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ce, Ag, and Pd, while an impregnation method was used to introduce the ions; Bi, Ti, V, Zr, Mo, and W. As a result of this study, the hydrocarbon distributions produced with the modified catalysts show appreciable yield in comparison to the performance of the unmodified H-ZSM-5 (80). Compared to H-ZSM-5(80), the catalysts doped with alkaline earth metal ions (Mg, Ca, and Ba) gave much higher ethylene yields, but propylene yields were significantly lower. Possibly, the decrease in the acidity of H-ZSM-5 produced by the incorporation of alkaline earth metal cations was responsible for this outcome; the reduced acidity hindered the secondary reaction that tends to result in the synthesis of higher hydrocarbons. A similar trend was observed by Xia et al. (2017a) with Zr Catalyst modified with alkaline earth metals. However, according to the study, NH₃-TPD did not provide concrete evidence for a reduction in acidity (Song et al., 2009). The catalytic activity of the ZSM-5(80) materials altered with Mn, Fe, Co, Cu, Zn, Ag, Bi, and V was similar to that of the ZSM-5(80) materials that were not modified. The introduction of Ni and Ga ions increased the synthesis of C₅+ aliphatic and aromatics, but the yields of ethylene and propylene were significantly decreased. This trend is similar to the result recorded by Van der Borght et al. (2015) and Makarfi et al. (2009b). Adding Cr, Ce, Pd, Ti, Zr, Mo, and W increased ethylene and propylene yields; propylene production was 26–31%. The maximum propylene yield (31%) was produced using Zr/ZSM-5(80) as a starting material, however, when H-ZSM-5(80) was employed for 5 hours, the yield of propylene plummeted below 30%, while the output of ethylene improved rapidly (Song et al., 2009). For the catalytic transformation of ethanol to propylene, Zr/ZSM-5(80) displayed more stability than H-ZSM-5(80), possibly because zirconium successfully protected the zeolite structure from undergoing dealumination with water, hence boosting the hydrothermal stability. The ZSM-5 zeolites doped with Zr and Ti proved to be the most efficient catalysts for propylene synthesis.

Similarly, the effect of (transition) metal loading on ZSM-5 was evaluated by Van der Borghet et al. (2015) for ethanol conversion. For the generation of hydrocarbons from ethanol, contrary to Song et al. (2009), only the impregnation approach was employed for the modification of the ZSM-5 catalyst with Ni, Fe, and Ga metals. All catalytic processes were conducted in the tubular reactor at T=170-390 °C with 0.5g of catalyst at P=0.01MPa. The study recorded ethylene as the only product when the temperature was raised to 250 °C. The ethylene content decreases when the temperature is raised over 250 °C and other hydrocarbons are produced. On HZSM-5, the transformation of ethanol stayed at 100 % for 12 hours. With time, the selectivity of ethylene declined while the selectivity of C₃-C₅ olefins increased. The selectivity of ethylene reduced as the space-time increased. This can be attributed to short contact/reaction time, which does not favour ethylene production. The influence of the metal content was also examined. Higher C₂ conversion was observed with rising amounts of metal content (up to 1Ga, 1Fe, and 1Ni/HZSM-5). As metal content was increased further (2, 4, and 7 metal (Ga, Fe and Ni) content), C₂ conversion was observed to decrease with increasing amounts of metal concentrations attributed to reduced acid strength of zeolite due to high metal loading (Lu et al., 2006a). In conclusion, lower metal concentration is assumed to favour lower olefin formation (Van der Borghet et al., 2015c). The review of zeolite catalyst for ethanol-to-olefin conversion at varying process parameters is presented in Table 2.6.

Table 2-6. Review on the application of zeolite catalyst for low alcohol conversion at different operating parameters

Catalyst	Process	Catalyst Synthesis Method	Operational Conditions	Results (%)			Inference	Ref.
				X	S	Y		
Zr/HZSM-5	ETE	IM	T =450 °C, P =1 bar, Mc=0.2 g	100	61	61	Addition of Zr to H-ZSM-5 zeolite results in an increase in the initial yield of C ₃ + olefins.	(Inaba et al., 2012)
HZSM-5	ETP	COM	T =400 – 500 °C, P =1 bar, Mc=0.2 g, W/F =0.05 g·min mL ⁻¹	100	-	-	Ethanol has significant adsorption on HZSM-5, which is principally responsible for the catalyst deactivation	(Wang et al., 2018b)
HZSM-5	ETE	HTM	T=450 °C, P =0.1 bar, W/F =0.01-	100	-	-	A process temperature above 300°C is required to produce C ₅ + hydrocarbons, which correlate to the amount of gasoline generated	(Gayubo et al., 2001)

			0.4 g·min mL ⁻¹					
HZSM-5	ETE	HTM	T =250-500 °C, P=0.5 bar, Mc=0.3 g, WHSV =1 h ⁻¹	100	10 0	10 0	There was a significant rise in the generation of ethene but a corresponding decline in the amounts of aromatics.	(Schulz and Banderma nn, 1994a)
Fe/HZSM-5	ETE	IM	T =500-700 °C, Mc=0.2 g	100	98	98	Metals, including Cr, Fe, and Ni, are efficient for synthesising C ₃ + olefins and paraffin, which may be precursors to aromatics.	(Inaba et al., 2006a)
HZSM-5	ETE	COM	T =225-425 °C, 0.5 g·min mL ⁻¹	100	95	95	Contrary to a lower temperature (280 °C), 400 °C increased the production of olefins attributed to cracking.	(Gayubo et al., 2010a)
HZSM-5	ETE	COM	T =350 °C, P =20 bar, Mc=0.3 g	100	75	75	Due to the operating parameters, the transformation of ethanol is followed by a significant decrease in acidity and microporosity caused by coking. This coke is liable for active site poisoning and access blockage.	(Ferreira Madeira et al., 2012)
HZSM-5	ETE	COM	T =350 °C, P =30 bar, Mc=0.3 g	100	35	35	At 350 °C. and 30 bars, it was shown that HZSM-5 zeolite was a remarkably stable catalyst for ethanol transformation into hydrocarbons.	(Madeira et al., 2010)
HZSM-5	ETE	HTM	T =325 °C, P =0.7 bar, LHSV=3 h ⁻¹	98	97	94	The HZSM-5 catalyst, which demonstrated the maximum initial activity at 93.1%, exhibited a discernible reduction in ethylene output after 60 hours of process time.	(Zhang et al., 2008a)
ZSM-deSi	ETE	DST	T =200 °C, P =1 bar, Mc=0.2 g, WHSV =0.4 h ⁻¹	80	12	10	The desilication process improved the proportion of weak to strong acid sites of ZSM-deSi with enhanced selectivity higher than the parent ZSM-5	(Xin et al., 2014)
HM90	ETE	COM	T =180 °C, P =1 bar, W/F =25g·min mmol ⁻¹	100	10 0	10 0	During dehydration, ethanol transformation and selectivity to C ₂ H ₄ and (C ₂ H ₅) ₂ O remained nearly constant.	(Takahara et al., 2005)
Fe/HZSM-5	ETE	IM	T =400 °C, Mc=0.2 g, flowrate=60 mL.h ⁻¹	100	98	98	The specificity of aromatics was shown to decrease with time-on-stream (TOS), with an increase in the specificity of ethylene	(Inaba et al., 2007)
P-ZSM-5 (P/Al =0.5)	ETP	IM	T =550 °C, P =1 bar, W/F =0.01 g/cm ³ min ⁻¹	100	31	31	Incorporating P improved the hydrothermal stability of the ZSM-5, which led to a considerable improvement in the catalyst's durability during the ethanol transformation.	(Takahashi et al., 2012b)
Sc ₂ O ₃ - In ₂ O ₃ /Beta Zeolite	ETP	DEP	T =260 °C, P =1 bar, Mc=0.8 g,	100	52	52	Adding Sc ₂ O ₃ to In ₂ O ₃ /Beta improves the stability of the catalyst, owing to the	(Xue et al., 2019)

			WHSV =0.2 h ⁻¹					prevention of the lowering of In ³⁺ to In ⁰ caused by Sc ₂ O ₃ alteration.	
HZSM-5	MTO (E+P)	COM	T=310 °C, WHSV=7 h ⁻¹ , P=1.3 bar, Mc=0.06 g	5	18	-	+	Low methanol conversion can be attributed to low operating temperature	(Bjorgen et al., 2007b)
HZSM-5	MTO (E+P)	COM	T=330 °C, WHSV=7 h ⁻¹ , P=1.3 bar, Mc=0.06 g	52	14	-	+	Methanol conversion increases to 52% when the temperature is increased by 20 C (310 °C)	(Bjorgen et al., 2007b)
HZSM-5	MTO (E+P)	COM	T=350 °C, WHSV=7 h ⁻¹ , P=1.3 bar, Mc=0.06 g	73	10	-	+	Operating temperature affects methanol conversion and olefin yield	(Bjorgen et al., 2007b)
HZSM-5	MTO (E+P)	COM	T=390 °C, WHSV=7 h ⁻¹ , P=1.3 bar, Mc=0.06 g	91	5+	-	35	Methanol conversion increases with an increase in temperature	(Bjorgen et al., 2007b)
HZSM-5	MTH	HTM	T=380 °C, WHSV=2 h ⁻¹ , P=10 bar, Mc=1.40 g	98	-	41		Methanol conversion and olefin yield increase with increasing temperature	(Di et al., 2013)
Hierarchical ZSM-5	MTH	HTM	T=350 °C, WHSV=1.2 h ⁻¹ , P=11 bar, Mc=0.7 g	100	59	-		The hierarchical ZSM-5 zeolite exhibited less coke formation and deposition over 24 hours, significantly less than the conventional ZSM-5 zeolite	(Wan et al., 2014)
ZSM- 5/MCM-48	MTH	HTM	T=380 °C, WHSV=1 h ⁻¹ , P=10 bar, Mc=2 g	97	-	42		The composite catalyst showed high performance and stability during the MTH reaction	(Di et al., 2013)
ZSM- 5/MCM-48	MTH	HTM	T=420 °C, WHSV=1 h ⁻¹ , P=10 bar, Mc=2 g	100	-	41		The catalyst results in increased methanol conversion at high temperature	(Di et al., 2013)

Processes: *ETE* – Ethanol to Ethylene; *ETP* – Ethanol to Propylene, *MTO (E+P)* – Methanol to Olefin (Ethylene + Propylene), *MTH* – Methanol to Hydrocarbon

Catalyst Synthesis Methods: *CPM* – Co-precipitation method; *PM* – Precipitation Method; *IM* – Impregnation Methods; *DST* - Desilication treatment; *DEP* - Deposition-precipitation

Results: *X*, *S*, *Y* – Conversion, Selectivity, and Yield respectively

W/F & *WHSV* – Space velocity; *M_c* – Catalyst weight

2.4.4.3.2 Application of Zeolite Catalyst in Oligomerization

A unique category of silica-aluminas is the crystalline, microporous zeolites (Perego and Carati, 2008). The utilization of MFI zeolites in the oligomerization of olefins is among the most extensively researched classes of catalytic materials, partly attributed to the earlier industrial application of MFI zeolites in the Mobil Olefins to Gasoline and Distillate (MOGD) and PetroSA for the transformation of Olefins to Distillate (COD) mechanisms, however, the flexibility of these class of materials availed scientists in selecting the pore size, connectivity

and thus the shape specificity (Moliner et al., 2015, Martínez and Corma, 2011). The zeolite catalysts, MTT, MFI, and MTW have 18, 23, and 26.2 pore openings, respectively, representing a progression from significantly restrained to less restrained. Solid phosphoric acid was designated a value of 50 because it is an unrestrained solid that can be used as a benchmark. High pore wall constraints (smaller pore openings) result in more linear products due to the increased pore wall constraints. With decreasing pore constraint, branching in the C₈ fraction, measured as the average branch number or trimethyl pentene percentage in the C₈ fraction, rises drastically. As a result of this, the linear olefin % in the C₈ components declines by an exponential factor. However, as the pore constraint reduces, the cetane number of the distillate boiling point range product obtained significantly reduces. Cetane number is a bulk characteristic that relies on branching, with linear molecules favoured for high cetane number and depending on branching. Consequently, impacts on branching are evident all over the molecular weight range, rather than easily described C₈ region. It is also feasible to see the effects of pore constraint through replacement around the double bond, with the percentage of C₈ olefins with three substituents (out of a prospective four) on the double bond reducing as pore constraint decreases (Nicholas, 2017, Nicholas et al., 2017).

At the elevated temperature (573 K), Iwamoto and Kosugi (2007) demonstrated that Ni ion loaded-MCM-41 synthesised by model ion exchange could effectively transform ethylene to propylene through selective dimerization to 1-butene, isomerization of 1-butene to 2-butenes, and cross-metathesis between 2-butenes and ethylene to produce synthesis gas. The latter metathesis stage is a rare Ni-based heterogeneous catalyst process (Iwamoto and Kosugi, 2007, Iwamoto, 2008, Ikeda et al., 2008, Iwamoto, 2011, Tanaka et al., 2012). Burattin et al. (1999) suggested that nickel phyllosilicates, a species generated at the catalyst interface, are active sites for ethylene dimerization and alkene metathesis. However, the exact form of the active sites has been a source of contention for some time (Tanaka et al., 2012, Lehmann et al., 2011, Lehmann et al., 2012). Control investigations with propylene have lately revealed that the metathetic performance of these catalysts has been seriously questioned (Perea et al., 2017). Every one of these investigations has shown, once again, that incorporating aluminium into the walls of mesostructured materials to produce AlMCM-41, AlMCM-48, or AlSBA-15, for example, boosts the catalytic activity for the oligomerization of ethylene. It has been proposed that increasing acidity is directly related to increased olefin conversion and isomerization rates, while simultaneously stimulating the synthesis of larger molecular weight products and coke, which may result in catalyst deactivation.

With the discovery of amorphous aluminosilicates as carriers for nickel in the oligomerization of ethylene, nickel-promoted zeolites were found as promising alternatives for the oligomerization of ethylene rather quickly. Adsorption/separation procedures can be enhanced by using zeolites, which are microporous, crystalline minerals that exhibit unique catalytic activity and structure specificity features. When it comes to selective oligomerization under moderate circumstances, nickel promotion is required, just as with amorphous aluminosilicates. The use of zeolites and prototype materials for discovering nickel active sites and kinetic or Density-functional theory (DFT) studies has been investigated. The application of bifunctional Ni-H-Beta for olefin oligomerization was examined lately by Martínez et al. (2013) and is an uncommon instance of this nanocrystalline zeolite being used for this purpose. Ion-exchange or IWI of a commercial H-Beta zeolite ($\text{Si}/\text{Al} = 12$) with $\text{Ni}(\text{NO}_3)_2$ solutions produced the catalysts used in this study. The performance of the catalysts increases with nickel dosage up to a maximum of 2.5wt.% before plateauing. Branched octenes are produced through carbocationic routes in which Brønsted acidic sites work concurrently with metallic sites to form branched octenes. Contrary to expectations, no deactivation of such microporous zeolites ($V_{\text{micro}} \text{ approx. } 0.2\text{cm}^3$) was perceived during the examined parameters, even at reasonably significant ethylene transformations, including 60–80% within 10 hours on stream. Although, the authors did not state if the higher stability is due to the unique textural features of Ni-H-Beta catalysts or to changes in operating parameters. However, it was proposed by the same researchers to conduct a comparative investigation between this nanocrystalline Ni-H-Beta, a commercial aluminosilicate (Siralex 30), and a mesoporous mesostructured Ni/Al-MCM-41 material to evaluate catalyst features and performance (Moussa et al., 2016). Moreover, compared to other mesoporous Ni/Al-MCM-41 materials, the most active Ni/Al-MCM-41 exhibits the highest efficiency under the same operating parameters. Jan et al. (2018) recently conducted a systematic investigation using a comparable Ni-H β catalyst in a continuous packed bed reactor. The $\text{Ni}(\text{NO}_3)_2$ was steadily dripped into a commercial zeolite (in the NH_4^+ form, $\text{Si}/\text{Al} = 25$) to produce a zeolite solution. In a lengthy trial, it was discovered that ethylene conversion remained constant at 50% for several days after adjusting the parameters. The low ethylene conversion can be correlated to the low catalytic activity compared to the Ni-H-Beta catalysts (Jan et al., 2018, Jan and Resende, 2018). Table 2.7 shows a review of the ZSM-5 catalyst for olefin oligomerization.

Table 2-7. Review of zeolite-based catalysts for olefin oligomerization

Feedstock	Catalyst Type	Operating Conditions	Products	Inference	Ref.
Ethylene	Ni/ZSM-5	250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	9 & 92 % ethylene conversion at 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)
Ethylene	Micro-sized HZSM-5 zeolite and nano-sized HZSM-5 zeolites catalysts	2.0 ± 0.1 g of catalyst, 3.0 MPa, 275 – 300°C, 3.0 MPa, and WHSV of 1.0 h ⁻¹	C ₆ -C ₁₀	In terms of activity (62.5 % transformation) and deactivation resistance, nano-sized HZSM-5 zeolites surpassed micro-sized HZSM-5 zeolites.	(Zhang et al., 2020a)
Ethylene	Ni-MCM-41/ZSM-5	250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	19 & 63 % ethylene conversion at 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)
Ethylene	Ni-ZSM-5/MCM-41	T=250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	30 & 29 % ethylene conversion at 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)
Propylene	Fentone-ZSM-5	T=280°C, WHSV=4.0 h ⁻¹ , P=40 bar	C ₅ +	propene conversion and diesel selectivity were as high as 98.3% and 92.4%, respectively	(Zi et al., 2020)
Ethylene	Ni/MCM-41	250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	7 & 49 % ethylene conversion 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)
Ethylene	HZSM-5	250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	13 & 80 % ethylene conversion 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)
Propylene	Zr-ZSM-5	T=260°C, P=40 bar, WHSV=1 h ⁻¹	C ₅ +	Liquid yield of 88 % and diesel selectivity 61 %. was obtained	(Li and Jiang, 2013)
Ethylene	H-MCM-41/ZSM-5	250–450°C. 1.5-20 bar, 0.5 g catalyst	C ₅ +	3 & 28 % ethylene conversion 250°C & 20 bar, & 450°C & 1.5 bar respectively	(Jin et al., 2020)

Propylene	FeSO ₄ -ZSM-5,	T=280°C, WHSV=4.0 h ⁻¹ , P=40 bar	C ₆ +	98% propene conversion	(Zi et al., 2020)
Propylene	H ₂ O ₂ -ZSM-5	T=280°C, WHSV=4.0 h ⁻¹ , P=40 bar	C ₆ +	97 % propene conversion	(Zi et al., 2020)

2.4.4.4 *Factors that influence the catalytic performance of zeolite catalysts*

Most of the chemical reactions that occur during heterogeneous catalysis take place on the superficial part of the catalyst nanoparticles. To obtain inherent perspectives into how a particular chemical or structural component affects catalytic efficiency, it is necessary to develop innate correlations between clearly described chemical and framework properties of catalyst nanoparticles and their catalytic activity via the bridge of chemistry and framework of the surface of the catalyst nanoparticles. By doing so, an intrinsic perception of how a particular chemical or morphological component affects catalytic activity can be attained. Owing to this knowledge, we may fabricate catalysts using a logical design approach rather than by trial and error, as is currently the case. In many circumstances, the structure, size and shape of a catalyst affect the catalytic efficiency of that catalyst. Nanoparticles of a catalyst with varied forms could have various crystallographic structures; the packing, density, and even the electrical form of atoms on several surfaces could all be extremely distinct (Cao et al., 2016b). Size and shape-reliant parameters are intimately linked to the superficial chemistry and catalyst nanoparticle morphology, which primarily controls the nanoparticle's catalytic efficiency. This can be attributed to catalytic activity at a solid-gas or solid-liquid contact on a catalytic site of the catalyst surface due to essential fundamental processes known as surface adsorption occurring on the catalyst interface. Since each facet of a catalyst nanoparticle has a unique binding arrangement and strength, each aspect of the catalyst nanoparticle can create distinct surfaces with terraces, steps, and corners on the surface of the catalyst nanoparticle. Consequently, the effects of the size and shape of a catalyst nanoparticle on its catalytic efficiency are mostly represented by variations in the chemical and morphological variables of the catalyst nanoparticles' surfaces. Furthermore, the effects of the various promoters used on the chemical characteristics of the resultant catalyst, as well as the activity of the resulting catalyst in terms of increasing the preference to lower olefins, have been investigated. It has also been described how several parameters, including the acidity of the zeolite, the Si/Al, and the working conditions, affect the process pathway (Cao et al., 2016b).

2.4.4.4.1 Acid Amount: Brønsted acid site and Extra-framework species

Zeolites containing different heteroatoms have demonstrated a wide range of catalytic activity. Brønsted acid sites are formed in the pores of zeolites when trivalent atoms, such as aluminium (Al), replace silicon (Si) in the framework and are balanced by protons. The types and locations of heteroatoms play a role in generating these acid sites. Recent studies have also revealed that extra-framework species, which often form during post-synthesis hydrothermal treatments, can impact neighbouring Brønsted acid sites' activity and, consequently, zeolites' cracking activity (Ji et al., 2017b).

In conventional zeolites, acid sites are crucial for catalytic processes. However, determining the locations of these acid sites and managing their distribution within zeolites pose significant challenges. Studies have shown that the placement of Al atoms in zeolites is influenced by both the Si/Al ratio and the fabrication process (Gounder and Iglesia, 2009, Sklenak et al., 2009). Depending on the fabrication technique, this can result in varying catalytic activity for zeolites with similar structures. Therefore, caution is necessary when comparing research data from different groups due to potential conflicts arising from the various sources of zeolites employed. Researchers have examined the impact of the Si/Al ratio on the distribution of framework Al and its effect on butane cracking and dehydrogenation in H-MFI zeolites. They found that Brønsted protons were more likely to be detected at channel junctions as the Al content increased. This spatial arrangement favours dehydrogenation over cracking due to differences in the transition state geometries. By modifying the Si/Al ratio of the zeolite, the product specificity of alkane cracking and dehydration can be altered. The positions of the protons and confinement effects also affect the acid characteristics of the solution. The deprotonation energies (DPE) at specific T-sites in various zeolites have been determined through theoretical simulations. DPE measures the energy required to remove a proton from a Brønsted acid site and indicates intrinsic acid strength. The findings indicate that DPE values can vary significantly between different T-sites in zeolites. There is a direct correlation between Brønsted acidity and alkane cracking activity, and the preference for cracking products can be altered by adjusting the acid strength distribution (Lin et al., 2014, Katada et al., 2015, Niwa et al., 2013). The Brønsted acidity of zeolites can be modified by introducing various heteroatoms into their structure. The strength of Brønsted acid decreases in the following order among zeolites altered with trivalent elements: Al-ZSM-5 > Ga-ZSM-5 > B-ZSM-5 (Jungsuttiwong et al., 2011). The addition of alkali metals, alkaline earth metals, rare earth metals, transition

metals, phosphorus, and other elements can also impact the acid characteristics. Studies have examined the effect of different promoters on the chemical properties of zeolites, as well as their catalytic performance and selectivity for light olefins. It has been observed that introducing alkaline and rare earth elements can reduce the reabsorption of cracking products and enhance dehydrogenation, leading to higher yields of light olefins. On the other hand, introducing transition metals can increase dehydrogenative cracking and, consequently, the yields of light olefins. Moreover, modifying ZSM-5 zeolites with phosphorus can alter the number of acid sites and the ratio of Lewis to Brønsted sites, ultimately resulting in higher yields of light olefins (Ji et al., 2017a, Furumoto et al., 2011).

Extra-framework species play a role as Lewis sites and interact synergistically with nearby Brønsted sites (Ghorbanpour et al., 2015). Different metal-exchanged zeolites exhibit varying stability levels, affecting the propensity of framework metals to migrate outside the framework. During hydrothermal treatments, zeolites substituted with gallium (Ga) or iron (Fe) are less stable compared to those substituted with aluminium (Al), allowing Ga and Fe to move to extra-framework regions more easily. Through periodic density functional theory (DFT) computations, it has been demonstrated that mononuclear oxygenated cations in the extra-framework are less stable than bi- or multinuclear cationic complexes in modified MOR and ZSM-5 zeolites containing Ga, zinc (Zn), Al, copper (Cu), and Fe (Miyake et al., 2016). Among the various extra-framework species, extra-framework aluminium species have been extensively studied. A synergistic effect between these species and neighbouring Brønsted acid sites has been proposed to cause the improved catalytic activity observed in the presence of extra-framework species (Ghorbanpour et al., 2015). It has been found that the presence of extra-framework aluminium species enhances the Brønsted/Lewis synergy in dealuminated HY zeolites, as confirmed by solid-state nuclear magnetic resonance (NMR) and DFT computations. Experimental results from ^{2-13}C acetone NMR and theoretical simulations indicate that these extra-framework aluminium species can increase the acidity of Brønsted acid sites in direct contact with them (Li et al., 2021). Additionally, including larger extra-framework aluminium species, as suggested by Gounder and Iglesia (2009) may lead to smaller void sizes in the functional supercages, thereby contributing to greater stabilization of the transition states.

2.4.4.4.2 Si/Al ratio - HZSM-5 zeolites with different Si/Al ratios

The catalytic performance of HZSM-5 zeolites is significantly influenced by the Si/Al molar ratio and the presence of modifying promoters (Rahimi and Karimzadeh, 2011b). The exceptional hydrothermal stability of ZSM-5 zeolite is closely related to its high Si/Al ratio, which limits aluminium separation from the framework structure and reduces framework breakdown during steam treatment. Consequently, increasing the Si/Al ratio enhances the stability and crystallinity of the zeolite (Hagen, 2015, Gates, 1991). Upon dealumination, the quantity of acidic sites decreases, but the acidity of the remaining centres increases until reaching a dealumination degree of approximately 50%. The opposing effects of acid centre concentration and their strength overlay lead to the highest reactivity at a specific $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Hagen, 2015). Han et al. (2004) investigated the catalytic cracking of heavy naphtha for the selective production of light olefins using various zeolites, including HZSM-5 with Si/Al ratios of 20, 25, 40, and 75, H-mordenite with Si/Al ratio of 12.5, H-beta with a Si/Al ratio of 150, and SAPO-11. Among these catalysts, HZSM-5 exhibited the highest efficiency for light olefin synthesis, with a yield of around 48.5 wt.% of $\text{C}_2\text{-C}_3+$ ($\text{C}_2/\text{C}_3=0.90$), even at the lowest Si/Al ratio of 20 (Han et al., 2004). The preferential production of propylene was achieved without compromising the overall olefin yield (Han et al., 2004). The cracking of naphtha range alkanes and naphthenes over the 8-12-member ring (MR) zeolitic catalysts was explored. Among the tested catalysts, 10-MR zeolites such as ferrierite demonstrated the highest yields of light olefins, particularly ethylene and propylene, with an 83% naphtha transformation and a 54 wt.% preference (Kustova et al., 2007a). The selectivity of catalysts for $\text{C}_2\text{-C}_3$ varied as follows: ferrierite > ZSM-22, ZSM-23 > ZSM-35, Y > EU-1 > beta (Kustova et al., 2007a). The specificity for light alkanes and coke was higher in 12-MR zeolites compared to ethylene and propylene, resulting in increased selectivity for light alkanes and coke at the expense of ethylene and propylene (Kustova et al., 2007a).

Lu et al. (2008) investigated the influence of the Si/Al ratio on the activity of ZSM-5 catalysts for light olefin production in C_4 alkane catalytic cracking. The study encompassed HZSM-5, Fe/HZSM-5, and Cr/HZSM-5 zeolites with Si/Al ratios ranging from 25 to 150. NH_3 -TPD investigations revealed a significant decrease in the catalysts' overall acid quantity, density, and strength as the Si/Al ratio decreased. However, the weak acid sites increased with lower Si/Al ratios. The three systems of catalysts (HZSM-5, Fe/HZSM-5, and Cr/HZSM-5) with Si/Al ratios below 50 exhibited comparable or higher isobutane transformations than other

systems. However, the changing trends in isobutane transformations varied among the three catalyst systems when the Si/Al ratio was less than or equal to 80. Higher Si/Al ratios (≥ 80) favoured increased yields of light olefins (C_2-C_4+) for Fe/HZSM-5 and Cr/HZSM-5 zeolites (Lu et al., 2008). The optimal Si/Al ratio to maximize the production of specific light olefins, such as ethylene, propylene, and butene, could not be determined based on the catalytic performances of HZSM-5, Fe/HZSM-5, and Cr/HZSM-5 zeolites with various Si/Al ratios at the referenced temperatures (550-600 °C). For example, at 550 °C, the maximum yield of light olefins (59.8 wt. %) was obtained over Cr/HZSM-5 zeolite with a Si/Al ratio of 150, while the maximum yields of light olefins (54.6 wt. %) over Fe/HZSM-5 and HZSM-5 were achieved with ratios of 80 and 50, respectively. Increasing the Si/Al ratios reduced BTX yields in all samples, indicating decreased hydride transfer and aromatization reactions due to fewer acid sites.

The effect of the Si/Al ratio on the production of light olefins was also investigated in catalytic cracking. Jung et al. (2004) observed a significant decrease in the conversion of n-octane with increasing Si/Al molar ratio (25, 75, and 100) of ZSM-5 zeolites across a temperature range of 200-600 °C. Regardless of the Si/Al ratio in the synthesis mixture, the specificity for olefins gradually increased with higher reaction temperatures. However, the number of acid sites with increased acidity had a major influence on the conversion but not the specificity (Jung et al., 2004). Consistent with previous findings (Kustova et al., 2007a), Abrevaya showed that increasing the Si/Al ratio from 24 to 66 reduced the occurrence of hydride exchange and aromatization reactions. Zhu et al. (2005) found that increasing the Si/Al ratio affected the catalytic cracking of butene to propylene over ZSM-5 zeolites, leading to improved propylene selectivity and total yields of propylene and ethylene (Zhu et al., 2005). Furthermore, higher Si/Al ratios significantly enhanced the stability of the catalysts. For instance, with a Si/Al ratio of 50 in ZSM-5, the conversion decreased from 96.6% to 67.5% (a 29% decrease) after 10 hours of operation, while with a Si/Al ratio of 366, the conversion only decreased from 84.5% to 81.4% (a 3% decrease) over the same duration. In contrast to the previous findings, Han et al. observed that as the Si/Al ratio decreased from 75 to 20, the yield of C_2-C_3+ increased from 29.3% to 37.5% (Han et al., 2004).

2.4.4.4.3 Modifications of ZSM-5 Zeolite catalysts.

Alkaline Earth Metal Modification of ZSM-5

Wakui et al. (1999b) investigated the effect of alkaline earth metals (Mg, Ca, Sr, and Ba) on the activity of HZSM-5 catalysts in the catalytic cracking of n-butane. The zeolites were modified by adding each alkaline earth metal's carbonate salt ($\text{AE}(\text{CO}_3)$) to the aqueous solution used for zeolite synthesis. The modified ZSM-5 zeolites showed higher ethylene and propylene yields than the non-modified HZSM-5 zeolites. Ba/ZSM-5 demonstrated significant results with a yield of $\text{C}_2 = + \text{C}_3 =$ of 4.5% (Wakui et al., 2002b). However, no information was provided regarding the stability of the modified catalysts (Wakui et al., 2002a).

2.4.4.4.3.1 Transition Metal Modified ZSM-5 Zeolites

Lu et al. (2006c) were the pioneers in evaluating the performance of Fe/HZSM-5 [91] and Cr/HZSM-5 [92] zeolites in the catalytic cracking of isobutane. At 625 °C, Fe/HZSM-5 (Si/Al = 32) and Cr/HZSM-5 (Si/Al = 32), catalysts loaded with trace amounts of 0.010 mmol/g Fe (Lu et al., 2006c) and 0.004 mmol/g Cr (Lu et al., 2006b) exhibited enhanced catalytic performance and selectivity in isobutane cracking. Olefin production ($\text{C}_2\text{-C}_4+$) over Fe/HZSM-5 and Cr/HZSM-5 zeolites reached 65.6% and 56.1%, respectively. Notably, Fe/HZSM-5 zeolites achieved significant production of ethylene (24.6%) and propylene (32.4%) (Lu et al., 2006c). The introduction of trace amounts of iron or chromium facilitated the dehydrogenation of isobutane, forming isobutene, which can be easily cracked to produce light olefins (Lu et al., 2006b, Lu et al., 2006c). In the dehydrogenative cracking of C_4 alkanes using cobalt oxide-impregnated HZSM-5 (5% Co/ZSM-5), butene selectivity was increased (Wakui et al., 2002b). Additionally, ZSM-5 zeolites (Si/Al = 200) doped with transition metals such as Cu, Zn, and Ag improved the yield of aromatics while decreasing the yield of $\text{C}_2\text{-C}_3+$ in the catalytic cracking of C_4 alkanes (Yoshimura et al., 2001).

2.4.4.4.3.2 ZSM-5 Zeolites Modified with Rare Earth (RE) Elements

Xiaoning et al. (2007) investigated the effect of rare earth elements (RE) on the morphology, acidity, and catalytic activity of HZSM-5 zeolite in the synthesis of light olefins. $\text{RE}(\text{NO}_3)_3$ aqueous solutions were used to impregnate HZSM-5 catalysts, and their performance was evaluated in the catalytic cracking of mixed C_4 alkanes (Xiaoning et al., 2007). Optimal propylene yields were obtained at 600 °C for Nd/HZSM-5, Ce/HZSM-5, and La/HZSM-5, with 25.9%, 25.2%, and 25.2%, respectively. Ce/HZSM-5 achieved an overall alkene production of 57.2 wt.% at 600 °C, while Nd/HZSM-5 reached 60.0 wt.% at 650 °C (Xiaoning et al., 2007). The ratio of propylene to ethylene varied significantly depending on the temperature and the specific rare earth element used. The addition of rare earth metals improved the specificity for

light olefins, leading to increased olefin production and reduced aromatic yields in the catalytic cracking of butane (Xiaoning et al., 2007). However, further research by Wakui et al. demonstrated a total C₂-C₃+ yield of 48 wt.% in the catalytic cracking of n-butane over La-impregnated HZSM-5 (Si/Al = 200) catalysts at 650 °C (Wakui et al., 1999a). The C₂-C₃+ yield increased to 58% at 650 °C by implementing a two-stage dehydrogenation and cracking process. The process utilized a dehydrogenation catalyst of Pt-Sn type and a cracking catalyst of RE-loaded HZSM-5 (Wakui et al., 2002c). The proposed procedure involved the initial dehydrogenation of n-butane to n-butene (1- and 2-butene) over a Pt-Sn/Ca-ZnAl₂O₄ catalyst (located at the top of the reactor), followed by consecutive conversions of n-butene to ethylene and propylene over a 10% Pr/ZSM-5 cracking catalyst (located at the lower part of the reactor).

2.4.4.4.3.3 Phosphorus and Lanthanum Modified ZSM-5 Zeolites

The combined influence of lanthanum and phosphorus is significant in achieving favourable outcomes for light olefin synthesis over P-La/ZSM-5 catalysts. When rare earth metals and phosphorus are used to modify zeolites, the formation of RE-P-O oxides on the zeolite's surface occurs, covering some surface acid sites (Liu et al., 2004). Lanthanum also prevents the leaching of phosphorus species from the zeolite at high temperatures and in the presence of steam. The modification with rare earth metals and phosphorus reduces surface acidity (Liu et al., 2004, Xue et al., 2010a), attributed to the interaction between rare earth metal cations and phosphate anions. Phosphorus adjustment is a commonly employed strategy to enhance the performance of HZSM-5 zeolites in the catalytic cracking of C₄ alkanes for light olefin production. Jiang et al. (2008) investigated the performance of P-modified HZSM-5 (using (NH₄)₂HPO₄ as the source of phosphorus) in the catalytic cracking of mixed C₄ alkanes to improve the yields of ethylene and propylene (Jiang et al., 2008). At a temperature of 650 °C, the highest yields of propylene and ethylene reached 25.6% and 33.9% wt.%, respectively, which were 7% and 4.5% wt.% higher than the yields obtained from the parent HZSM-5 zeolite. However, Wakui et al. (1999a) found that the yields of ethylene and propylene decreased when using P/ZSM-5 (2 wt.% P-loading) in the catalytic cracking of n-butane at 650 °C, suggesting a detrimental influence of added phosphorus on the cracking activity (Wakui et al., 1999a). Satisfactory results were obtained by impregnating the zeolites with aqueous solutions of La(CH₃COO)₃·5H₂O and (NH₄)₂HPO₄, achieving optimal outcomes over a 2% P-10%La/HZSM-5 (Si/Al = 200) mixture (Wakui et al., 1999a, Wakui et al., 2002a).

The addition of lanthanum has been found to contribute to the production of lower aromatics, although not entirely consistent with other findings (Rahimi and Karimzadeh, 2011b). Other elements, such as magnesium (Mg), calcium (Ca), and copper (Cu), were shown to yield lower quantities of benzene, toluene, and xylene (BTX) while increasing the yields of light olefins. The addition of cobalt (Co), nickel (Ni), iron (Fe), and zinc (Zn) to ZSM-5 zeolites significantly reduced the production of BTX but also decreased the yields of ethylene and propylene to some extent (Wei et al., 2005). P-La/ZSM-5 (Si/Al = 72) demonstrated the best results, with initial C₂-C₃+ yields of approximately 57-60%. The stability test showed that over P-La/ZSM-5, the C₂-C₃+ production remained above 50% for 30 hours, while on HZSM-5, it decreased from 47% to 31% after 10 hours (Wei et al., 2005). The catalytic cracking process under steam conditions (without N₂ stream) resulted in significantly higher yields of light olefins (C₂-C₃+ = 57%) and reduced BTX production (C₂-C₃+ = 56%) compared to the process without steam. The presence of steam enhanced the production of light olefins by reducing the synthesis of BTX and light paraffins, likely formed through hydrogen transfer reactions (Wei et al., 2005). Yoshimura et al. conducted a comprehensive study on the catalytic cracking of naphtha for light olefin production. They explored oxidative cracking over basic catalysts (aerobic process), oxidative and non-oxidative cracking over transition metal catalysts (aerobic/non-aerobic process), and catalytic cracking over solid acid catalysts (non-aerobic process). They obtained interesting results with an innovative La₂O₃-P/ZSM-5 (Si/Al = 200) zeolite-based catalyst, which produced ethylene (34 wt.%) and propylene (23 wt.%) at 650 °C in the presence of steam, representing a 10% increase compared to standard steam cracking techniques operating at higher temperatures (Yoshimura et al., 2001). A feasibility analysis for a naphtha processing capacity of 3000 tons/day showed that a fixed-bed catalytic cracking facility could reduce energy consumption per ton of ethylene and propylene produced by over 20%, leading to a roughly 20% reduction in CO₂ emissions (Yoshimura et al., 2001, Feng et al., 2010).

2.4.4.4.3.4 Fluorinated ZSM-5

Fluorinated HZSM-5 zeolites (F/HZSM-5) show great potential as catalysts for the catalytic cracking of naphtha to produce light olefins. HZSM-5 (Si/Al = 46) zeolite was immersed in an aqueous solution of NH₄F to develop the F-modified HZSM-5 samples. Feng et al. found that the highest yields of propylene (36.4%) and ethylene (20.2%) were achieved at 600 °C over 0.1F/HZSM-5, which had the highest Brønsted acid quantity. These yields were 7.3% and 4.3% higher than the highest yields obtained over the parent HZSM-5 zeolite (Liu et al., 2004). The

addition of fluorine significantly increased the acid content of HZSM-5, as observed in the FT-IR analysis of pyridine adsorption on F/HZSM-5. The BET surface area and pore volume of F/HZSM-5 increased, primarily due to the expansion of micropores. Fluorine adjustment not only regulated the pore properties of HZSM-5 zeolites but also controlled the quantity and density of acid sites, particularly Brønsted acidity, which could lead to increased conversion of naphtha and improved specificity for light olefins (Feng et al., 2010). Mao et al. found that the surface acidity of F-ion-exchanged ZSM-5 zeolite increased due to the generation of new Brønsted acid sites and the strengthening of existing acid sites in the parent zeolite. This was attributed to the proton attack of the zeolite surface by chemisorbed H^+F ion pairs. Under these conditions, the zeolite framework structure remained intact (Le Van Mao et al., 1999).

2.5 Economic Evaluation and Ecological Implication of Low Alcohol Feedstock: Current Production, Costs and Environmental Impact

Due to the increasing depletion of the world's fossil-fuel reserves, there has lately been a surge in research utilizing biofuel in compression-ignition engines. Environmental issues have indeed increased in the price of fossil fuels and regulations on exhaust emissions from internal combustion (IC) engines. Various nations, including the United States, have switched from fossil fuels to sustainable fuels (Traver, 1967). As a result, low alcohol is essential to substitute fuels that can be employed in conjunction with gasoline in internal combustion engines, either as a blend or as an additive. The cost of producing low alcohols can vary significantly depending on the feedstock used, the transformation approach used, the production level used, and the region in which the fuel is produced (Awad et al., 2018).

2.5.1 Economics of Low Alcohols

For this study, bioethanol production and cost will be discussed. Figure 2.8 illustrates global ethanol production by nation or area from 2007 to 2021. It can be observed that production climbed rapidly from 2007 to 2010, with the highest output occurring in 2019 after a dip in 2011 and 2012 and a further decline in 2020 due to the COVID-19 outbreak. The United States is the world's greatest ethanol manufacturer, having synthesised over 13.7 billion gallons (BG) in 2020 despite the pandemic and 15.1BG in 2021, representing 52 and 54% of the world's ethanol production, respectively. Brazil ranks second in world ethanol production with 7.9 and 7.5BG, representing 30 and 27.5% of world ethanol production in 2020 and 2021, respectively. The United States and Brazil manufacture 83% of the world's ethanol, while the remaining 17% is produced by European Union (EU), 1.3BG and other countries in 2021.

To determine the market costs of biofuels, the most important factors to consider are labour and land expenses, feedstock, the oil market, and agricultural incentives. As of 2020, the cost of ethanol from sugar cane and corn is approximately US \$0.60 to \$0.70 per LGE (litre per gasoline equivalent), which is significantly higher than the cost of gasoline, with an average cost price of US \$0.58 per L⁻¹ (US\$2.40 per gallon), making ethanol less competitive in the market (Figure 2.9) (EIA 2020). Likewise, sugar beet or wheat ethanol may cost between US\$0.6 and US\$0.8 LGE. However, in 2021 the cost of sugarcane ethanol showed an appreciable competitive average cost of US \$0.66 when compared to corn ethanol and gasoline (US \$0.80 and US \$0.84 average cost, respectively), which shows that sugarcane ethanol can compete with gasoline in the fuel market. Considering the energy cost, ethanol is presently more costly than gasoline in all countries considered. Only ethanol generated in Brazil comes close to competing with gasoline in terms of price and performance. A significant price difference exists between the ethanol generated from corn in the United States and that of sugar cane in Brazil, with ethanol made from grain and sugar beet in Europe being even more costly (Anekwe et al., 2021b). Owing to the significant production of corn (USA) ethanol, its comparatively expensive cost is a significant barrier to its widespread use and commercialization as an alternative energy source and gasoline additive. Consequently, ethanol has not been economically competitive with gasoline; however, with government subsidies, the cost of ethanol manufacturing will be reduced significantly (Yacobucci, 2007). Moreover, when compared to fossil fuels, biofuel use will reduce fuel's net cost. The most significant difficulty is that increasing the use of biofuels will, in the short term, increase the overall fuel cost, making it more expensive than fossil fuels. The long-term savings in fuel expenditures, on the other hand, may assist in mitigating this challenge.

These discrepancies in the cost of ethanol result from various parameters, including scale, operational efficiencies, biomass costs, capital and labour expenses, co-product accounting, and estimates (Awad et al., 2018). These parameters influence the cost, pricing, and profitability of biofuel synthesis. The price of biomass resources remains a significant factor in determining the cost of biofuel synthesis. The wide majority of U.S. ethanol is generated from corn, Brazil mainly utilizes sugarcane, while the EU employs wheat and sugar beet for ethanol production. The costs of these agricultural products are determined by factors such as planted area, outputs, harvest variables, and market characteristics, all of which are prone to year-to-year variations. The technological complexity of manufacturing facilities and the price of the fuels utilized for process energy impact the cost of biofuel production. In Brazil, the cost

of sugar cane ethanol varies according to the harvest period, with prices increasing during the inter-harvest season from January to March. Other factors influencing biofuel pricing include frequent modifications of current gasoline and diesel prices. The expense of commercial-scale bio-based product synthesis is now prohibitively expensive in developed nations. For instance, the price of producing biofuels may be three times greater than that of producing petroleum fuels without considering the non-market advantages. In contrast, the costs of manufacturing biofuels in developing nations are far lower than in Organization for Economic Co-operation and Development (OECD) countries and are quite close to the world market cost of petroleum fuel (Abbasi and Abbasi, 2010).

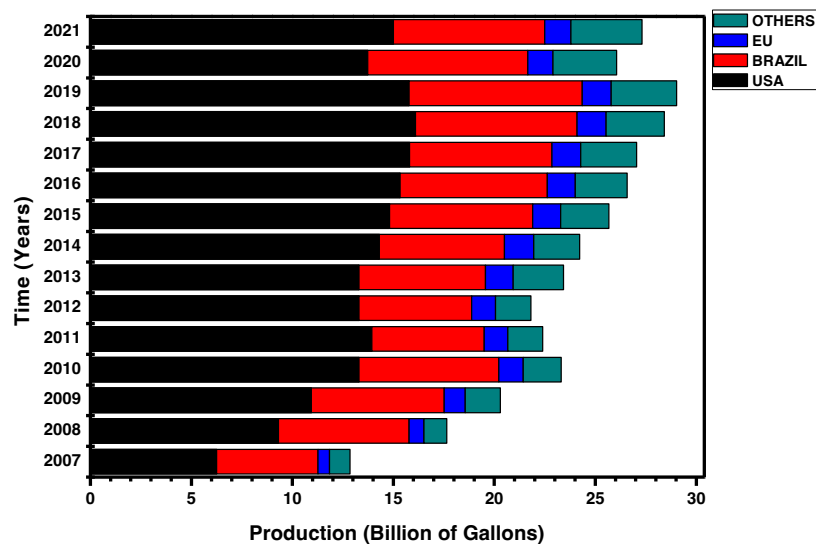


Figure 2-8. Global ethanol production from 2007 – 2021 (*Source: US Energy Information Administration (2021); (United State Department of Agriculture, 2020))*

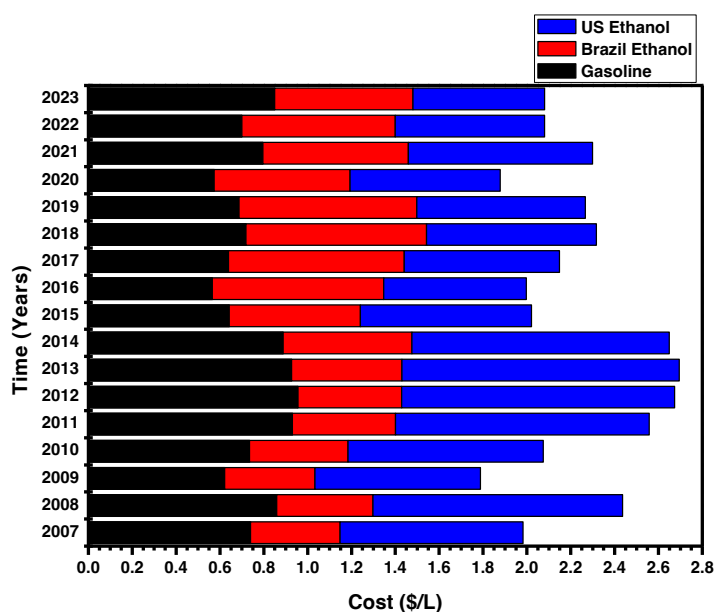


Figure 2-9. Comparison of the average retail fuel prices of Gasoline, Brazil ethanol and US ethanol in litre per gasoline-equivalent (LGE) from 2007 to 2021 (*Source: US Department of Energy (2021); Brazil Ethanol (2019); (US Energy Information Administration, 2022)*)

2.5.2 Environmental and Health Impact of Low Alcohols

Global acknowledgement of the severe long-term consequences of climate change offers a critical premise for using low-alcohol fuels. This implies that alcohol fuels should be ready to embrace opportunities to reduce greenhouse gas emissions (CO₂, CH₄, N₂O, etc.). Low bioalcohols have proven to be quite successful in lowering greenhouse gas emissions. Compared to pure gasoline, bioethanol derived from corn emits 43% fewer greenhouse gases than the latter. From a scientific perspective, ethanol can be manufactured from biomass generated from the CO₂ plants absorb during photosynthesis. As a consequence, it can be considered carbon neutral. In contrast to fossil fuels, which release a large quantity of CO₂ from their internal carbon atoms during combustion, ethanol can be considered carbon neutral since it does not release nearly as much CO₂ from its internal carbon atoms during combustion. However, the growth of biomass crops and the production of alcohol fuels are responsible for many greenhouse gas emissions, both directly and indirectly. When alcohol fuels are employed, there is a wide range of potential CO₂ reduction. According to Alckmin–Governor and Goldemberg–Secretary (2004), the values range between 0.5 kg CO₂-equivalent/litre of ethanol for wheat-derived ethanol and as high as 2.24 kg CO₂-equivalent/litre of sugar cane-derived ethanol.

Natural environments disintegrate ethanol at an alarmingly fast rate. Biodegradation of ethanol is quick in soil, groundwater and surface water, which can be retrieved within 10 days. As a result, it poses little threat to the environment and living organisms. However, there have been a few isolated instances in which the degradation of oxygen in surface water due to large amounts of ethanol has resulted in the death of fish in surface water. Ethanol, on the other hand, is not assimilated by soil particles (Council, 1993). Furthermore, it has been asserted that ethanol enhances air quality by assisting ozone formation (Vallinayagam et al., 2017).

Methyl alcohol (methanol), on the other hand, is a toxin that is colourless and flammable, and it is employed as a solvent, an alternative fuel for motors, as a feedstock for catalytic processes or as a basic fuel for picnic stoves, as an antifreeze (by decreasing the freezing point of water) for automobile radiators, and as a pesticide (Goswami et al., 2015, Sheng and Azevedo, 2005). Methanol is a low-toxicity compound for aquatic and most terrestrial species, and adverse consequences from exposure to methanol in the environment are unlikely to be noticed except in the event of a spillage. Non-primate animals have low acute toxicity when exposed to methanol. However, methanol is associated with several health hazards, including blindness, mobility difficulties, and mortality (Sheng and Azevedo, 2005). The intake of 10 mm of methanol results in lifelong visual impairment, while 30 mm of methanol leads to death when consumed as part of a beverage. Methanol toxicity in humans (methanol poisoning) is a result of its metabolism (in the liver) via alcohol dehydrogenase, which triggers the formation of formaldehyde (Gribble, 1989), and subsequently converted to formate (formic acid), a highly poisonous substance responsible for metabolic acidosis and end-organ toxicity (Polss, 1973). These transformations cause damaging impacts on the central nervous system. Methanol can be absorbed into the human body through various routes (ingestion, inhalation, eye or skin contact).

Various sources release methanol into the atmosphere, including volcanoes, microorganisms (especially bacteria), insects, animals, and the breakdown of organic substances. Moreover, methanol can be discharged into the air due to the human impact, mostly due to using methanol as a solvent or feedstock for catalytic conversion processes for fuel and petrochemical production, which results in evaporation. The presence of methanol in water and soil is less significant since methanol exists in natural organisms such as fresh and saltwater, groundwater, sediments, and soil, and its source is bioaccumulation, presumably from other sources. Methanol can also be found in synthetic products such as ethanol. It is possible to establish that

methanol is less damaging to terrestrial and aquatic organisms than other pesticides. Compared to petroleum-based fuels, it can be claimed unequivocally that methanol is significantly safer and less hazardous (Mohammed et al., 2017).

Allowable alcohol exposure limits for general industry in the air (40 hours per week) in the United States are 1900 mg/m³ for ethanol, 900 mg/m³ for gasoline, and 260 mg/m³ for methanol, according to the EPA. Because ethanol has a characteristic smell and methanol does not, it is difficult to distinguish methanol in air concentrations greater than 2,000 ppm (about 1500 mg/m³). As a result, extra measures for the refuelling system and the gasoline station are required (Atnaw et al., 2014). To be classified as renewable, a fuel or its source must be biologically recycled by combining carbon dioxide and water in photosynthesis. However, while H₂O and CO₂ are necessary for methanol production, a mechanism can be developed to supply CO₂ (a GHG) from the atmosphere or flue gases, both needed for methanol production. Because H₂ is required to initiate synthesis, water electrolysis is carried out to kick-start the renewable energy system. A substantial quantity of CO₂ is required to synthesise methanol from various resources such as natural gas, coal, biomass, and flue gas. To generate methanol, natural gas and coal need less CO₂ (Demirbaş, 1997).

2.6 Challenges, Development and Prospects in Catalytic Conversion of Low Alcohols to Fuel and Petrochemicals

2.6.1 Challenges in the Catalytic Conversion Processes

Despite the potential of low bioalcohol as a renewable energy source, its production, conversion to higher hydrocarbons (for fuels and petrochemicals), and applications still face some challenges.

2.6.1.1 *Biomass and Land Availability; Food and Water Security*

Technologies for producing biofuels will only be effective and beneficial to the general public if there is a sustainable supply of biomass feedstock available, considering ecological implications and the "food vs fuel" controversy (Cheng and Timilsina, 2011, Lin et al., 2011, Luthra et al., 2015, Painuly, 2001). A sustainable and environmentally favourable approach to developing oil crops has been proposed in one of the reviews by Groom et al. (2008). They also urge that zero-carbon, more sustainable, and virtually entirely non-fodder feedstock are promoted so that biodiversity and the preservation of critical and native food crops are not jeopardised or compromised in any way. The issues associated with the long-term supply of

biomass= resources for biofuel synthesis have also been discussed in other publications (Demirbas, 2009a, Demirbas, 2009b), in which the authors have specifically emphasised the dispute between food and biofuel. The need for food and water will continue to rise with the world's increasing population. It is among the reasons that food costs have risen substantially worldwide. Historically, there was no substantial relationship between biofuel costs and food prices; however, the number of food crops (sugarcane, maize, soybean, and rapeseed, among others) used to make biofuels has increased, and this relationship has also become stronger. The constant rise in and generation of biofuel, as well as the increased competitiveness of the biofuel industry, results in a spike in the costs of raw materials used to manufacture biofuel. In light of these rising tendencies, the food and biofuel industries will become increasingly intertwined in the coming years, which will almost probably impact food costs (Joshi et al., 2017).

As a result, the focus of biofuel study is changing away from fodder raw material and toward the development of biofuel synthesis from non-fodder biomass (like *Jatropha*, *Karanja*, *Polanga* oils etc., for biodiesel production and agro and forestry residue cellulosic biomass for bio-ethanol synthesis). For this purpose, much of the study on biofuel generation concentrates on the possible consequences on food security, land use variations, and water sources (Lin et al., 2011, Luthra et al., 2015, Painuly, 2001). Farmers, especially in developing countries such as India, have begun to adjust their farming practices away from producing food crops and toward producing biofuel crops on agricultural land to increase their incomes and employment opportunities in the agriculture sector, even if humans do not consume the new crops. Consequently, food accessibility and security would deteriorate, while the price of food would rise (Lin et al., 2011, Luthra et al., 2015). Moreover, several other impediments to the long-term development of present biofuel technology exist. The energy density of biomass-derived fuels is low, and the cost of gathering and transporting biomass is expensive. Furthermore, increasing the development of biofuel-based crops without considering the quality and accessibility of water in each location could burden water resources, particularly in developing nations. Such agricultural transitions toward the production of biofuel crops can alter the supply of clean and potable water while drastically increasing the burden on regional water resources (Lin et al., 2011, Luthra et al., 2015). Aside from that, the high input requirements for biofuel synthesis (land use, water use, crops, energy use, etc.) are primarily fully liable for the poor economics related to these biomass-derived fuels, which is recognised as one of the significant

barriers in their long term development (Demirbaş, 2010, Escobar et al., 2009, Luthra et al., 2015).

The above impediment can be summed up as follows:

- Because biomass production is always dependent on various conditions, developing biofuel synthesis may necessitate the acquisition of additional land to ensure long-term viability.
- Increased demand for water resources due to the expansion of biofuel feedstock production.
- Preserving biomass has proven to be a significant difficulty, and including storage costs has reduced cost efficiencies.
- Technological advancements in manufacturing equipment result in a cleaner, more consistent, and smoother output.
- The applications of by-products should be properly delineated and categorised.

The utilisation of organic chemicals, which are damaging to the ecosystem, in the majority of procedures and green process development with substantial output has therefore become an issue of great concern.

2.6.1.2 The Influence of Low Alcohol Water Content on the Catalytic Conversion Process

Many investigations (Xiang et al., 2022, Wu et al., 2014, Kyriienko et al., 2021) have demonstrated that water and pollutants that may be evident in low alcohols can impact the catalytic efficiency and stability of catalysts during the bioalcohol transformation into various chemicals and fuels. It was revealed that water significantly influenced ethanol dehydration on alumina-based catalysts when using bioethanol as a feedstock (10 wt.% ethanol in water). The study by Kochar and AS (1981) reported that the presence of water, with exceptionally high water content, significantly slows the efficiency of ethanol transformation. The researchers revealed that in a microchannel reactor and at decreased temperatures (i.e., 380 °C), the rate of ethanol transformation decreased from 86 % to 65 % as water content increased from 5 wt.% to 90 wt.% over $\text{TiO}_2/\text{-Al}_2\text{O}_3$, while the specificity of diethyl ether increased at the expense of ethylene conversion. The use of extremely high temperatures ($> 420\text{ }^\circ\text{C}$) can potentially eliminate the influence of water. In the course of so many years of thorough studies, it has been discovered that the process temperature on alumina-based catalysts should be set high (>400

°C, especially in the existence of high water content) (Chen et al., 2007b, Kagyrmanova et al., 2011) to preclude the production of diethyl ether and achieve appreciable ethylene selectivity (Chen et al., 2007b, Kochar and AS, 1981, Pearson, 1983).

H-ZSM-5 has a peculiar pore structure and an acidic characteristic, making it one of the most promising catalysts for transforming ethanol into gasoline. However, coke deployment (which prevents the entry of active sites) and dealumination, on the other hand, triggers the immediate deactivation (i.e., loss of acidity) of H-ZSM-5. There is a complex relationship between the presence of water in the system and the deactivation of the catalyst. The hydration of Brønsted acid sites diminishes the acidic strength of the catalyst. Since water and coke precursors compete for adsorption on the acid sites during coke generation, water can restrict coke formation at mild temperatures (Gayubo et al., 2011). In the presence of water, however, at high temperatures (greater than 450 °C.), zeolite dealumination can occur, resulting in a considerable reduction in the active sites of the catalyst (Aguayo et al., 2002a, Aguayo et al., 2005). Hence, the design and tuning of catalysts for ethanol transformation should consider acidity and mesoporosity modifications to address the effect of water in alcohol conversion as well as the introduction of metal promoters, especially for catalysts with excellent specificity and hydrothermal stability at tolerable temperatures (Xiang et al., 2022).

2.6.1.3 Catalyst Deactivation - Carbon and Coke Deposition onto the Catalyst Surface

During catalytic processes, the deposition of different components onto the catalyst's surface occurs, leading to catalyst deactivation and a decrease in catalytic performance due to blocking sites and pores on the catalyst. The sintering process is the most critical component in the deactivation of the catalyst. A significant reduction in the active surface area characterises the deactivation of a catalyst. The sintering procedure led to a substantial improvement in the metal–support interaction, which had a negative influence on the catalyst activity as a consequence. An activity typically known as fouling can have severe implications if it progresses to a later stage, such as breaking the particles and blocking the spaces in the catalyst. Carbon and coke deposits in porous catalysts are fouling that has garnered considerable awareness recently. Notably, the perception of carbon and coke deposition is relatively ambiguous in terms of description and is tied to their sources. For example, coke formed by the decomposition and condensation of hydrocarbons has a different structure on the catalyst surface. The result can range from longer polymerized hydrocarbon chains to a stratified structure such as graphite. On the other hand, carbon fouling is an exceptional result of CO

disproportionation, which is a peculiar process. The chemical structure of deposited species varies based on the kind of reaction, catalyst, and environmental variables present throughout the generation process (Bartholomew, 2001). Presently, there is an arrangement that classifies catalytic processes, which are followed by coke and carbon generation, into two categories: structure-sensitive or structure-insensitive. In the case of coke-sensitive reactions, the unreacted coke will overlay the active phase, decreasing activity. Catalytic cracking and hydrogenolysis are examples of reactions that fall into this group. In the coke-insensitive processes, the reactive deposits can be eliminated to a significant amount by hydrogen or other gasifying agents, depending on the reaction. Examples of this type include methanol synthesis, methanation, steam reforming, and Fischer-Tropsch synthesis. It can be concluded that the structure and position of coke are far more significant than the impacts of catalytic activity (Rostrup-Nielsen, 1974, Schmidt et al., 2013).

Figure 2.10 depicts how carbon fouling affects supported metal catalysts. Potential outcomes can be broken down into three main categories. The first involves carbon chemisorbing on metal surface sites, which prevents reactants from reaching the metal; the second involves enclosing the entire metal particle, which results in complete deactivation. The last scenario involves clogging micro- and mesoporous materials, limiting entry to those sites. The rate at which deactivation continues for a specific catalyst and process highly depends on the variables present, including the process temperature. The discrepancy in rates of formation and gasification of carbon or coke precursors primarily determines the deactivation rate in the coke-insensitive process on metals. As a result of the presence of hydrocarbon reactions in metal oxide and sulfide catalysts, coke forms not only in the gas phase and on the catalytic surface but also in the non-catalytic component of the catalyst structure. There are many various types of reactions that can occur when hydrocarbons are involved. Polymerization/oligomerization of olefins, cyclization of alkenes, and production of polynuclear aromatics are all examples of reactions in which coke condenses on the catalyst surface.

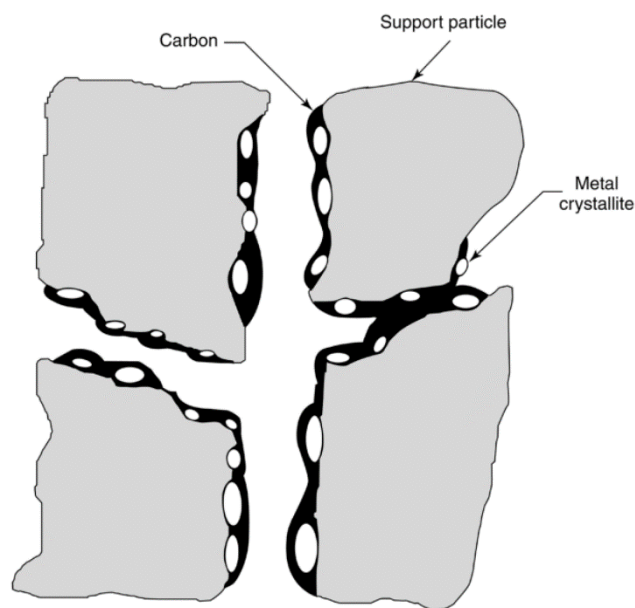


Figure 2-10. The development of carbon deposition on a supported metal catalyst results in fouling, crystallite encapsulation, and pore blocking, as seen in this schematic illustration adapted from Bartholomew (2001).

Much research on ethylene oligomerization has looked at catalyst deactivation (a severe concern in heterogeneous catalysis). Catalyst deactivation can be caused by significant product adsorption on active sites and pore blockage by heavy molecules. As a result, the pore size and process conditions have the most critical influence on the catalyst deactivation and lifespan. For instance, the Ni–Y and Ni–MCM-22 microporous Ni–exchanged zeolites (Ni–Y, Ni–MCM-22) experienced rapid deactivation during conversion (Lallemand et al., 2006, Lallemand et al., 2008b). It was reported that at a process temperature of 323 and 70°C, NiY lost around half of its initial reactivity after 120 –180 mins time-on-stream (TOS), while the Ni–Beta nanocrystalline zeolite with a substantial exterior surface area was an exception (Martínez et al., 2013). Under process parameters (120 °C and 35 bar), this catalyst showed no evidence of deactivation. Catalysts having mesopores, including Ni–amorphous silica-alumina, Ni–mesostructured silica-alumina, and Ni/sulphated alumina, on the other hand, demonstrated extreme deactivation resistance. The degree of catalyst deactivation (around 50 and 70% during 100 hours on stream) was unaffected by the space velocity, although it increased with pressure and temperature. According to Scurrrell (2001), Ni-exchanged silica-alumina showed just a slight deactivation under more extreme situations (35 bar, 120–180 °C) during 900-hour TOS tests (Heydenrych et al., 2001). The Ni–MCM-41 catalyst was much more active (with

ethene transformation of >95%) and quite resistant against deactivation during catalytic studies conducted at 30 °C and 35 bar for 170 hours on stream, according to Lallemand et al. (2011).

2.6.1.4 Catalyst Recovery Challenges

Catalyst recovery is one of the primary challenges associated with asymmetric homogeneous catalysis. Since homogeneous catalyst technologies are used in some commercial operations, recovery of homogeneous catalysts such as nickel complexes has become difficult, especially with no significant progress on heterogeneous catalysts since then. Although the homogeneous Dimersol approach has a modest initial investment, the nickel catalyst is not recycled, which has a negative impact on global economics by increasing operational expenses. However, it is usually a major problem in current catalysis studies to modulate the performance and selectivity of heterogeneous catalysts to achieve the best possible results in a specific process (Thomas et al., 2009). Zeolites take centre stage in this discussion since they are used in many acid-catalyzed processes. Another fundamental aspect that makes catalyst recovery difficult is that the bonds between metal and ligand are frequently broken and re-established in catalytic processes. If this happens, the catalyst can detach from the support and end up being dissolved. When the catalyst is recovered through filtration and recycled or employed with a continuous liquid flow, the "leaching" process causes the catalyst to lose its activity (Cole-Hamilton, 2003). However, when the catalyst was embedded inside the pores of zeolites or mesoporous materials, leaching was significantly reduced. Despite these benefits, reactions in which ultrafiltration has been performed have, in most cases, demonstrated a decline in activity following recycling (de Groot et al., 1999).

To this end, there is no clear answer to the query of which catalyst recovery and recycling methods ought to be made commercially available. Every one of the procedures has at least one drawback, and most do not yet demonstrate the level of activity necessary for widespread commercial use. The catalyst, solvent, or procedure may be highly costly; the leaching rate of the catalyst is too high; the solvent or ligand is exorbitant; or the pressure is excessively high. There are many techniques, but only a few thorough cost evaluations have been conducted. Before any commercialization is even considered, they will be necessary. Some methods may have a lower environmental impact due to reusing most of the materials and avoiding contaminating volatile organic solvents. However, the effects that certain solvents (such as fluoruous and ionic liquids) have on the surrounding environment are not yet fully understood (Cole-Hamilton, 2003).

2.6.1.5 *Zeolite Commercialization Challenges*

Zeolite catalysts have been promising in the catalyst conversion of low alcohol into fuels and petrochemicals. The most often used acid zeolites in industrial processes are bifunctional acid zeolites, which include tiny mono- or bi-metallic particles, and microporous acid zeolites (FAU, MOR, MFI, BETA, and in lesser amounts of other frameworks, including FER, LTA, LTL, MTW, CHA, AEL, and TON) (Bellussi et al., 2012), accompanied by zeolites having additional transition metals (especially Ti or Fe in little quantity) in place of Al in their framework or sometimes extra-framework positions (Cu-zeolites). Despite recent advances, basic-type zeolites (Hunger, 2010) and bigger pore zeolites and mesoporous materials have restricted uses. Zeotype materials, such as silica alumina-phosphate (SAPO) (Bricker et al., 2007), have some applications, but very few of them have significant industrial catalytic applications; however, many of these catalysts, including other zeolite catalysts, are used in fine chemical synthesis (Fechete et al., 2012). Other than for specialized uses, metal complexes housed within zeolites or anchored/tethered to mesoporous components have failed to achieve widespread application in the industry (Čejka et al., 2012). This is primarily because the cost-effectiveness and stability of the system are still poor under realistic conditions. Hence, the reasons for the relatively small number of zeolites available for commercial use. The higher manufacturing costs are mainly due to organic structure-directing agents (OSDAs), i.e. molecules with sizes and structures that are congruent with the zeolite channels or cages and promote their development. Most zeolite frameworks can only be synthesised with OSDAs. However, the cost and inability to recycle OSDAs due to the post-synthesis calcination required to remove the entrapped molecules is highly costly and limits their broader application in commercial settings (Rimer et al., 2014). Consequently, there exists a disparity between the wide range of micro- and mesoporous materials that have been designed (due to extensive research and development) and the limited variety of materials currently available for industrial application (Corma et al., 2010).

2.6.2 *Developments and Viewpoints in Low Alcohol Catalysis*

2.6.2.1 *Reactor Design for Low Alcohol Conversion*

Studies of low alcohol conversion, including ethanol dehydration to ethylene, oligomerization of olefins, etc, are currently focused on facets including the production system/facilities, the reaction pathway, and an extremely effective catalyst. The reactor is an essential apparatus in the entire production unit of ethanol dehydration to ethene synthesis. When likened to the fixed

bed reactor, which is presently the most frequently employed in commercial facilities, the fluidised bed reactor has several benefits, including a higher heat and mass transfer rate, a more homogeneous bed temperature, and a more reliable mechanism. It is particularly well suited for large synthesis involving a significant thermal effect. On the other hand, the catalyst is easily worn out due to the friction and collision between the catalyst particles and between the catalyst particles and the reactor. Moreover, in conjunction with a wear-resistant, effective, and stable catalyst, this kind of reactor will be the reference for further investigation (Zambrano et al., 2020).

2.6.2.2 *Development in Zeolite Catalyst*

2.6.2.2.1 *Exploring Zeolite Versatility and Application*

With the application of zeolites, it is feasible to eliminate many processes dependent on mineral acids and stoichiometric/toxic reactants and improve the processes' material efficiency (reduced secondary products and energy use) (Ranu and Chattopadhyay, 2009). Actually, with the advances in zeolite development, it's presently feasible to apply zeolites in over 100 commercial operations, and the present global synthesis of zeolites (as of the year 2010) accounts for approximately 4 million tons per year, with a market value of approximately 3 billion USD. Catalysis is the most profitable of the three major application areas for synthetic zeolites (detergents, adsorbents/desiccants, and catalysis), accounting for around 20% of the total volume but approximately 50% of total revenue. The production of fuels, petrochemicals, and fine chemicals, particularly for pharmaceutical, fragrance, and agrochemical applications, is a field in which significant attempts are being made to apply growing understanding in a modified design of zeolites and associated materials. This is relevant in the pharmaceutical, fragrance, and agrochemical industries (Climent et al., 2011b, Climent et al., 2011a, Lucarelli and Vaccari, 2011, Čejka et al., 2012, Wenten et al., 2021). It has been demonstrated that acid zeolites with Brønsted or Lewis acid in carbonium ion reactions and metallosilicate (particularly titanosilicate) in oxidation reaction sites may be employed in a wide range of organic syntheses. Apart from the well-known shape selectivity features of zeolite catalysts, there are various benefits, ranging from clearly identified secluded areas with adjustable acidity to a controlled polarity. It's worth noting that, despite the size of the channels, which decelerates diffusion (resulting in slower reaction rate and deactivation), rapid improvements are underway to establish hierarchical zeolites, nanocrystalline and nanosheet zeolites, as well as to develop large pores zeolites (Galarneau et al., 2022, Kurmach et al., 2022, Yu and Xiao, 2022, Iadrat

and Wattanakit, 2021). However, since sophisticated models and multistep methods are needed, the synthesis of these materials is frequently prohibitively expensive.

2.6.2.2.2 *Improvement in Zeolite Framework*

Zeolites are among the significant class of commercial heterogeneous catalysts, with widespread use in refining and petrochemistry, as well as growth potential in ecological catalysis and the production of fine chemicals (Corma et al., 2010, Čejka et al., 2008, Centi and Perathoner, 2009, Maheria et al., 2021, Mitchell et al., 2021). Zeolites are crystalline microporous aluminosilicates that can be modified in various ways, providing a wealth of possibilities for the further development of their characteristics (Yu and Xu, 2010, Otto et al., 2018, Wang et al., 2021a). Over 200 different structural kinds have been identified, each with a unique size, shape, and connection of their channels, with the majority ranging from 8 to 30 rings (Čejka et al., 2012). Although the size of zeolite channel openings can occasionally exceed 1nm, it should be noted that the largest channel size for commercial processes is still 0.74 nm (12-ring). The ability to modify the textural features of zeolites, in conjunction with tunable acidity (type, concentration, and strength of acid sites), is the most significant aspect of zeolites (Xiao et al., 2021, Remperová, 2021, Suttipat et al., 2021). Although zeolites are typically 3D materials, it has lately been shown that some zeolites can be generated from layered precursors. Post-synthesis treatment of the precursors can result in the formation of 3D zeolites from the precursors. To gain an insight into the fabrication process, it was necessary to examine variations in X-ray powder diffraction trends after the fabrication and following calcinations (Lawal et al., 2022, Roth and Dorset, 2011, Roth et al., 2011). This structural discovery opens the door to new opportunities for customizing the textural characteristics of zeolites. Unlike the first conversions of 2D zeolitic precursors to a 3D framework, which were discovered by chance, the fabrication of 2D (lamellar, single-nanosheet) zeolites using designed structure-directing agents by Na et al. (2013) depicts a significant step forward in this field with substantial utilization potentials (Na et al., 2010).

2.6.2.2.3 *Exploration of Tunable Nature and Synthesis Mechanisms of Zeolite Catalyst*

The prospects for the continued use of zeolite catalysts in various disciplines of the chemical industry largely depend on the ability to fine-tune the zeolite features to match those needed for the intended operations. From the perspective of actual catalysts, zeolites are significantly more than just a perfect 3D systematic organization of TO_4 tetrahedral with channels and cavities that retain suitable active centres for the approaching guest molecules to react. The

zeolite components are composed of microscopic crystals with distinct structures, often including defects, sometimes in large quantities, and a specific nanoscopic (at the unit cell level) and macroscopic (at the crystal level) distribution of active sites, which can be acidic, basic, or redox, or a mixture of these to make the catalyst even more complicated. A review of recent studies on the fabrication of zeolite catalysts shows that the experimental methodologies used to achieve these materials are becoming incredibly complex. It is more straightforward to categorize all these findings into distinct groups, which may then be reduced to a single question, to have a thorough grasp of the information available. The synthesis of zeolites is predicted to yield several benefits. Five possible approaches have been suggested for classification: Firstly, there is little uncertainty that the crystallization of novel zeolitic frameworks is the most attractive long objective. Each new framework represents a new opportunity for refining a current operation or inventing a completely innovative approach, following extensive technical efforts (Martínez and Corma, 2011). Faujasite-based FCC (fluid catalytic cracking) catalysts are currently the best illustration of the significant variations induced by the employment of a synthetic zeolite material on a commercial scale (Choudary and Newalkar, 2011, Luan et al., 2021, Roberie et al., 2002).

Secondly, novel chemical components of current zeolites frequently provide the path for developing wholly new usage areas. TS-1, the Ti-comprising all-silica MFI topology material, illustrates this facet well (Wang et al., 2020, Bellussi and Millini, 2017). More recently, the effective fabrication of zeolite beta comprising Sn-atoms in tetrahedral coordination has been recognized as a notable milestone in zeolites (Tang et al., 2020, Jin et al., 2014). In the activation of carbonyl groups, these materials are highly effective and selective, as demonstrated by their activity in the Baeyer–Villiger oxidation of ketones to esters in the existence of H_2O_2 and their specificity in the Meerwin–Ponndorf–Verley reaction, which results in a decrease of carbonyl compounds to alcohols (Palai et al., 2022, Corma and Renz, 2005). Román-Leshkov et al. (2010) demonstrated that Sn-beta catalysts are adequate for converting sugars. Controlling the heteroatom position at the unit-cell scale and the macroscopic scale would be highly attractive for a particular framework, and the desired heteroatom (structure T-atoms other than Si) would be achievable in concept with suitable mastery of the synthesis parameters. It is also necessary to perform T-atoms properly situated and placed within a zeolite crystal (Mlekodaj et al., 2021, van Bokhoven and Lamberti, 2014, Dědeček et al., 2012). Since it is possible to migrate from a framework position to an extra-framework position and back again, the siting/position is not fixed but rather hinges on the

degree of hydration and process temperature. In fourth place, crystal size and shape are also important for many operations, and both are dependent on the synthesis conditions. Finally, genuine zeolites have a variety of flaws that originate from various sources, all of which have the potential to affect their catalytic function (Sazama et al., 2011, Barbera et al., 2011). It can be noted that various synthesis techniques have been developed to address one or more of these fundamental objectives, keeping in mind that modifying a single synthesis factor might impact multiple objectives. Some of these aspects have been thoroughly examined by Strohmaier (2010), while some observations on the hurdles in the synthesis of zeolitic materials have also been highlighted (Coronas, 2010, Wang et al., 2012).

Various synthesis techniques have been developed to circumvent the drawback given by zeolites' narrow channel openings while maintaining their chemical features. One method is fabricating hierarchical materials, which combine micro- and mesoporosity (Hartmann et al., 2021, Mumtaz et al., 2021, Martins et al., 2022). Several synthetic approaches have been suggested, with the following two being the most attractive approach: (i) the formation of zeolite seeds and their subsequent self-assembly into a mesoporous framework; and (ii) the production of mesopores in zeolites by primary or post-fabrication methods. Self-assembling approaches have also been presented to create one-of-a-kind structures (Al-Jubouri, 2020, Zhang et al., 2020b, Etim et al., 2016). Mesoporous molecular sieves attributes include integrated chemical diversity and large surface areas with pores with dimensions ranging between 3 and 30 nm (Čejka et al., 2012). Regrettably, their walls are primarily amorphous, and their structure has no significant acid sites (especially in the case of the Brønsted type). Mesoporous materials have grown substantially in chemical structure recently, resulting in mesoporous carbons, metals, carbides, and other compounds (Chen et al., 2011b, Platschek et al., 2011). Furthermore, the framework of the amorphous surface has not yet been entirely defined, and it is very dependent on the preparation and calcination processes used to create them. The formation of "surface roughness" (Zukal et al., 2008), as well as the existence of a corona area in the inner walls and channel-to-channel microporosity, are the results of this process, which can be utilised to design improved nanostructured materials for catalytic processes, such as TiO_2 @SBA15-like mesoporous nanocomposite (Perathoner et al., 2007).

2.6.2.2.4 Zeolite Catalyst Promotion and Stability Improvement

As a common norm, microporous zeolites can experience quick deactivation due to pore blockage induced by the production of higher oligomers, which might result in coking.

Increased acidity at the micropores' surface may sometimes contribute to coking formation (Catizzzone et al., 2015). The study of zeolites has enabled researchers to gain a comprehensive knowledge of the factors that control activity and stability in low alcohol conversion. This has been made possible by the wide range of structural and textural characteristics achieved through neutralization, dealumination, doping or promotion (Menon et al., 2020, Singh et al., 2020b, Palizdar and Sadrameli, 2020). The promotion of zeolite catalysts using metals, including transition metals (Li et al., 2016, Sánchez-López et al., 2021, Kosinov et al., 2018), alkali and alkaline earth metals (Song et al., 2009a, Klein et al., 2016, Inaba et al., 2012, Eman and Chand, 2015), and rare earth metals (Ouyang et al., 2009, Liu et al., 2017, Abdullayeva, 2020, Sarve et al., 2022) has proven to enhance the catalytic performance of the zeolite catalyst (Wang et al., 2018c). However, great care is required to avoid high metal content, which may have a detrimental effect on the catalyst performance (Julian et al., 2020). The metal promotion process can be carried out by incorporating the promoter (metal) into the catalyst using appropriate synthesis techniques. Post-treatments, such as alkali ions or steaming, can reduce surface acidity and open the porous framework, resulting in improved, but still insufficient, stability without significantly influencing the performance or olefin transformation rate. In this context, using structured aluminosilicates with mesoporous networks that are less geometrically constrained appears to be especially promising for producing effective, selective, and more stable catalysts (Olivier-Bourbigou et al., 2020).

Also, other elements have been employed as a promoter. As evidenced by the various patents, including all the leading refining businesses, phosphorus' promotional benefits are prevalent in the petrochemical sector (van der Bij and Weckhuysen, 2015). Many researchers have examined the impact of phosphorus on zeolites. Regarding basic research in this area, the actual form of phosphorus–zeolite association has long been debated, making it an essential subject to study (Nicholas et al., 2017). Models of probable interactions have been suggested over time, but there is disagreement about whether phosphorus is permanently linked to the structure (Blasco et al., 2006, Lischke et al., 1991, Göhlich et al., 2011, Cardoso et al., 2005, Damodaran et al., 2006). H-ZSM-5 is more stable hydrothermally by adding phosphorus as a promoter (Alabdullah et al., 2020). However, as phosphorus combines with zeolite acid sites, the quantity and strength of zeolite acid sites decrease (van der Bij and Weckhuysen, 2015).

2.6.2.2.5 *Improvement in Transition Metal Catalysis*

The problems associated with the catalyst separation from the oligomerization products and the difficulty of reusing transition metals catalysts are major drawbacks of this catalyst system. To overcome these drawbacks, a thorough study has been carried out recently to develop olefin oligomerization techniques that include the involvement of ionic liquids is being considered (Thiele and de Souza, 2010, Thiele and de Souza, 2011, Nifant'ev and Ivchenko, 2020). This necessitates the utilization of transition metal (including Ti, Zr) precursor complexes having ionic liquid-type ligands in their coordination spheres. They operate as reusable heterogeneous oligomerization catalysts when paired with aluminium-organic activators and can be used in different solvents, such as molecular organic and ionic liquid solvents (Azizov et al., 2010). Moreover, the application of ionic liquids for "hydrogenizing" homogeneous catalysts has been gaining more attention recently. The primary benefit of employing ionic liquids includes (1) facilitating the reaction by acting both as solvents and as catalysts (Wasserscheid and Welton, 2008). Most of the research has been done on the chloroaluminate type of ionic liquid systems under this section (Azizov et al., 2015, Göksu et al., 2020, Berton et al., 2022, Liu et al., 2022a), and (2) to enhance the separation of reaction products from process medium and the reusability of the catalyst in a cyclic process (Earle and Seddon, 2000, Wasserscheid et al., 2001).

To ensure effective transformation and product selectivity in heterogeneous catalysis, temperature and pressure are essential factors, just as they are for homogeneous catalysis. Additional conventional characteristics associated with the heterogeneous system, including morphological and textural qualities of the metal, surface density of the metal, acido-basic strength, and carrier density, are considered for a more comprehensive knowledge of the catalytic process. Moreover, in heterogeneous catalysis, stability difficulties occurred quickly due to the use of amorphous or crystalline aluminosilicates or alumina supports. To achieve scalability and efficiency in conformity with industrial requirements, many innovative catalyst designs and technological advancements were created expressly for this purpose. For a long time, the significant divergence between active heterogeneous and homogeneous systems has triggered debates concerning the nature and origin of active sites, Ni speciation, and the oxidation rate in active heterogeneous processes. To determine the processes' location, regular and innovative multi-technique attributes have been used (Olivier-Bourbigou et al., 2020).

2.6.2.2.6 Nickel Catalyst Potential for Oligomerization

The Ni-based solid catalysts for the oligomerization of light olefins have piqued the curiosity of academics for a while, and they have been the main research focus (Finiels et al., 2014, Nicholas, 2017, Ghashghaee, 2018, Hulea, 2018). For synthesising somewhat effective and selective catalysts, particularly for ethylene, propylene, and butene conversions, heterogeneous nickel-catalyzed oligomerization has received much interest. It has the potential to offer immobilized models of effective homogeneous catalysis. With the silica supports with low activity and Ni-doping, material research advances have enhanced efficiency with lower nickel percentages when nickel is deposited into aluminosilicates and aluminas. An appropriate selection of Ni precursors and aluminic conveyors has permitted oligomerization using moderate parameters with improved selectivity for dimerization, particularly for ethene, which is usually challenging to attain dimer selectivity (Hulea, 2018, Karpova et al., 2021). Contrary to the significant progress in recent years, homogenous ethylene and propylene dimerization remain preferable for commercial applications. Butene dimerization is the sole process in which a technical alternative is available in homogeneous and heterogeneous forms. However, the selectivity to short and total-terminal olefins at significant transformations for ethylene oligomerization continues to be a considerable problem in Ni heterogeneous catalysis. Since effective Ni catalysts are frequently composed of an acidic surface (aluminosilicates, sulfated alumina), the isomerization of 1-butene to 2-butenes is simple and straightforward (Karpova et al., 2021, Aid et al., 2017). Aside from this, surface acidity promotes the cationic oligomerization of reactive olefins, including propylene or butenes, which results in coke generation and the deactivation of catalysts. To prevent pore filling, an optimized balance between monitored acidity and meso/macroporosity must be achieved. Additionally, the exact localization of promoters, including arranging silicon close to the Ni site, are essential factors for achieving effective and stable catalysts.

Furthermore, $\text{NiSO}_4/\text{Al}_2\text{O}_3$ has the potential to contend with homogeneous Phillips catalysts, $\text{NiCl}_2(\text{PBU}_3)_2$ in the manufacture of 1-butene and 2-butene blends with little hexene formation since it is an effective and uncommon catalyst that induces selectivity for butenes, particularly 2-butene. Exothermicity of the reaction must be addressed for ethene transformation with significant efficiencies in the heterogeneous form, however, this constitutes a difficult barrier that current process techniques cannot meet. As a result, homogeneous approaches allow for more efficient heat outflow during the reaction, making processability at high selectivities a

realistic possibility. This means that procedure development must occur simultaneously with increased catalyst stability and specificity. Many concerns about the type of Ni active centres in the heterogeneous system have been debated for a long time. Other doubts include the systematic routes that can be undertaken to explain identified specificity. Significant advancements in the areas of analytical technologies, whether ex-situ or in-situ, in conjunction with the rapidly increasing power of surface molecular modelling and DFT computations, have currently sparked revived attention in identifying the active sites that regulate the activity and specificity of olefin oligomerization. By drawing comparisons between homogeneous and heterogeneous catalysis, it is possible to understand better the determination of the real active sites and the discovery of the process influencing specificity in heterogeneous catalysis. While thermal techniques have lately been re-examined, and radical-assisted oligomerization is also a viable option, catalytic approaches continue to monopolize the market due to the level of precision they provide over the final product (de Klerk, 2005, Cowley et al., 2007).

2.6.2.2.7 *Mitigation of Catalyst Deactivation*

Aside from the reaction parameters, the structure of the catalyst, which includes the metal type, metal size, and support material, impacts the pace at which carbon or coke accumulates in the process. It has been observed that supported active phase metals such as Fe, Ni, and Co can promote the generation of filamentous carbon from CO and HCs at their active temperatures of 350-400 °C. The following is the order in which the activity drops at that temperature region: Fe>Co>Ni (Bartholomew, 2001, Argyle and Bartholomew, 2015). In contrast, metal active types such as platinum, ruthenium, and rhodium have been proven to generate negligible coke or carbon when subjected to steam reforming. Noble metals have demonstrated the ability to reduce the mobility and solubility of carbon, thus preventing the coking process. The addition of noble metals such as platinum reduces the rate at which carbon is formed during some processes like methanation. Adding Cu or Au to Ni in steam reforming can reduce the amount of deposition (Bartholomew, 2001). Comparing this to the addition of Sn to Co in the absence of a noble metal, it was found that the rate of filament formation from ethylene accelerates significantly. This scenario shows that choosing a noble active phase is essential (Bartholomew and Argyle, 2015, Argyle and Bartholomew, 2015).

Apart from the possibility of an active phase, changes in catalyst structure, particularly with respect to the support material, can affect the rate at which undesirable carbon or coke accumulates. Adding oxide additives or using oxide supports is a change that can increase

immunity to species deposition. The ability of support to control the orientation of metal crystallites is one explanation for its inhibitory behaviour; for example, the choice of silica prevents both CO dissociation and carbon hydrogenation. Choosing the right support can make a big difference. In addition, catalyst deactivation can be avoided by making the best possible choices for catalyst design and process parameters. Placing an electrostatic precipitator on the hot side or adding an effective low-temperature catalyst at the end of the process can avoid abrasion, fouling and/or poisoning. Sintering is reduced to a minimum by employing catalyst promoters that improve thermal stability and keep process temperatures within limits (Argyle and Bartholomew, 2015). The kind and degree of chemical deactivation depend on various factors, including operating circumstances, fuel type, catalyst configuration, and boiler maintenance shutdowns, among others. Hence, system optimization is required to minimize catalyst deactivation and improving catalytic performance (Argyle and Bartholomew, 2015).

2.6.2.2.8 *Development in Catalyst Synthesis Techniques*

With the evolution of catalytic processes, the techniques of catalyst fabrication have been enhanced and got more intricate. Consequently, the term catalyst synthesis encompasses such phrases as conventional and novel ways of catalyst synthesis. Some studies argue that current techniques can be enhanced and that only novel, unorthodox techniques to catalyst fabrication can advance the production of catalytic systems with substantially innovative features. However, conventional methods should not be considered as some permanently constituted complex processes. Given the present rate of research development, these approaches can be constantly augmented with innovative concepts and substantially enhanced, restoring relevance. There are so many novel, unorthodox catalyst synthesis techniques that it seems complicated to analyse their fundamentals in a single article, much less examine their characteristics and appraise their prospects for each catalytic process. However, some of these approaches are still in the research phase (either in the preliminary research stages or being investigated) and not all of them will prove worthwhile for advancement.

The present and emerging catalyst synthesis methods comprise the processes of conventional techniques in an innovative combination of engineering-modified approaches. These involve the stacking of various ions on the support surface by a set of chemisorption cycles, the pyrolysis of volatile metal compounds on a heated surface, and the disintegration of colloidal dispersions of salts of greater acids in alcohol on the support surface (Munnik et al., 2015). Other technologies are relatively new in catalyst synthesis but have been applied for a long

time in preparing dispersed materials that are extensively employed in producing chemicals and other commodity products. These techniques depend on either condensation or dispersion; as a result, they can be chemical (physicochemical) or physical procedures. This emergence of methodologies, on the other hand, can open up innovative options. Some current promising techniques are discussed below.

2.6.2.2.8.1 *Colloidal Catalyst Synthesis Method*

The colloidal fabrication method presents a unique opportunity to regulate nanoparticle size, shape, and content in the liquid phase by modifying their surface tension (Losch et al., 2019, Tao et al., 2008). A gradual parameter variation in a homogenous metal precursor solution is typically used to produce nanoparticles. In this case, a nucleation burst occurs, which is proceeded by the formation of nanoparticles from the leftover precursor in the solution. While the presence of ligands in the solution is critical for controlling aggregation, coalescence, and development of nanoparticles, the shape of the nanoparticles can be influenced by the presence of ligands (Park et al., 2007). Although the fabrication of colloidal nanoparticles for catalysis has been investigated (Guo et al., 2013, An and Somorjai, 2012, Jia and Schüth, 2011), few studies have focused on incorporating preformed particles on support, although this step is critical for achieving effective and stable heterogeneous catalysts. Furthermore, the range of colloidal synthesis processes accessible and the diversity of stabilizing ligands that must be eliminated before or after deposition makes a deduction from existing studies challenging (Munnik et al., 2015).

2.6.2.2.8.2 *Melt Infiltration (MI)*

The melt infiltration process involves physically mixing a metal or metal precursor salt with a support framework, and then heating the mixture above the melting temperature of the metallic salt (Cho et al., 2022a, Cho et al., 2022b). Due to capillary pressure, the melt is drawn into the pores of the support, with the temperature discrepancy between the melt and decomposition temperatures being critical. There are many parallels between this synthesis method, impregnation and drying, however, the physical concepts of wetting and capillary pressure are particularly significant in this preparation method (de Jongh and Eggenhuisen, 2013). As a result of the relatively simple technique and the absence of the requirement for a solvent, melt infiltration can be a viable alternative in certain situations. The approach can also be called the solid-solid technique, solid-state impregnation, or solvent-free approach. The MI has been used extensively in manufacturing catalysts, primarily using transition-metal nitrate hydrates. These

have low melting temperatures because melting happens as a result of dissolving in their crystal water, which is typically between 50 and 100 °C, whereas the usage of metal precursors without crystal water generally is less effective (Munnik et al., 2015).

2.6.2.2.8.3 *Electrochemical Catalyst Synthesis Technology*

Catalytic materials and chemicals that can be utilized as precursors for supports and catalysts can be synthesised electrochemically under the influence of current, initially originating from either metal salts via bottom-up fabrication or from bulk metals via top-down synthesis, depending on the application (Gao et al., 2022, Xing et al., 2022, Hersbach et al., 2018, Gao et al., 2019). In some instances, applying these procedures revealed unique characteristics of the techniques that made manufacturing catalysts with enhanced attributes possible. The framework, content, and morphology of intended catalysts for a specific metal depend on various characteristics, including the electrolyte, pH, and additive and how potential/current is delivered. Electrochemical synthesis differs from wet chemical fabrication in that it uses potentials and currents to accelerate the reduction of metal salts instead of an extensive array of reducing reagents, as in wet chemical synthesis (Ramimoghadam et al., 2014). During the electrochemical synthesis, potentials and currents can accurately regulate the nucleation and development processes that dictate cells' framework, composition, and morphology. It has been shown that successive oxidation-reduction treatments can drive crystal growth in specific orientations, forming structured nanostructures (Grosse et al., 2018). In electrochemically produced materials, the pulse induces relatively complicated disturbances that impact adsorption and desorption behaviours that emerge at the electrode/electrolyte interfaces, providing the potential to modify the frameworks and characteristics of electrochemically generated materials (Casebolt et al., 2021). Additionally, this approach demonstrates its unique capacity to rebuild catalysts in situ under process parameters (Gao et al., 2022, Engelbrecht et al., 2018, Arán-Ais et al., 2020).

Furthermore, electrochemical fabrication at an industrial scale has been reported to produce aluminium hydroxide with a pseudo-boehmite framework, an improved surface, and remarkable thermal resilience amid basically non-equilibrium parameters. Moreover, the pore structure created by this method is said to be advanced in various ways than the pore structure produced by the traditional fabrication of $\text{Al}(\text{OH})_3$. Most notable among these are the electrochemical fabrication of metal oxides in an electrolyser chamber, electrochemical synthesis of complicated catalytic processes that are typically achieved by co-precipitation,

electrochemical adjustment of surface and bulk characteristics of supports and catalysts, creation of supports with required morphological and acid-base characteristics, manipulation of the acid-base characteristics of zeolite materials, and electrochemical synthesis of silica gels and sols of silicic acid etc. Electrochemical techniques based on ion-selective membranes provide innovative solutions to technological, economic, and environmental issues (Gao et al., 2022).

2.6.2.2.8.4 *Catalyst Cleaning, Rejuvenation and Regeneration*

Catalysts that have been deactivated may be cleaned, rejuvenated, or regenerated. Catalyst cleaning is frequently used to describe the elimination of physical constraints, including fly ash-clogged monolith channels or channel surfaces coated with a loose dust layer; these constraints are readily eliminated in situ with compressed air, however, cleaning can be performed as a preliminary phase in the other procedures. Rejuvenation pertains to moderate operations that eliminate poisons or foulants within the catalyst pores while restoring some of the catalytic processes; these procedures are frequently carried out on- or off-site, depending on the circumstances. Rejuvenation entails the elimination of blinding layers and the partial elimination of some poisons; as a result, the process is partially returned, but no new activity is introduced. Essentially, regeneration is the ex-situ, total renewal of catalytic process+ by using a sequence of comparably advanced processes, some of which eliminate not only poisons and foulants but also a portion or a significant portion of the active catalytic components from the support; therefore, regeneration is the resuscitation of active catalytic components to their original state or a condition with even greater activity. Selective catalytic reduction (SCR) catalysts are frequently and periodically cleaned or "blown out" while in operation, whereas rejuvenation or regeneration is usually performed when around 50–60 % of the catalyst's original activity has been degraded, depending on the operating conditions. In situ rejuvenation (ISR) techniques have been widely employed, but off-site regeneration (OSR) is presently the preferred method due to its superior efficacy and lower cost of operation (Argyle and Bartholomew, 2015).

McMahon (2006) reported that rejuvenating SCR catalysts such as vanadium oxide or metal-substituted zeolites may be cheaper than regenerating SCR catalysts if the catalyst is relatively new or if the SCR process does not constantly work (as in the event of facilities that solely function during periods of high pollution levels, referred to as the "ozone season"). Several examples of rejuvenation procedures are to be found in the scientific and patent literature.

Several researchers ((Khodayari and Odenbrand, 2001, Khodayari and Ingemar Odenbrand, 2001, Du et al., 2016b, Wang et al., 2021b, Liu et al., 2019, Shen et al., 2016) on regeneration]) have found that the performance of poisoned catalysts can be partially restored by washing with water, sulfuric acid, NH_4Cl , and/or catalyst precursor solutions and also by washing and treatment with gaseous SO_2 . When restoring a substantial proportion of the original catalyst activity, the amount to which these rejuvenation approaches are effective varies considerably from one catalyst to another (Argyle and Bartholomew, 2015).

2.6.3 Prospects and Future Work Considerations

Low-alcohol fuels are readily available and are sourced from renewable biomass feedstock. The "blending wall" in low bioalcohol synthesis, combined with increased productivity and biomass diversity, would likely result in large quantities of bioalcohols being generated at competitive costs and made available for use as fuel and in fabricating various commodity chemicals. In a wide range of methods, liquid fuel can be produced utilising fundamental and applied techniques that are now readily available commercially. To design both financially sustainable and promising approaches when commercialising, the employment of presently accessible techniques for low alcohol fuel production should be attempted. This is valid even though liquid fuel generation is generally more expensive than directly mining fossil fuel. Rather than focusing on the technologies, it is more about problem-solving for low-cost approaches than the mechanism itself. Adopting viable and profitable methods rather than marginally lucrative techniques or only technically possible to achieve large-scale production of low lignocellulosic alcohols in large quantities is necessary. However, bioalcohol, such as bioethanol, is an enterprise with a cheap cost of synthesis per unit of output. A sufficiently large-scale production capacity is required to achieve exceptional low-cost competitiveness with other liquid fuels (Takei et al., 2011). Due to the intrinsic restrictions of applying low-energy-density biomass and the sophisticated transformation procedure into alcohol fuels, plant construction costs are prohibitively high. Furthermore, the climates and soils of a large portion of Africa are strikingly comparable to Brazil's (Graschinsky et al., 2012). Both regions have substantial untapped potential in terms of expanding the use of bioenergy commodities, such as the production of alcohol fuels in their respective economies. This will enhance the transition to bioeconomy and global application commercialization of low-alcohol fuels.

The oligomerization of lower olefins remains an important field of study and commercial interest 80 years after Ipatieff's early discoveries (Ipatieff et al., 1935). Acidic catalysts,

including solid phosphoric acid and zeolites, are employed in several industrial operations and are still being studied as novel material kinds and procedures emerge. The most prevalent zeotypes have been studied extensively, and broad criteria concerning stability and resultant shape specificity have been created based on pore size and interaction. As novel zeotypes are identified, further work is necessary, partially to check that the criteria hold for emerging zeotypes and to investigate zeolites with different channel sizes in a material. This work should address the following questions and concerns, including but not limited to (i) Does oligomerization with a catalyst with both a 10MR and a 12MR route yield products similar to those produced with a 10MR or a 12MR? (ii) How does oligomerization work in a material with many rings of different sizes in a single network? (iii) What is the linearity of 8MR uni-dimensional zeolite's product? These problems require attention, generally involving shape selection, which will almost always necessitate material identification before being answered. The capacity to evaluate the product generated by the new acid catalyst has been a bottleneck in establishing innovative acid catalysts. While GC procedures, especially GCxGC, have come a long way since their inception, further molecular-based descriptions and classification of the chemicals obtained are still required. It is now feasible to closely examine the molecules produced by oligomerization in a particular range of carbon numbers, including the C₈ fractions. Since these data are sometimes unavailable for the C₉ and C₁₀ hydrocarbons, the product distribution of the C₉ and C₁₀ fractions is assumed to be identical to the C₈. This may be valid for a specific catalyst or begin to disintegrate, as Exxon investigators have reported for some catalysts like MFI (Busca, 2007). Further work is required to reduce the time invested in characterizing a specific portion of the product and to determine the identification of molecules within that area.

While different studies demonstrate that the catalytic process has a significant perspective as a feasible approach for green low-alcohol conversion, questions surrounding effective catalyst design and the catalyst synthesis technique's effect must be considered and tackled correctly. Catalysts are highly efficient when changing the reaction rate and controlling the process pathway. Increased knowledge and ability to understand the reaction process can aid in the configuration and filtering of the fundamental aspect of the catalyst. An activated Al₂O₃-based catalyst is the most commonly used catalyst in the industrial plant for low alcohol conversion, such as ethanol to ethylene. Moreover, some byproducts are unsuitable for downstream product synthesis at a reasonably high reaction temperature. The present area of interest on zeolites as a catalyst for low alcohol conversion, which can be accomplished at lower temperatures. But

its application is limited by low stability, quick deactivation by carbon deposition, high cost, and the time-consuming fabrication method. As a result, its utilization in the research facility is still in the exploratory phase and a bit far away from being used on a large scale in commercial production. However, future research will be devoted to gaining a thorough knowledge of the activated alumina catalyst currently being used on a large scale, with a rational design and proposed amendment development to minimize the process temperature and improve product distribution. Furthermore, the improvement of the stability of the zeolite catalyst under varied process parameters should be pursued to enhance its commercial application, facilitate the development of a catalytic low-alcohol conversion system, and offer robust assistance for the market competitiveness of the overall process. This will necessitate more systematic research to fine-tune the co-existing acidic and redox-active sites needed to attain improved specificity of the target product. Greater knowledge and optimization of process parameters require thorough kinetic investigations, which are now lacking, and modeling trials, which are currently insufficient in this area. The identified initiation effect may represent a promising remedy to the coking issue and a step forward in developing the process. There is a pressing need for further innovative studies and explorations that use various catalytic systems.

Metal-based catalysts have gained relevance in the last decade, especially with the discovery of homogeneous catalysts that can preferentially dimerize or trimerize to 1-butene, 1-hexene, or 1-octene. Going forward, it is necessary to establish targeted oligomerization to long-chain oligomers (C_{12} , C_{14} , or C_{16}), which is currently only possible by fractionating the entire product of a full-range LAO process. In addition, further studies are required on the formation of linear oligomers from substituted olefins and the high specificity for linear octenes. The head-to-tail connection has long been the focus, thus, further research into the remedial measure and the framework-property link will be beneficial. Furthermore, establishing heterogeneous catalysts that can deliver the same rigid framework-characteristic correlations as homogeneous catalysts would make preferential oligomerization procedures more commercialised. Researchers have designed several mechanisms where oligomerization is among the phases or essential processes and oligomerization-only procedures. The establishment of oligomerization catalysts able to operate under various operating conditions or the design of appropriately upgradable dual-batch systems will undoubtedly facilitate advancement in this field.

Since the Nickel catalyst has been viable in the oligomerization process, the development of viable, selective, and upgradable Ni-doped heterogeneous oligomerization catalysts will facilitate the advancement of this approach. Numerous improvements have been made in the search for framework/performance relationships for Ni-doped heterogeneous oligomerization, resulting in the design of more effective and selective catalysts. No heterogeneous catalyst for ethylene or propylene has yet demonstrated α -olefin specificity and chain length management that are now supplied by homogeneous catalytic technologies under the effective industrial working parameters currently provided by homogeneous catalytic techniques (Olivier-Bourbigou et al., 2020). Overall, low alcohol conversion has been an industrially valuable process for upgrading low-value light olefins to high-value products over the past decades. It will continue to be so with the development of the proposed advances outlined within. The ethanol conversion to olefins has reached a more advanced stage of development. The current emphasis of continuing research should focus on process intensification, which includes reactor enhancement, process simulation, and optimization, among other operating conditions.

Separation of the organic products and catalyst recovery are the primary challenges associated with asymmetric homogeneous catalysis. A wide range of techniques is currently being investigated to achieve this goal. The use of catalysts immobilised on a solid substrate may be one answer to the problem. Also, employing a two-phase system, where the desired phase differs for the catalyst and the organic product, is another possible approach to enhance product separation and recovery. In this case, structural adjustments must often be made to the catalyst (Baudequin et al., 2003). Periodic regeneration or recycling of catalysts becomes economically necessary to extend catalyst life and reduce operating costs for catalytic processes. On the other hand, it is common for the recycled catalyst's performance and/or selectivity to degrade to some degree. To restore the lost catalytic performance of zeolite, an oxidation regeneration strategy has been employed by burning coke at elevated temperatures in the air (Vitolo et al., 2001, Valle et al., 2010, Karnjanakom et al., 2016). To prevent the irreversible loss of acidity, the temperature at which the catalysts are regenerated should not be higher than at which the catalysts are calcined. The performance of the regenerated HZSM-5 catalyst was decreased after five upgrading and regeneration cycles due to a decrease in Brønsted acid sites after regeneration (Vitolo et al., 2001). However, Valle et al. (2010) noted that the regenerated Ni/HZSM-5 catalysts retained similar activities for ten reaction-regeneration cycles for a catalyst regenerated by burning coke with air at 550 °C for two hours. The homogeneity of the catalysts combined with their moderate acid strength and low density of acid sites primarily

contributed to the catalysts' ability to maintain their stability after modification (Cheng et al., 2016). The long-term stability of the performance of Al_2O_3 doped with Zn, Ce, and Ni metals catalysts was demonstrated by a five-cycle reusability test. During the fifth cycle, the used catalysts were subjected to a calcination process in which they were heated to 650 °C in air for half an hour (Karnjanakom et al., 2016). The stability of the catalyst may be due to the fact that some metal species catalysed the oligomerization of intermediates. This was done by promoting the migration of hydrogen atoms through C-H activation. These intermediates prevent coke forming on the catalyst's surface during the reaction (Karnjanakom et al., 2016).

Ionic liquids (IL) have only recently been proposed as an alternative method for separating and recycling spent catalysts (Baudequin et al., 2003). In these solvents, catalysts with polar or ionic behaviour can be immobilised to be easily separated from the organic product. The ILs significantly improved the complex process of recovering the product and recycling the catalyst. ILs are more than simple neoteric solvents because of their extraordinary properties. The thermodynamic and kinetic properties of processes conducted in ILs differ from those performed in conventional solvents. As a result, the performance of the reaction can often be improved using ILs. In addition, ionic liquids can increase the shelf life of organometallic reagents and biocatalysts, facilitate product recovery, and recycle homogeneous catalysts (Baudequin et al., 2003). Therefore, the existing catalyst system needs to be further developed to achieve more significant preferential activity, extended durability, and flexible regeneration properties and procedures without substantial activity loss before testing in a commercial-scale biofuel production plant can be completed (Cheng et al., 2016). To exploit suitable heterogeneous catalysts for large-scale biofuel production, suggestions for further research include (i) deepening knowledge of the processes responsible for catalyst deactivation and regeneration and (ii) creating catalysts that are efficient, highly stable and have improved regeneration properties.

2.6.4 Concluding Remarks and Outlook

Low alcohols are commercially available fuels derived from renewable biomass sources. Low alcohols have emerged as a foundational chemical for the manufacture of fuels and petrochemicals in the near future, owing to the dwindling fossil fuel supplies and the improved accessibility of low alcohol transformation technologies in recent years. The "blending wall" in low alcohol synthesis, along with improvements in production capacity and lignocellulosic biomass diversification, would likely result in excess low alcohols being produced at

competitive costs and made available for use in manufacturing various commodity products. Moreover, the decision of the most potential products is still based on the local market and a prompt evaluation of their long-term viability. Due to the limitations of low alcohols as a viable transportation fuel, the catalytic conversion offers the potential to transform low alcohol into gasoline equivalents and value-added chemicals. Due to the substantial concentration of water in low alcohol crude, the effect of water on the framework and efficiency of catalysts and catalytic processes must be tackled with great care.

The research and development on modifying aluminosilicates from amorphous to microporous/mesoporous zeolites and then to mesoporous aluminosilicates provide valuable information regarding the fundamental parameters controlling performance and stability for low alcohol conversion. Acidity, average pore diameter, porosity distribution, and the precursor ratio to acid sites are important metrics for effective low alcohol conversion into fuels and petrochemicals. Mesoporous materials offer a promising remedy in prospective industrialization potential: a workable balance between efficiency and stability. This is due to the flexibility of the fabrication of siliceous materials using different alumination methods. The accompanying aspects should be given proper consideration in this context: extrapolation of material synthesis and processability with exogenous solvents to cope with the exothermicity of the dehydration and oligomerization processes. Consequently, zirconium oxide, amorphous aluminosilicates (such as zeolites), and lately mesoporous and mesostructured aluminosilicates have had a significant performance for catalytic conversion (dehydration and oligomerization) processes and as carriers for metal oxides including nickel oxide in the context of olefin oligomerization. A peculiar pore structure and acidic feature of H-ZSM-5 make it one of the most attractive catalysts for low alcohol conversion. Due to deactivation to a greater or lesser degree, the inherent acidity of aluminosilicates can sometimes be a stumbling block. On the other hand, coke deposition (i.e., preventing access to the active sites) and dealumination triggers the easy deactivation of H-ZSM-5 (i.e., loss of acidity). Even though aluminas have lower acidities, they usually have mesoporosity. In this regard, they have seen increased interest from academic and industrial sectors in developing active and stable catalysts for catalytic conversion processes, including olefin oligomerization.

However, although research has been carried out extensively to improve low alcohol transformation and selectivity towards a preferred product, as well as the catalyst stability, additional studies into catalyst structure-activity correlations and the respective process

conditions are still considered necessary for the logical design of catalysts and the effective upgrading of low alcohols to fuels and value-added chemicals. It is also necessary to study and evaluate the economic consequences of low alcohol valorisation compared to alternative synthesis pathways to facilitate the commercialization of the newly developed low alcohols conversions processes.

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CHAPTER 3

METHODOLOGY

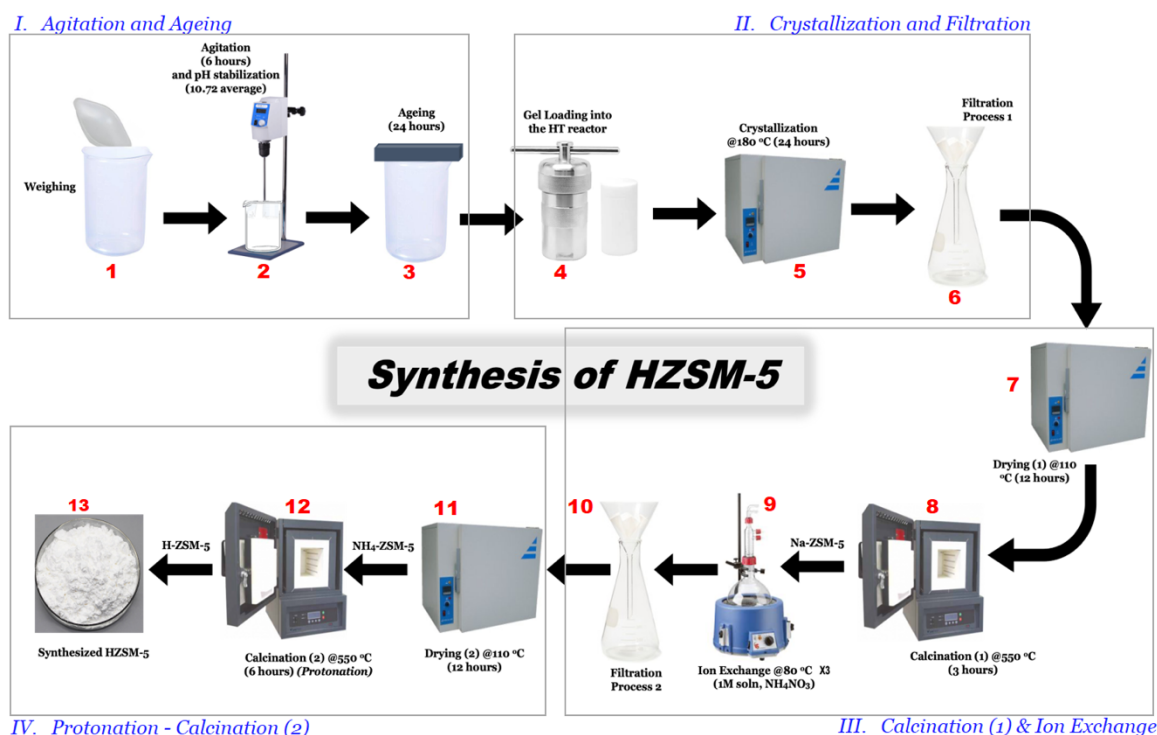
Synthesis and Characterisation of a Newly Developed Tunable and Transition Metal-doped Mesoporous ZSM-5 (Si/Al = 40) Zeolite Catalyst

Abstract

This chapter focuses on the hydrothermal synthesis of a novel HZSM-5 zeolite catalyst with a Si/Al ratio of 40 and modification with transition metals. The synthesis process was carried out under specific operating conditions, including an ageing time of 12 hours, a crystallisation time of 24 hours, and a temperature of 180°C. The dry impregnation method was applied to introduce different concentrations (0.5 – 10 wt%) of transition metals (Co, Fe and Ni) into the ZSM-5 support catalyst. The synthesised catalysts were extensively characterised using various analytical techniques to evaluate their structural, morphological, and chemical properties. X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), N₂ adsorption, particle size distribution (PSD) analysis and NH₃ temperature programmed desorption (NH₃-TPD) analysis were performed. The characterisation results confirmed the successful synthesis and incorporation of transition metal species into the framework of the ZSM-5 zeolite. The presence of doped metals in the zeolite matrix had noticeable effects on the catalysts' crystallinity, structure, structural properties, and acidity. These effects were particularly pronounced at higher metal contents. Importantly, despite the metal doping, the MFI zeolite framework was preserved, highlighting the stability and structural integrity of the synthesised catalysts. The characterisation results revealed the promising potential of the synthesised HZSM-5 zeolite catalyst doped with transition metals for the efficient catalytic conversion of low alcohols into valuable hydrocarbons. These findings demonstrate the capability of the catalysts to facilitate the desired hydrocarbon reaction, making them suitable for catalytic applications involving the conversion of low alcohols into high-value hydrocarbon products.

Keywords: Catalyst, Mesoporous, Transition metals, Zeolite, ZSM-5

Graphical Abstract



3.1 Introduction

Zeolites are natural aluminosilicates characterised by their crystalline and microporous structure (Bekkum et al., 1991, Dyer, 1988). Their unique structure has facilitated their use in various fascinating applications, including catalysis, adsorption and water filtration (Corma, 1997, Ozin et al., 1989, Egeblad et al., 2008). Zeolites, known for their exceptional properties such as high activity, strong acidity, shape selectivity, thermal stability and cation exchange capacity, occupy a prominent position as solid acid catalysts in oil refining and petrochemicals. Zeolites possess remarkable catalytic capabilities in petrochemical processes such as cracking, isomerisation, aromatisation and alkylation, which has motivated researchers to explore their potential for future catalytic applications (Clerici, 2000, Kim et al., 2010, Zhao et al., 2006b). The extensive use and successful commercialisation of zeolite catalysts have led to continuous advances in hydrothermal synthesis methods. Since developing the first zeolite synthesis technology in the 1940s, various microporous and macroporous materials with different structures and morphologies have become accessible (Pang et al., 2009). These materials have found applications in various fields. In hydrothermal synthesis, the predominant technique for zeolite production, reaction media containing ionic solutions are subjected to non-ideal and

non-equilibrium conditions in hermetically sealed vessels at supercritical or near-supercritical temperatures. These conditions effectively activate the reaction media, leading to significant changes in their physical and chemical properties and the formation of unique microporous structures (Pang et al., 2009). However, most hydrothermal processes for zeolite synthesis require a certain temperature (80-200 °C), pressure (1-100 MPa) and reaction time (1-20 days), which contributes to the high energy requirements of the process (Pang et al., 2009, Arafat et al., 1993, Kang et al., 1999, Newalkar et al., 2000).

Reports from several studies have highlighted the crucial factors for synthesising an active catalyst in converting low alcohols into liquid hydrocarbons. These factors, including ageing, crystallisation, and temperature, are critical parameters influencing the catalyst's performance (Wang et al., 2014, Chou et al., 2006, Ma et al., 2020, Che et al., 2021, Che et al., 2019a, Goodarzi et al., 2020, Che et al., 2019b). The optimal ageing time typically falls within the 12 to 48 hours range, ensuring sufficient time for the desired chemical transformations and for the catalyst to reach its maximum activity. This period allows for forming essential catalytic sites and the necessary structural changes and crystallinity within the catalyst matrix. Similarly, the crystallization time is vital in developing an effective catalyst. Typically, 24 to 48 hours is considered appropriate for promoting the growth and formation of well-defined crystal structures within the catalyst. This extended duration facilitates the desired crystalline framework, which is crucial for the catalyst's stability and catalytic efficiency. Furthermore, the operating temperature during the catalyst synthesis process is a key factor influencing catalyst performance. The temperature range of 160 to 200°C has been identified as optimal for promoting the desired chemical reactions and facilitating the required crystallisation and other necessary transformations. This temperature range allows for the activation of the catalyst and provides the necessary energy for the desired catalytic reactions. By carefully controlling these critical factors, including ageing time, crystallization time, and temperature, researchers can optimize the catalyst synthesis process and develop highly active catalysts for converting low alcohols into valuable liquid hydrocarbon products. In addition, ensuring the safety of the process is a problem because the synthesis conditions, including the high pressure and temperature, must be maintained for an extended time. To maintain these demanding reaction conditions, special reaction vessels such as steel autoclaves lined with poly(tetrafluoroethylene) are used (Corma et al., 2010, Pang et al., 2009). Exploring alternative

approaches to zeolite synthesis holds significant potential for improving energy efficiency and process safety.

Among the zeolites studied, ZSM-5 or modified ZSM-5 has shown promising catalytic performance in the ethanol dehydration process for ethylene production, primarily due to the hydrophobic nature of their surfaces (Le Van Mao et al., 1987, Le Van Mao et al., 1989). The synthesis of ZSM-5 zeolites occurs in a multistep process in which a silicon source, an aluminium source, an alkali, and a structure directing agent (SDA) are combined in a suspension to form a gel, which is then converted to a crystallised aluminosilicate under specific temperature and pressure conditions (Yan et al., 2015). Structure-directing agents, also known as "templates", are commonly used to control the growth of zeolites and stabilise their framework (Mintova et al., 2013). For example, in the synthesis of SDA for ZSM-5, the tetrapropylammonium cation is commonly used in three possible forms: as a hydroxide (TPAOH), as a salt (preferably as a bromide, TPABr), or as a combination of both (Anthonis et al., 2001).

To further improve the catalytic performance of ZSM-5 catalysts, the introduction of metal species has been used to modify ZSM-5 zeolites and increase the selectivity of aromatics and liquid fuel hydrocarbons in the reaction of low alcohol to hydrocarbon (LATH) (Conte et al., 2012, Ono et al., 1988, Zaidi and Pant, 2004, Zeng et al., 2007, Yang et al., 2016, Lai et al., 2016, Pinilla-Herrero et al., 2021). The introduction of metals into the ZSM-5 zeolite framework has improved the catalytic activity during the LATH process. Metal modification of HZSM-5 catalysts, such as through impregnation or ion exchange, alters their acidity and texture, leading to varying levels of catalytic activity (Calsavara et al., 2008b, Gayubo et al., 2010b, Bun et al., 1990). For example, introducing nickel into ZSM-5 catalysts led to an appropriate acid strength and improved hydrothermal stability, reducing coking and dealumination during ethanol-to-gasoline conversion (ETG) (Gayubo et al., 2010b). Metals play a crucial role in the dehydrogenation of alkanes, leading to the formation of olefins. Subsequently, the olefins are protonated on acid sites, forming carbenium ions, which undergo isomerisation and cracking, followed by reverse stages (Thybaut and Marin, 2003). While the functions of both the metal and acid in certain processes, such as hydrocracking, are well understood, there are many other processes where the role of the metal remains incompletely understood or unexplained (Zakaria et al., 2012a, Conte et al., 2012). Nickel has been recognised for its influence in catalytic cracking reactions (Maia et al., 2010b), while gallium

has shown positive results in light alkene and alkane aromatisation and cracking reactions (Viswanadham et al., 2004, Hagen and Roessner, 2000). Nickel-catalysed reaction pathways have been extensively described in the literature, particularly for olefin oligomerisation and ethylene oligomerisation to linear olefins, where Ni^{2+} ions are identified as the active species (Heveling et al., 1998). The influence of iron modification in catalytic cracking has also been speculated (Lu et al., 2006c). Calsavara et al. (2008a) synthesised iron-doped ZSM-5 zeolites through a combination of direct synthesis and post-ion exchange, and regardless of the iron inclusion method, the partial substitution of framework Al^{3+} by Fe^{3+} (0.3–0.5 wt% iron) resulted in prolonged catalyst life and improved yield of liquid hydrocarbons. This is attributed to the lower acidity of framework Fe^{3+} compared to framework Al^{3+} since framework Fe^{3+} replaces framework Al^{3+} (Calsavara et al., 2008a). Wang et al. (2016a) synthesised mesoporous Zn/ZSM-5 zeolite by directly introducing zinc into the alkali treatment process. The presence of ZnOH^+ species in the material gradually improves the selectivity of benzene, toluene and xylene (BTX) and liquid hydrocarbons as the amount of incorporated zinc increases (Wang et al., 2016a). Similarly, Ni et al. (2011) synthesised nano-H [Zn, Al] ZSM-5 by a one-step hydrothermal synthesis, resulting in a catalyst with high selectivity for liquid hydrocarbons and robust catalytic stability. The nano-H [Zn, Al] ZSM-5 exhibits crystalline aggregates of 250 x 50 x 25 nm (Ni et al., 2011). Wang et al. (2018d) successfully synthesised nano-ZSM-5 zeolite with a shortened B-axis, effectively reducing carbon deposition during the methanol-hydrocarbon process (Wang et al., 2018d, Ma et al., 2016). While the selectivity of aromatic hydrocarbons over ZSM-5 usually reaches about 30 %, impregnation with zinc increases the selectivity to over 90 %. Incorporating metals such as zinc into ZSM-5 can create new Lewis acid sites and improve the material's ability to aromatise methanol (Wang et al., 2016a, Niu et al., 2022).

A limitation of zeolites is their limited pore size, which significantly restricts the passage of large molecules, making them unsuitable for the catalysis reactions involving such molecules (BjØrgen et al., 2008). The preparation of zeolites with meso/macroporous pore structures represents an optimal solution to overcome this limitation. Some zeolites with larger surface area and porosity have better catalytic performance than normal zeolites (Sabarish and Unnikrishnan, 2019). Therefore, this study aims to synthesise a novel ZSM-5 zeolite catalyst with improved meso/macroporous pore structures and modify the catalyst with a transition metal to improve the catalytic performance.

3.2 Materials and Methods

3.2.1 Materials

The following compounds were employed to synthesise the ZSM-5 (Si/Al = 40) zeolite catalyst used in this study: sodium silicate solution ($(\text{Na}_2\text{O})\text{SiO}_2 \cdot \text{H}_2\text{O}$) as the silica source, aluminium sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) - the aluminium source, tetrapropylammonium bromide - TPABr as the structure directing agent (SDA), sodium hydroxide (NaOH, 97%), sulfuric acid (H_2SO_4 , 98% concentration) - synthesis gel pH stabiliser, ammonium nitrate (NH_4NO_3) - for ion exchange, and the precursor compounds for transition metal doping, namely, nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). Methanol, ethanol, and propanol were used as feedstocks for the conversion process. All chemicals were of analytical grade and were purchased from Sigma-Aldrich. A Teflon-lined stainless steel hydrothermal reactor (HTR) with a volume of 200 mL and a working volume of 150 mL was used for catalyst synthesis. A fixed bed reactor was used to convert the low alcohol conversion to hydrocarbons.

3.2.2 Methods

3.2.2.1 *Synthesis of Transition Metal-doped Mesoporous HZSM-5*

The hydrothermal catalyst synthesis method described in Figure 3.1 was used to prepare the ZSM-5 catalyst support. The newly developed batch formula used for the catalyst synthesis is **10Na₂O:40SiO₂:1.0AlO₃:10.5TPABr:3740.6H₂O**. The operating conditions chosen for the catalyst synthesis were informed by previous studies that have identified the optimal parameters for improving catalyst mesoporosity and producing ZSM-5 catalysts with high activity in converting low alcohols into liquid hydrocarbons (Wang et al., 2014, Chou et al., 2006, Ma et al., 2020, Che et al., 2021, Che et al., 2019a, Goodarzi et al., 2020, Che et al., 2019b). The desired catalyst was achieved by carefully implementing the optimum operating conditions while controlling other influential factors.

The synthesis solution was divided into three, with the first consisting of a mixture of sodium hydroxide and sodium silicate solution dissolved in deionised water. The structure directing agent, tetrapropylammonium bromide, was dissolved in deionised water, and the resulting solution was assigned solution 2. A third solution contained the required aluminium source dissolved in deionised water. Solutions 1 and 2 were mixed and stirred continuously, then solution 3 was added after stirring for one hour. The mixture was then vigorously stirred at

2000 revolutions per minute (rpm) for another five hours at room temperature until a homogeneous gel mixture was obtained. The initial pH of the gel, which was 11.53, was lowered to an average pH of 10.73 with 98 % sulfuric acid. The resulting solution was allowed to age undisturbed at room temperature for 12 hours before being transferred to a Teflon-lined stainless-steel reactor for hydrothermal crystallisation at autogenous pressure and a temperature of 180 °C for 24 hours. After the crystallisation step, the reactor was cooled to room temperature, and the solid product was recovered by filtration and washed thoroughly with deionised water to a stable pH. The solid product obtained was dried overnight at 110 °C and then calcined at 550 °C for three hours to remove the organic template, resulting in Na-ZSM-5. The Na-ZSM-5 sample was then subjected to ion exchange at 80 °C with 1M of ammonium nitrate (NH_4NO_3) at a volumetric concentration of 10 mL per gram of catalyst for one hour. The sample was recovered via filtration, washed with deionised H_2O , and dried overnight at 110 °C to obtain NH_4 -ZSM-5. The ion exchange procedure was repeated two more times. The ammonium ions in NH_4 -ZSM-5 were then decomposed by calcination at 550 °C for six hours, forming the hydrogen (protonated) form of ZSM-5, known as HZSM-5. The transition metal-doped HZSM-5 catalyst was prepared through incipient wetness impregnation. The HZSM-5 support catalyst was impregnated with transition metals at 0.5, 1, 5 and 10 wt% concentrations. For this study, the metal-modified HZSM-5 catalysts were designated as xM/HZSM-5, where x is the weight percentage of the metal, and M is the transition metal (0.5Ni/HZSM-5, 1Fe/HZSM-5, 10Co/HZSM-5, etc.).

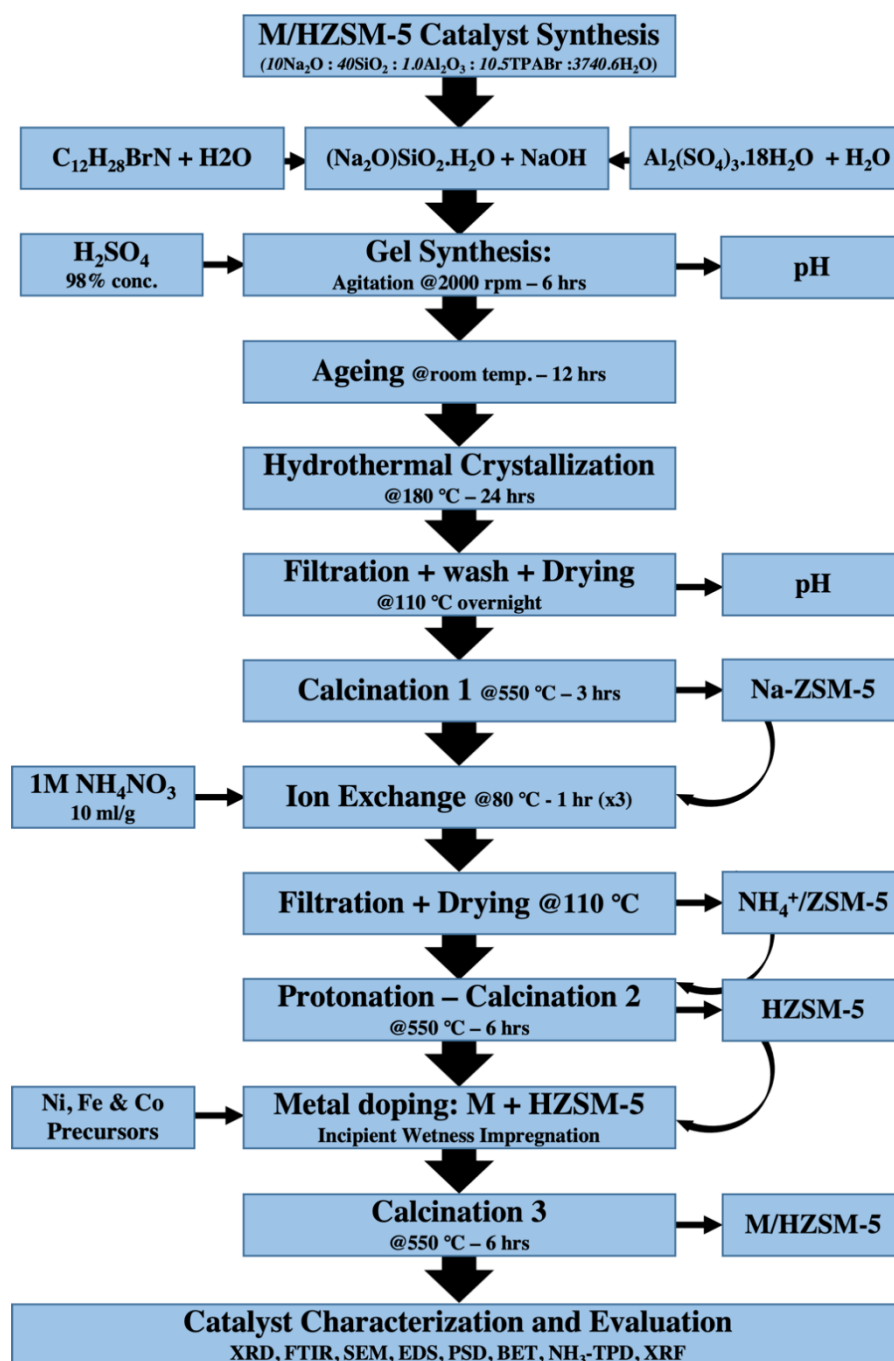


Figure 3-1. Synthesis procedure for metal-doped mesoporous HZSM-5

3.2.2.2 Catalyst Evaluation

The catalytic performance of the pure and metal-modified catalysts in the conversion of low alcohol to hydrocarbons was evaluated, and the results were presented in subsequent chapters. The experiments were carried out in a fixed bed reactor (Figure 3.2) at temperatures of 350 and 400 °C and hourly weight-space velocities (WHSV) of 5 - 12 h⁻¹. Glass beads and glass wool were used for structural support of the catalyst bed. Low alcohols (methanol, ethanol and

propanol) were used as the feedstock. After the initial activation of the catalyst at 400 °C, low alcohols were fed into the reactor using a high-pressure liquid chromatography (HPLC) pump. The product selectivity (S_i) and conversion (X) calculated based on the work of Sun et al. (2020) and other basic calculations are shown in Eqs. 3.1-3.5.

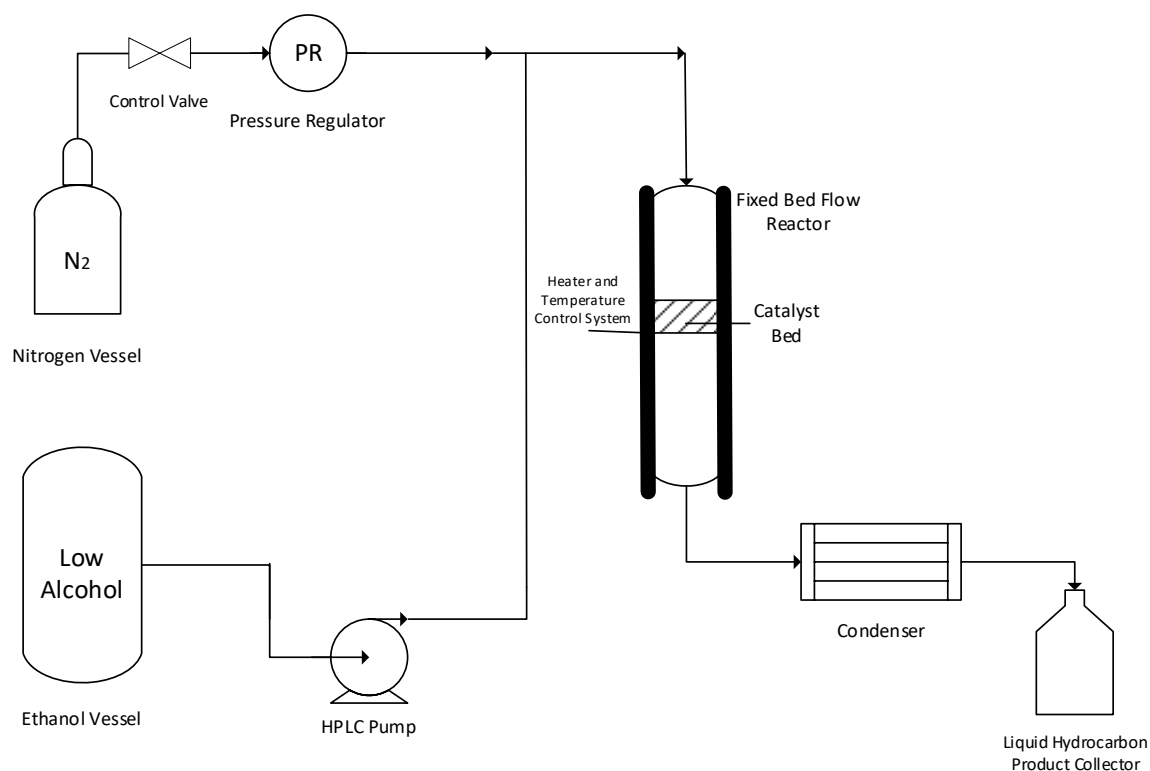


Figure 3-2. Schematic Diagram for the Catalytic Conversion of Low Alcohols to Hydrocarbons

3.2.2.2.1 Calculations

The *Weight Hourly Space Velocity (WHSV)*, *Selectivity, S_i* , *Conversion, X* , *Liquid and Coke Yield* will be calculated as follows:

- i. **Weight Hourly Space Velocity (WHSV):** the weight of feed flowing per unit weight of catalyst per hour.

$$WHSV(\text{per } h) = \frac{\text{hourly mass feed rate}}{\text{catalyst mass} \times \text{hr}} \quad \text{Equation 3.1}$$

- ii. **Selectivity, S_i** shows the degree of specificity or preference of a compound over all the measured compounds in the product. The selectivity will be reported by the number of carbon atoms in the molecule (C_9 , C_{10} , etc). It is denoted by:

$$\text{Selectivity, } Si \text{ (wt. \%)} = \frac{\text{mass of compound, } i}{\text{mass of all measured compounds}} \times 100 \quad \text{Equation 3.2}$$

- iii. **Conversion, X** determines the rate of feedstock transformation to target products and will be determined using the equation:

$$\text{Conversion, } X \text{ (mol. \%)} = \frac{\text{molar flow rate of alcohol (in)} - \text{molar flow rate of alcohol (out)}}{\text{molar flow rate of alcohol (in)}} \times 100 \quad \text{Equation 3.3}$$

- iv. The **Liquid yield**, the amount of liquid product recovered from the process, will be calculated thus:

$$\text{Liquid yield (wt. \%)} = \frac{\text{mass of liquid product collected}}{\text{mass feed rate of alcohol} \times \text{time}} \times 100 \quad \text{Equation 3.4}$$

- v. The **mass of coke** accumulated throughout the process will be determined as follows:

$$\text{Coke yield (wt. \%)} = \frac{\text{final mass of catalyst bed} - \text{initial mass of catalyst bed}}{\text{mass feed rate of alcohol} \times \text{time}} \times 100 \quad \text{Equation 3.5}$$

3.2.3 Characterisation of Synthesised Catalysts

Bruker D2 Phaser Diffractometer X was used to identify the X-ray diffraction (XRD) patterns. The Cu-K1 radiation was employed at 40 kV and 40 mA, and the XRD patterns were recorded in the angle range (2θ) of 0° to 90° at a scanning rate of $2.0^\circ/\text{min}$. FTIR spectra were collected on a Perkin Elmer Fourier Transform-Attenuated Total Reflectance-Infrared Spectrometer Spectrum-2 (FT-ATR-IR-2) spectrometer in the range of $4000\text{--}400 \text{ cm}^{-1}$ to determine the functional groups in the sample. The morphology of the materials was studied using scanning electron microscopy (SEM) with a ZEISS Sigma 300 VP equipped with a field emission gun. Energy dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments x-act PentaFET Precision EDS instrument to map the presence of various elements in the metal-doped ZSM-5 zeolite. The particle size distribution (PSD) data was obtained using equipment from Malvern. An X-ray fluorescence (XRF) study was conducted to determine the elemental composition. Trace element (Co) was determined via Moviol solution binder method and analysed using Philips PW2404 X-ray spectrometer. The major elements, Ni, and Fe were identified using the Norrish Fusion 1 method and quantified using PANalytical X-ray

fluorescence spectrometer. In-house correction processes were applied, and trace and major elements were determined using the USGS and NIM series (United States).

The catalyst's specific surface area and porosity were determined through nitrogen (N_2) physisorption analysis at a temperature of -196 degrees Celsius. The Quantachrome Instrument: Autosorb iQ Station 3 from Anton Paar, USA, was utilised for this purpose. Prior to the measurements, each sample underwent a 10-hour degassing process at a temperature of 300 °C to remove any adsorbed substances. The Brunauer-Emmett-Teller (BET) equation was then applied to determine the surface area and pore diameter, while the Barrett-Joyner-Halenda (BJH) method was used to estimate the pore volume. The pore volume estimation was based on the relative pressure ($P/P_0 = 0.995$). A chemisorption analyser (NH_3 -TPD, AutoChem II 2920) was used to perform temperature-controlled desorption of NH_3 . To remove adsorbed water, a sample of approximately 100 mg was heated to 300 °C at a rate of 10 °C/min with a He flow of 40 ml/min for 2 hours. After reducing the temperature to 100 °C, NH_3 was substituted for He for 20 minutes. Finally, the sample was heated to a temperature of 700 °C at a rate of 10 °C/min, and a desorption NH_3 signal was obtained using a TCD detector.

A YL6500 gas chromatograph (GC) system was used to analyse hydrocarbon products. For the product quantification, standard curves were created to facilitate the analysis of hydrocarbon products. The GC column program consisted of the following steps: initially, the sample was injected at 40 °C, then the column was gradually heated to 50 °C at 3 °C/min and maintained for 3 mins. The column temperature was further increased to 60 °C at 2 °C/min and held for one minute. Subsequently, the temperature was increased at 5 °C/min until it reached 200 °C and was kept for 1 minute. Finally, the column temperature was raised to 315 °C at 15 °C/min and maintained for 5 minutes. The analysis results from the GC/MS were based on the peak area distribution.

3.3 Results and Discussions

3.3.1 Characterisation of Synthesised Catalysts

3.3.1.1 Identification of Crystalline Phases

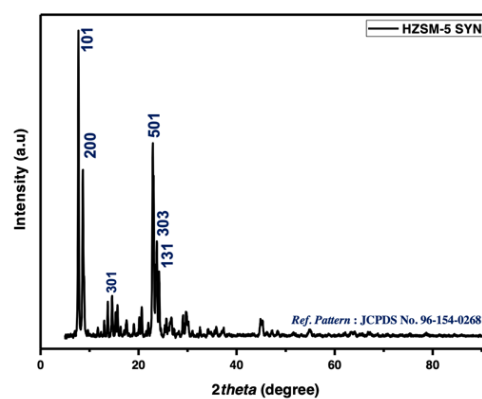
X-ray diffraction was employed to examine the crystalline phases of the samples. Figures 3.3 a-f depict the XRD patterns obtained from the metal-doped ZSM-5 after impregnation. While 3.3a & b showed the sample and XRD of the as-synthesised catalyst, Figure 3.3c showed that

the XRD pattern of the as-synthesised catalyst is comparable to the commercial catalyst. The patterns exhibited distinct peaks at specific angles ($2\theta = 7-9^\circ$ and $23-24^\circ$), namely 7.97° , 8.88° , 14.81° , 23.14° , 23.32° , and 24.00° , which corresponded to the crystallographic planes (101), (200), (301), (501), (303), and (131) of the MFI zeolite framework. The as-synthesised ZSM-5 correspond to the standard ZSM-5 with a chemical formula of $\text{Al}_{1.57}\text{Si}_{94.43}\text{O}_{208.00}$, crystal system: orthorhombic crystal system, and characterised by space group Pnma (#62) – a centrosymmetric with 8 point inversion per unit cell attributed to the orthorhombic space group (Liu, 2021, Vezzalini et al., 1997), with lattice constants: $a = 20.048 \text{ \AA}$, $b = 19.884 \text{ \AA}$ and $c = 13.352 \text{ \AA}$. The metal-doped ZSM-5 maintained its framework despite the incorporation of transition metals, as evidenced by the presence of characteristic peaks. However, the crystallinity of the M/HZSM-5 catalysts decreased with increasing metal doping, indicating the dispersion of metals on the HZSM-5 surface. Similar observations were reported by Vichaphund et al. (2014). Upon careful examination of the patterns of metal-doped samples (Figure 3.3 d-f) in Figure 3.3g within the range of $2\theta = 30-50^\circ$, the presence of metal oxides was detected in the metal-doped samples, specifically high metal-doped (5 and 10 wt%) samples. The visibility of the metal oxide peaks increased with higher metal doping percentages, ranging from 0.5 to 10 wt%. In the Co/HZSM-5 catalysts, the peaks observed at $2\theta = 19.05^\circ$, 31.35° , 36.94° , 38.64° , 44.92° , 55.80° , 59.51° , 65.41° , 74.32° , and 77.56° corresponded to the (111), (220), (311), (222), (400), (422), (511), (440), (620), and (533) planes of spinel Co_3O_4 (ICDD PDF No. 96-153-8532). In the Fe/HZSM-5 catalysts, signals detected at $2\theta = 24.13^\circ$, 33.12° , 35.61° , 40.84° , 49.42° , 54.01° , 57.51° , 62.39° , 63.97° , 71.82° , 72.17° , and 75.41° were attributed to the (211), (104), (110), (113), (024), (116), (112), (214), (300), (208), (010), and (220) planes of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) (ICDD PDF No. 00-024-0072). The Ni-doped catalysts exhibited peaks at $2\theta = 37.24^\circ$, 43.27° , 62.85° , 75.37° , and 79.36° , which corresponded to the (111), (200), (220), (311), and (222) planes of NiO (ICDD PDF No. 96-432-9324). The presence of these metal oxides in the samples became more pronounced with higher metal loading, indicating the formation of transition metal oxides during impregnation and calcination processes. These findings are consistent with previous studies (Bepari et al., 2017, Li et al., 2022a, Farhadi et al., 2013, Rakshit et al., 2013b, Rakshit et al., 2013a, Qiao et al., 2009, Ali et al., 2018, Jiráťová et al., 2019). In contrast, the 0.5 wt.% metal-doped samples did not exhibit noticeable peaks within the investigated angles, suggesting that these metals were in small amounts (Van der Borgh et al., 2015b, Li et al., 2018b).

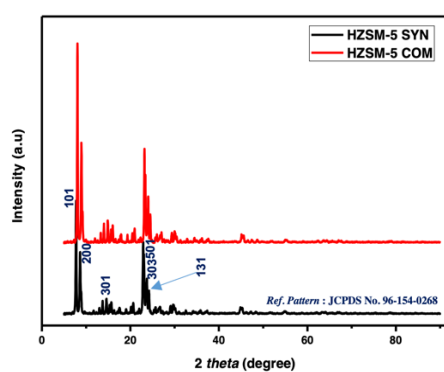
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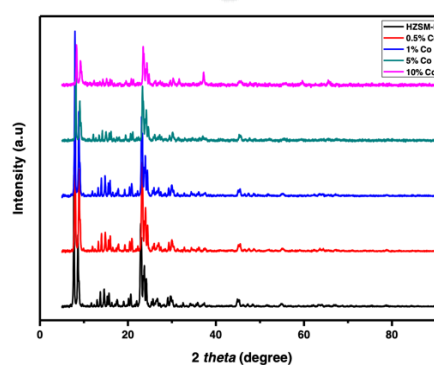
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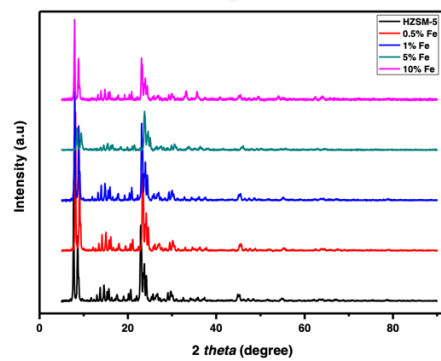
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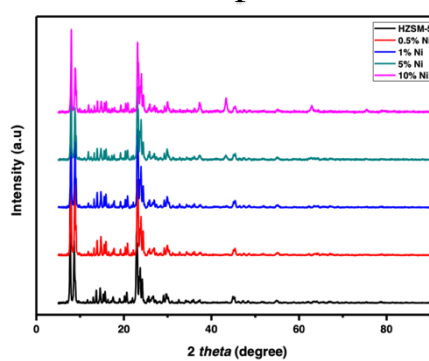
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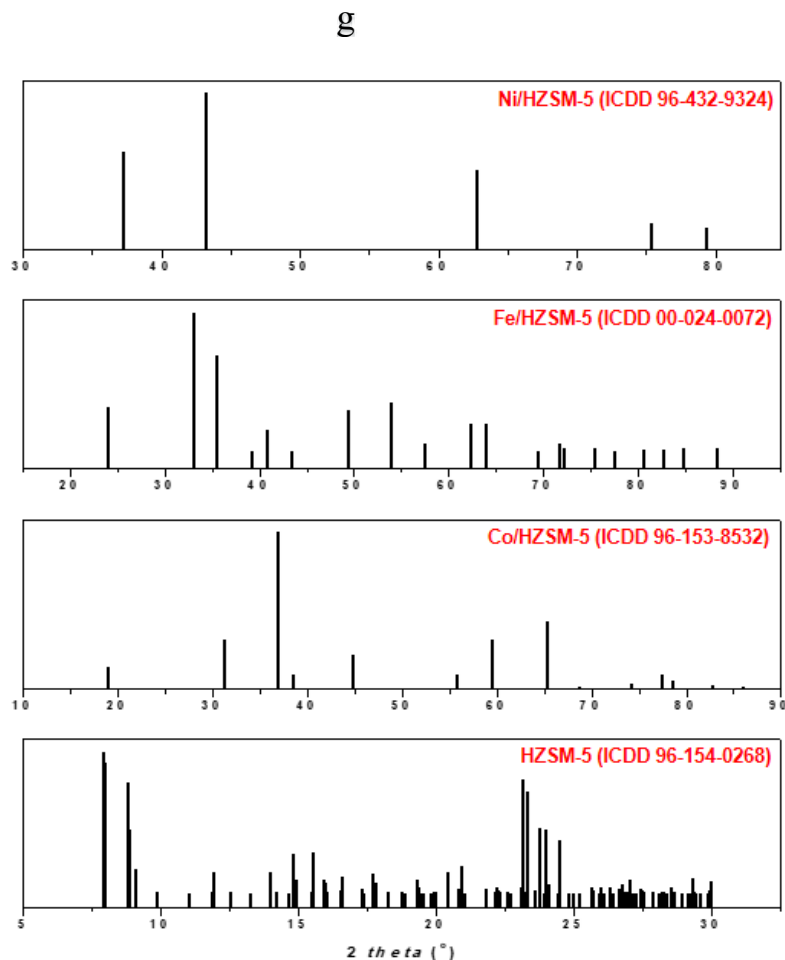
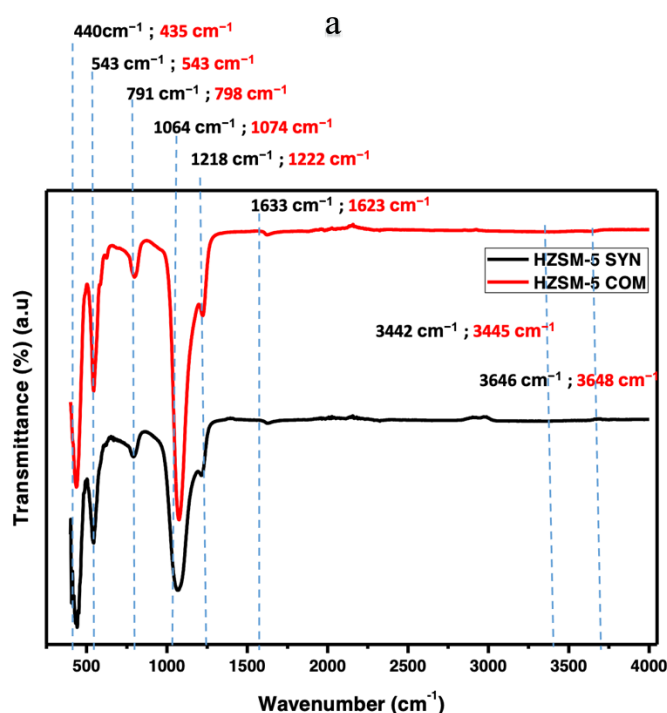


Figure 3-3. (a) Sample of as-synthesised HZSM-5 Zeolite Catalysts, (b-g) XRD patterns of pure and transition metal-doped HZSM-5 (b) as-synthesised HZSM-5, (c) as-synthesised and commercial HZSM-5 (d) Co-doped (e) Fe-doped (f) Ni-doped HZSM-5 and, (g) peaks of HZSM-5 and transition metal oxides

3.3.1.2 Functional Groups Identification

The FTIR findings in Figure 3.4 showed that all samples exhibited an IR spectrum characteristic of an MFI-type zeolite. The FTIR analysis showed that the as-synthesised catalyst is comparable to the commercial catalyst (Figure 3.4a). The peaks around 440 cm^{-1} were attributed to the vibration of internally located T-O bonds within the TO_4 tetrahedra. In this context, the letter "T" represents the presence of either Al or Si within the zeolite structure. The bands detected at a wavenumber of 543 cm^{-1} were primarily associated with the outer bonds of the double five-membered rings, similar to what was described in (Jansen et al., 1984). Similar to the observations reported by Allahyari et al. (2014), the peak at 791 cm^{-1} corresponded to the symmetrical stretching of the internal bonds connecting the tetrahedral units. The bands identified at 1218 cm^{-1} indicated the asymmetric stretching vibration of the T-

O bond, specifically referring to the external bonds between the TO_4 tetrahedra (Ali et al., 2003). The most prominent peak at 1064 cm^{-1} was attributed to the internal asymmetric stretching of the Si-O-T bonds. Additionally, the presence of adsorbed H_2O on the catalyst surface was confirmed by a peak at 1633 cm^{-1} , consistent with the results reported by Barros et al. (2008) and He et al. (2017). The band at 3442 cm^{-1} suggests the stretching of internal tetrahedral Si-OH-Al hydroxyl groups on extra framework Al and strong Brønsted acid sites. Likewise, the presence of terminal Al-OH groups was confirmed by the band at 3646 cm^{-1} , consistent with the findings of other studies (Liu et al., 2015a, He et al., 2016). The metal oxide peaks were identified by the bands at 661 , 587 and 668 cm^{-1} assigned to Co-O stretching mode, Fe-O vibrations and Ni-O bond for Co_3O_4 , Fe_2O_3 and NiO, respectively (Figures 3.4 b-g). Previous studies have consistently reported similar results, indicating a strong correlation or trend in observed outcomes (Suresh, 2017, Šuligoj et al., 2021, Budipramana et al., 2014).



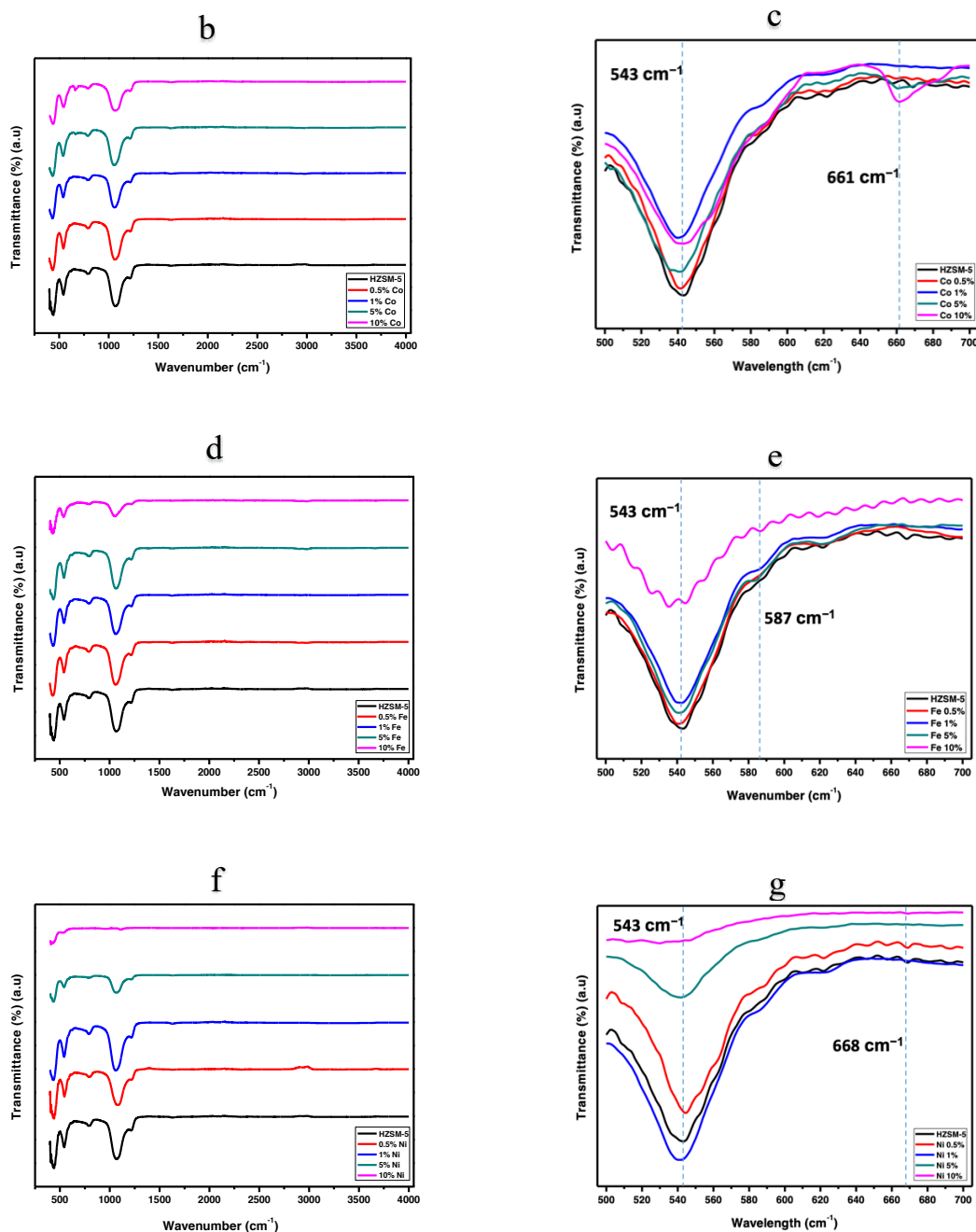


Figure 3-4. FTIR spectra of (a) as-synthesised and commercial HZSM-5 and metal-doped catalysts at wavelengths: 400-4000 cm^{-1} and 500-700 cm^{-1} (metal oxides) for (b & c) Co-doped, (d & e) Fe-doped and (f & g) Ni-doped HZSM-5 catalysts

3.3.1.3 Catalyst Morphology, Particle Size Distribution and Elemental Composition

Figure 3.5 presents a micrograph of the surface morphology of pure and transition metal-doped ZSM-5. The micrographs reveal that the zeolite particles form aggregates, interconnected in a manner that allows them to maintain a self-supporting configuration. The catalyst surfaces

exhibit pores with a wide range of size distribution, a finding consistent with a trend reported in a previous study (Vichaphund et al., 2014). Furthermore, the surface morphology of pure ZSM-5 and M/HZSM-5 (metal-doped) (0.5-10 wt%) samples displayed comparable prismatic particle shapes. However, the introduction of metals in some of the doped samples affected the parent catalyst's crystallinity, resulting in inconsistencies in catalyst morphology. This observation aligns with the XRD analysis, which indicated a decrease in crystallinity with increasing metal doping. Notably, the samples with high metal (Co, Fe, and Ni) doping exhibited rougher particle surfaces, particularly evident in the case of 5 and 10 wt.% Ni and Fe-doped catalysts. This surface roughness could be attributed to the production of metal oxide, which altered the structure of the particle surface. Differences in particle size and surface texture induced by the presence of metal oxides likely contribute to the distinct appearances of the transition metal-doped zeolites, corroborating findings from studies by Subramanian et al. (2016) and Vichaphund et al. (2014).

The SEM images also included an inset displaying the particle size distribution (PSD) curve. The analysis of PSD revealed that the synthesised catalysts exhibited a bimodal distribution of particle sizes, encompassing numerous irregular particles of small, medium, and large sizes, resulting from the introduction of transition metals (Di et al., 2013). The bimodal and multimodal (for 10 wt%Ni only) particle distribution may be due to various processes such as particle growth, particle breakup, and larger particles in the system. The larger mode of distribution results from redispersion or breakup of particles, while the smaller mode represents molecular condensation (Niu et al., 2014, Li et al., 2018a). Most of the ZSM-5 catalysts, including pure and metal-doped variants, displayed particle size distributions ranging from 0.55 μm to 100 μm (1000 μm for 10 wt% Ni only). Previous studies suggest that highly dispersed particles are due to transition metals (such as Ni and Fe species and Co cations or oxo cations) that were originally present in the zeolite channels. However, the introduction of these metal species is responsible for the formation of larger particles. The presence of doped metals can influence the size and morphology of ZSM-5 zeolite crystals. Some metal ions may promote the growth of larger crystals, while others may inhibit crystal growth. This can impact the overall crystallinity of the zeolite. Similar trends have been reported in other studies (Shilina et al., 2023, Shilina et al., 2019, Bryzhin et al., 2020, Rostovshchikova et al., 2021). With reference to the unmodified catalyst, the introduction of transition metals increased the average particle size of the modified samples. This size increment can be attributed to the larger

ionic radii and crystal sizes of the incorporated transition metals (M = ionic radii, crystal size): Fe^{2+} (0.61 Å, 0.75 Å), Fe^{3+} (0.55 Å, 0.69 Å), Co^{2+} (0.65 Å, 0.79 Å), Co^{3+} (0.55 Å, 0.69 Å), and Ni^{2+} (0.69 Å, 0.83 Å), which exceed the ionic radii and crystal sizes of Al^{3+} (0.54 Å, 0.68 Å) and Si^{4+} (0.26 Å, 0.4 Å) ions. The coagulation of metal moieties on the catalyst surface is believed to contribute to the observed increase in particle size (El-Bahy et al., 2008). This finding aligns with the study conducted by Saeidi and Hamidzadeh (2017), which demonstrated a similar increase in particle size upon introducing transition metals in ZSM-5. The EDS spectra of the metal-doped catalyst revealed the presence of metal species (Figure 3.6). Additionally, a quantitative analysis using EDS and XRF provided the metal-doped catalysts' weight percent (wt%) elemental composition and particle size (mean) of all catalysts (Table 3.1). XRF analysis was employed to validate the results obtained from EDS, as the latter method was considered less reliable.

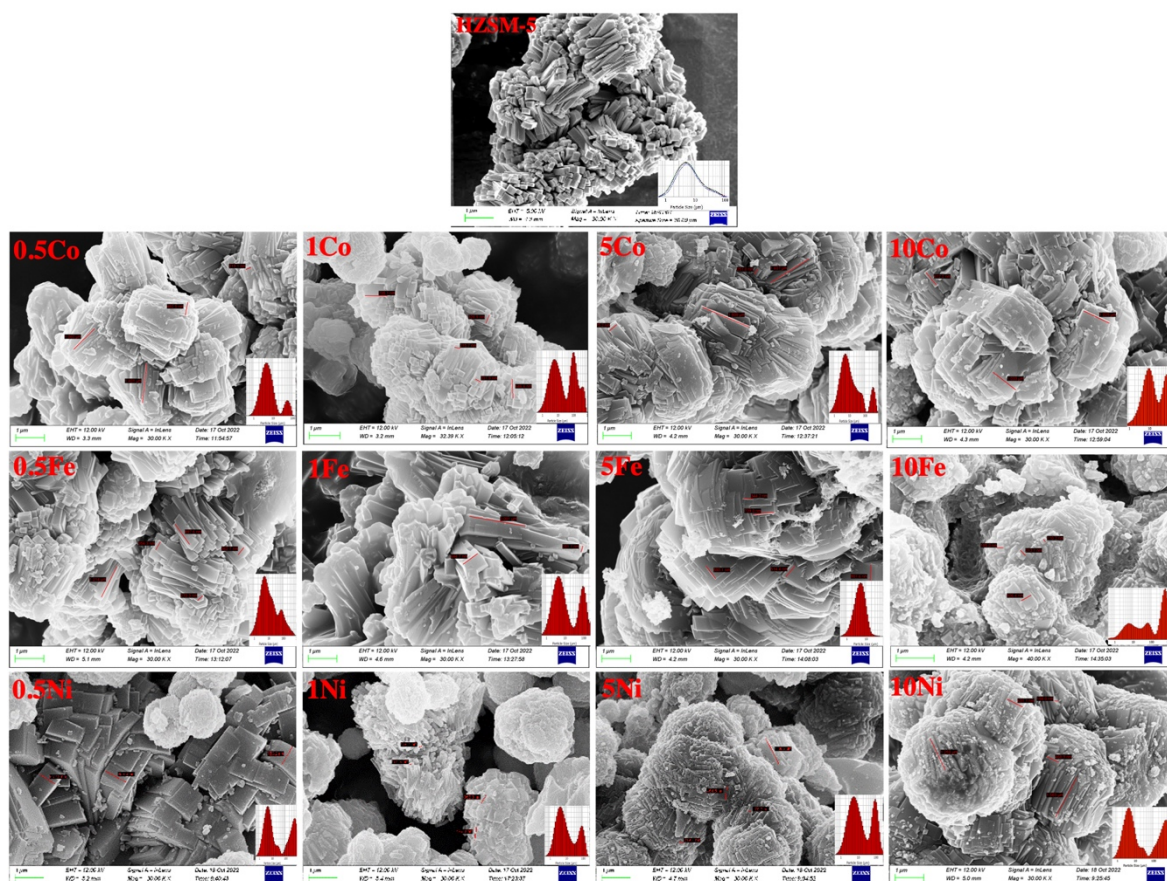


Figure 3-5. SEM and PDS (inset) of pure and transition metal-doped HZSM-5

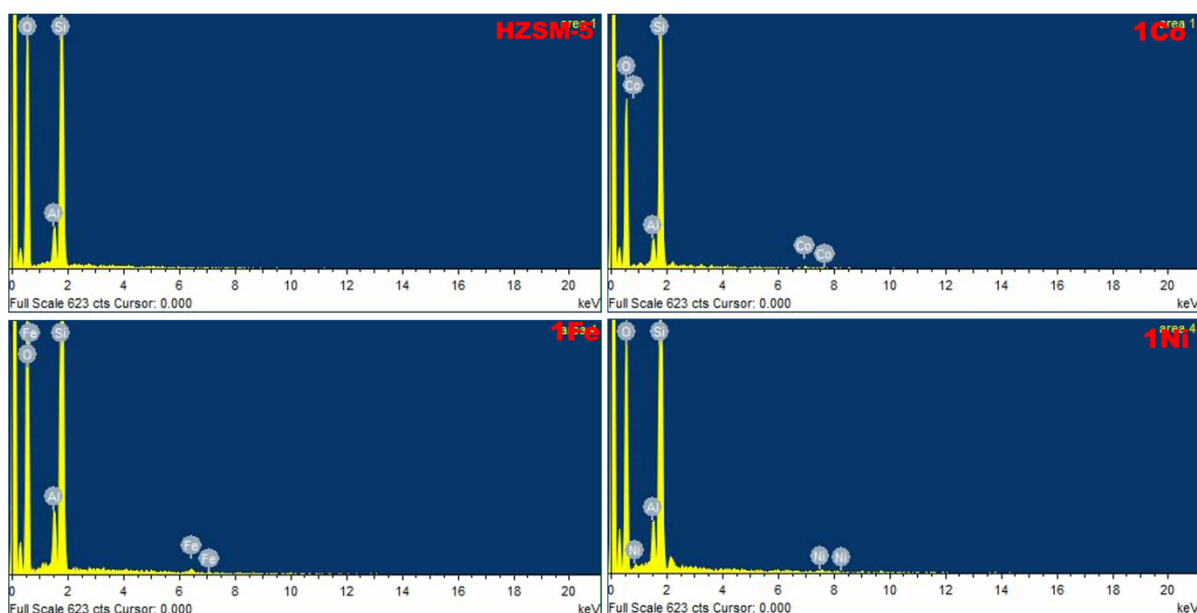


Figure 3-6. EDS Spectra of (1 wt%) metal-doped catalysts

Table 3-1. Transition metal composition of catalysts

Catalysts	Metal Loading (wt.%)			Particle size (Mean) (μm)
	Amount Loaded	EDS Avg.	XRF	
HZSM-5	0.00	0.00	0.00	4.55
0.5Co	0.5	ND	0.48	4.85
1Co	1	1.41	0.95	7.99
5Co	5	6.37	5.73	5.68
10Co	10	9.97	11.74	8.86
0.5Fe	0.5	0.54	0.55	5.74
1Fe	1	1.36	1.02	7.08
5Fe	5	4.38	4.70	4.94
10Fe	10	10.16	9.32	12.67
0.5Ni	0.5	0.71	0.50	6.33
1Ni	1	0.75	1.01	5.23
5Ni	5	5.12	4.53	6.61
10Ni	10	11.77	9.23	9.23

3.3.1.4 Textural Properties of Synthesised Catalysts

Figure 3.7a illustrates the N₂ physisorption isotherms and pore size distributions of the original and (0.5-10 wt%) metal-modified HZSM-5. Both the M/HZSM-5 catalyst and the parent catalyst exhibited Type-1V isotherms, with the M/HZSM-5 catalyst showing a significantly increased uptake in the P/P₀ range of 0.9-1.0. The hysteresis loop observed in all catalysts suggests the presence of mesoporous structures attributed to capillary condensation (Li et al., 2019b, Chen et al., 2011a, Imperor-Clerc et al., 2000). Increasing the relative pressure increased the adsorbed volume. However, introducing transition metals such as cobalt, iron, and nickel reduced the amount of adsorbed gas among the metal-doped samples, except for the 1 wt.% Ni-doped catalyst, the adsorbed volume exhibited a declining trend with increasing metal doping in the order of 0.5 > 1 > 5 > 10 wt%. A similar observation has been reported (Singh et al., 2020a). Notably, the Ni-doped HZSM-5 demonstrated the highest overall adsorbed volume compared to its counterpart, while 5 - 10 wt% metal-doped catalysts adsorbed the lowest volume, likely due to its smaller surface area compared to the pure catalyst, as shown in Table 3.2. The substantial volume adsorbed by 1 wt% Ni/HZSM-5 catalysts may be attributed to its high surface area, which provides sufficient surface area per unit for adsorption. A hierarchical macro-mesoporous network in the samples is supported by the multiple peaks and pore size distribution ranging from <2, 2-50, and >50 nm observed in all samples (Figures 3.7 b & c). The significant reduction in the volume of mesopores in the 25-50 nm range contributed to the decrease in pore volume. The effect of metal modification on pore size in the 1-25 nm range varied depending on the type of metal. Samples with 5 -10 wt% metal doping displayed smaller peaks in this range, while samples with 0.5 wt% doped catalysts showed larger peak intensities. This can be attributed to the optimum quantity of metal oxides (nickel, cobalt and iron) oxide, which have more prominent mesopores in this range, a similar trend reported by Li et al. (2018b).

Metal impregnation resulted in a reduction in the specific surface area of the metal-doped samples. For example, the surface area of Fe/HZSM-5 decreased with increasing metal doping, from 397.5 m²/g (for the parent catalyst) to 387.2, 366.3, and 368.6 m²/g for 0.5, 1, and 5 wt.% Fe, respectively. Additionally, the catalyst demonstrated a remarkable hierarchical meso-macropores structure, predominantly consisting of mesopores, as illustrated in Table 3.2. This unique characteristic contributes to enhanced performance and catalytic efficiency. The abundance of mesopores further facilitates improved mass transport and accessibility

for reactants, making these catalysts exceptionally promising for a wide range of applications. The modified samples exhibited lower mesopores volume, total pore volume and average pore diameter than the parent catalyst. This reduction can be primarily attributed to the presence of metal species that triggered the clogging of zeolite pore channels. Hence, it is reasonable to hypothesise that most of the metal was absorbed only on the outer surface of HZSM-5. Furthermore, larger nickel species could grow on the catalyst's surface as the metal loading increased, leading to substantial pore blockage and decreased surface area. These larger metal species have the potential to agglomerate and form metallic nickel particles at metal loadings of > 1 wt.%, covering the zeolite surface and further reducing the surface area. Interestingly, compared to other modified HZSM-5 catalysts, an increase in S_{BET} to 440.28 m^2/g and total pore volume was observed at 1 wt.% Ni could be attributed to the development of additional pores during the metal incorporation process or the formation of NiO species outside the zeolite pores. Incorporating a small quantity of nickel (1 wt.%) into ZSM-5 zeolite produced smaller nickel species on the catalyst's surface, increasing surface area. It was suggested that smaller nickel species acted as nuclei for the formation of smaller zeolite crystals, creating mesopores that contributed to the increased surface area. This indicates that increasing the amount of Ni to 1 wt.% is optimal for enhancing the catalysts' surface area. However, further increasing the metal doping to 5 wt.% resulted in a reduction in surface area by 92.74 m^2/g (347.5 cm^3/g). A similar trend has been reported by (Mohamed et al., 2005).

The process of metal impregnation resulted in a variation in the average pore diameter of the metal-doped ZSM-5 catalysts, which ranged from 1.78 to 2.68 nm, in contrast to pure ZSM-5 with an average pore diameter of 2.22 nm (Table 3.2). Compared to the unmodified HZSM-5 catalyst, a decrease in total pore volume and average pore diameter was observed with increasing metal loading. However, the enrichment of metal species in the 5 and 10 wt% Fe-modified HZSM-5 mesopores likely contributed to the slight increase in average pore size observed after modification. This confirms that the presence of metals in the catalyst formulation promoted an increase in pore diameter within the ZSM-5 structure, indicating structural changes due to metal doping. These changes in pore size are a critical factor affecting the surface area of the catalyst, the accessibility of the active sites, and its suitability for certain catalytic reaction.. Thus, the incorporation of metal ions may influence the crystallinity and size of the zeolite crystals, which in turn may affect the porosity and pore size of the catalyst. It can be inferred that the addition of certain metals can lead to the opening or narrowing of the pores, which affects reactant diffusion and product desorption (Saeidi and Hamidzadeh, 2017, Chiosso et al., 2023). The findings presented align

with the results reported by Saeidi and Hamidzadeh (2017), Güleç et al. (2019), and Zakaria et al. (2012). These studies support the observations made in this study regarding the N₂ physisorption isotherms, pore size distributions, and the impact of metal modification on surface area and pore characteristics. These consistent findings strengthen the validity and reliability of the current study's results.

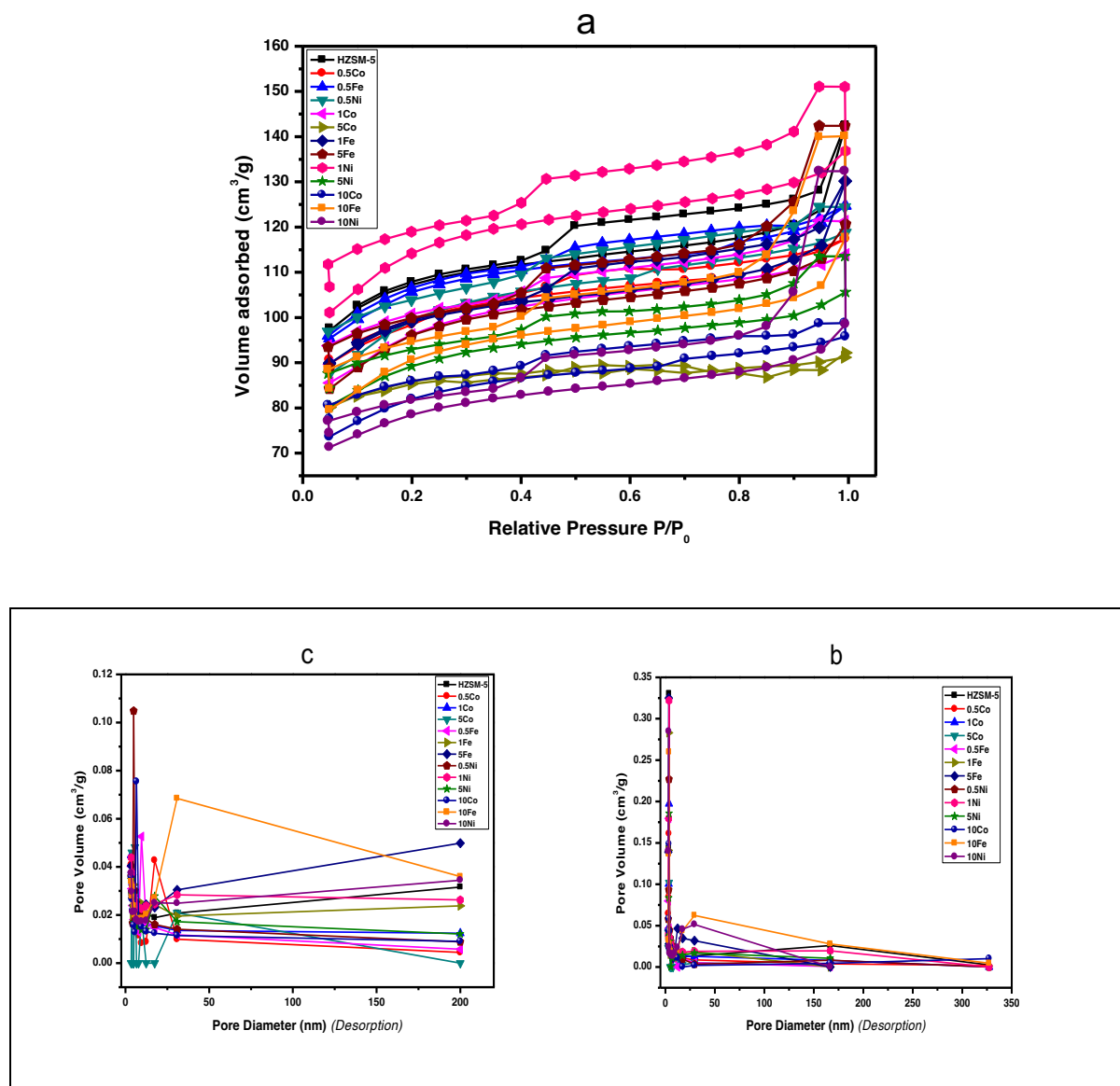


Figure 3-7. N₂ adsorption-desorption isotherms (a); BJH pore distribution for adsorption (b) and desorption (c) of pure and modified catalysts

Table 3-2. Textural properties of transition metal-modified catalysts with different metal contents

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	V_{macro} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	Avg pore dia. (nm)	Volume@ STP ($\text{cm}^3 \text{g}^{-1}$)	Metal loading (wt.%)
HZSM-5	397.47	0.706	0.678	0.0285	2.22	109.94	0.00
0.5Co	362.60	0.461	0.456	0.0057	2.01	102.39	0.5
1Co	369.85	0.545	0.536	0.0080	2.03	101.36	1
5Co	318.21	0.231	0.229	0.0015	1.78	87.04	5
10Co	319.29	0.420	0.405	0.0147	1.92	85.75	10
0.5Fe	387.20	0.448	0.448	0.0006	1.20	108.58	0.5
1Fe	366.27	0.633	0.633	0.0001	2.21	101.59	1
5Fe	368.60	0.710	0.709	0.0001	2.40	100.71	5
10Fe	348.02	0.701	0.668	0.0325	2.50	92.14	10
0.5Ni	381.36	0.590	0.582	0.0083	2.02	104.61	0.5
1Ni	440.28	0.772	0.753	0.0197	2.13	119.62	1
5Ni	347.54	0.457	0.446	0.0105	2.03	93.26	5
10Ni	306.21	0.663	0.663	0.0002	2.68	82.01	10

3.3.1.5 *NH₃-TPD Results*

The acidity of HZSM-5 and transition metal doped HZSM-5 were determined by NH₃ temperature-programmed desorption (NH₃-TPD). The NH₃-TPD results showed the presence of three distinct peaks, which were identified and categorised as detailed in Table 3.3, per the methodology outlined by Zheng et al. (2014). The desorption of NH₃ in weak acid (WAs), moderate acid (MAs), and strong acid sites (SAs) corresponded to peaks centred around 100–300 °C (low temperatures (LT)), 300–500 °C (medium temperatures (MT)), and 500–700 °C (high temperatures (HT)), respectively. To gain more specific insights into the acidity shift, quantification was performed on acid content and acid sites to assess surface acidity. The total acidity was quantified by measuring the amount of NH₃ desorbed per gram of catalyst within a temperature range of 100 to 700 °C. The outcomes of these analyses are presented in Table 1.

The impact of metal doping on the acidic properties of the HZSM-5 zeolite catalyst was more evident when compared to the textural properties. The presence of Ni, Fe, or Co at loadings of 0.5, 1, 5, and 10 wt.% led to a reduction in the number of strong acid sites (SAs), also referred to as Brønsted acid sites (BAS), by approximately 60–98 %. Interestingly, higher nickel

loadings, specifically at 10 wt.%, resulted in a 60% increase in strong acid sites (SAs) compared to the pure HZSM-5 catalyst. It is noteworthy that during the dry impregnation technique, some of the acidic protons responsible for the Brønsted acidity of the crystalline zeolite ZSM-5 might have been ion-exchanged by Co, Fe, or Ni ions, explaining the significant reduction in SAs observed (Zakaria et al., 2012a). Similarly, a decrease in moderate acid sites (MAs), also known as moderately strong acid sites (mSAs), was observed with metal-loaded samples, ranging from 5 to 48%. This decrease became more pronounced with higher loadings of Co and Fe (5 and 10 wt.%), while increased Ni doping led to an increase in MAs, particularly at 5 and 10 wt.%, resulting in a significant (28 and 56 %) rise in MAs, respectively. However, the decline in MAs was less severe compared to the reduction in SAs. At lower metal loadings (0.5-1 wt.%), metal ions in the zeolite framework likely lead to substituting some acidic protons responsible for strong acid sites, decreasing their number. This ion exchange process between the metal ions and the acidic protons contributes to the observed reduction in strong acid sites. However, a different phenomenon occurs at a higher loading, especially for Ni metal species. At this higher concentration, the nickel species may form clusters or particles on the zeolite surface, which act as catalytic active sites. These nickel clusters can enhance the generation or preservation of moderate and strong acid sites, increasing their number (Zakaria et al., 2012a).

In contrast to BAS, the number of WAs or Lewis acid sites (LAS) increased by approximately 5–42% at lower metal loadings (0.5-1 wt.%). This increase may be attributed to the formation of corresponding oxides, such as NiO, Fe₂O₃, and Co₃O₄ (as indicated by XRD results), which can act as Lewis acidic centres. Additionally, it was reported that modifying a proton from zeolite with metal species can alter the distribution of acid sites (Aho et al., 2010). Specifically, the BAS experienced a more significant decline when the zeolite was doped with 5-10 wt% metal. On the other hand, medium BAS also decreased, albeit to a lesser extent, than the strong acid sites. In accordance with the trend explained above, while total acidity increased with lower metal loadings, a substantial decrease was observed with increased loadings in most catalysts with high metal loading (5-10 wt.%), primarily due to a decrease in LAS. The 10wt% Fe doping recorded the lowest total acidity. The change in the acidity of the catalysts can mainly be attributed to the coverage of acidic sites on the external surface and the reactivity of metal species with protonic acid or other groups on the external surface or in the channels. These factors have been identified as the primary contributors to the observed changes in acidity. The interaction between metal species and protonic acid likely resulted in the

transformation of strong acid into a moderate or weak acid (Wei et al., 2017, Abdelsayed et al., 2015). Moreover, incorporating Ni, Fe, and Co led to variations in peak temperature areas compared to undoped HZSM-5. The result of this study is consistent with other studies (Che et al., 2019c, Li et al., 2019b, Zheng et al., 2014, Iliopoulou et al., 2012).

The acid test result presented in this study provides evidence of weak acid sites, including both Brønsted and Lewis sites, in the catalysts, which aligns with the typical ZSM-5 peak characteristics (López-Fonseca et al., 2003). Brønsted acid sites are formed when aluminium atoms are linked to silicon through a "bridging hydroxyl," resulting in a negative charge balanced by a proton. These sites are considered dominant and are believed to be the primary catalytic centres for some reactions. Being acid sites, they can bind basic compounds such as ammonia through hydrogen bond formation [36]. On the other hand, Lewis acid sites consist of aluminium or BBSi⁺ ions with low coordination. These sites play a crucial role in various catalytic processes by acting as electron pair acceptors and facilitating charge transfer processes (Sonnemans et al., 1993). Based on the results obtained from the TPD-ammonia test, it can be deduced that metal impregnation modifies catalyst acidity by introducing new weak, moderate, or strong acid sites differently. The diverse acidity characteristics of catalysts can be attributed to the availability of crystallographic structures with various configurations and framework atoms occupying different environments (Damjanović and Auroux, 2009). These structural variances contribute to the wide range of acidity properties observed in the catalysts.

Table 3-3. Acidity of unmodified and metal-doped HZSM-5

Catalysts	Peak Temp (°C)			Acidity conc. (μmol NH ₃ /g)			Total acidity
	L.T.	M.T.	H.T.	Weak	Moderate	Strong	
HZSM-5	198	419	686	0.95	0.74	0.024	1.71
0.5Co	189	425	667	1.05	0.69	0.015	1.76
1Co	184	432	656	1.11	0.61	0.018	1.74
5Co	181	444	632	0.78	0.59	0.030	1.38
10Co	172	438	623	0.51	0.70	0.004	1.21
0.5Fe	194	436	678	1.01	0.79	0.017	1.82
1Fe	187	428	624	1.09	0.64	0.011	1.74
5Fe	182	437	621	0.64	0.41	0.026	1.06
10Fe	168	418	612	0.59	0.38	0.006	0.98
0.5Ni	190	435	688	1.06	0.69	0.014	1.76
1Ni	188	439	678	1.16	0.83	0.020	2.01

5Ni	184	442	642	1.17	1.04	0.035	2.21
10Ni	178	427	617	0.68	1.71	0.060	2.45

LT – Low temperature; MT – Medium temperature; HT – High temperature

3.4 Conclusion

Mesoporous ZSM-5 zeolites were hydrothermally synthesised using TPABr as an organic structural directing agent. Optimised operating conditions employed during the synthesis process resulted in improved mesoporous HZSM-5, while the incorporation of transition metal species into the zeolite framework was effectively achieved by dry impregnation. Comprehensive characterisation techniques provided valuable insights into the properties of the synthesised catalysts, revealing characteristic peaks and functional groups associated with a typical MFI zeolite framework. The characterisation results showed that low metal doping (0.5-1 wt%) had a negligible effect on the crystallinity and structural properties of the framework compared to high metal doping (5-10 wt%). However, at high metal doping, the peaks of metal oxides, such as Co_3O_4 , Fe_2O_3 , and NiO , became more evident, indicating the successful incorporation of Co, Fe, and Ni into the catalysts. The introduction of transition metal species also increased the particle size of the parent catalysts. N_2 adsorption results revealed the presence of meso/macroporous structures in contrast to the microporous nature of the catalysts. In addition, introducing metal species reduced the surface area due to the blockage of the zeolite channels. The acid test performed on the catalysts revealed the presence of three types of acid sites: weak, moderate and strong. Interestingly, an increase in weak acid sites was observed, accompanied by a significant decrease in strong acid sites. Overall, the comprehensive characterisation of the synthesised catalysts has provided valuable insights into their structural, morphological and chemical properties.

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CHAPTER 4

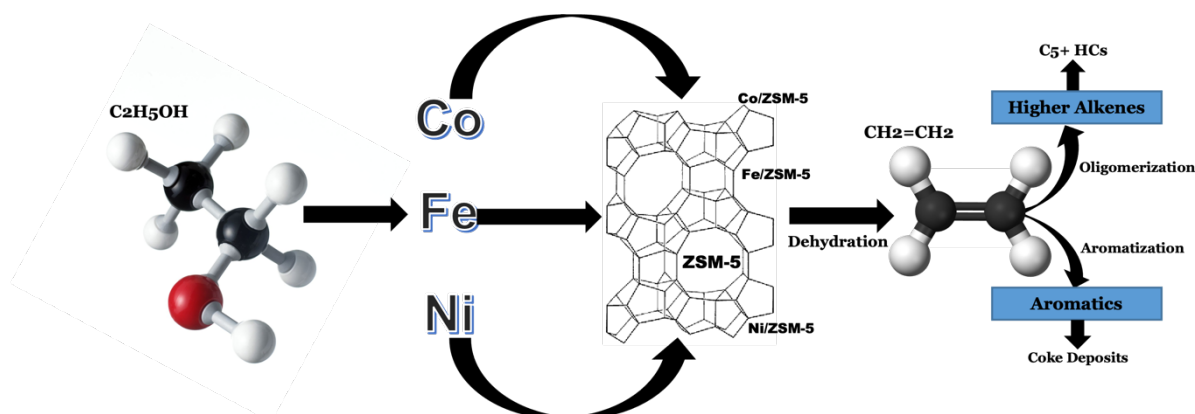
Effects of Transition Metal Doping on the Properties and Catalytic Performance of ZSM-5 Zeolite Catalyst on Selected Processes

Abstract

ZSM-5 is a viable catalyst for hydrocarbon reactions. The modification of this catalyst may affect its characteristics and application in catalysis. This chapter uses experimental data and secondary data from the literature to investigate the effect of transition metal-doping on the properties and catalytic performance of ZSM-5 on ethanol conversion. The ZSM-5 catalyst was hydrothermally synthesised and promoted with different concentrations (0.5 and 10 wt%) of transition metals (Co, Fe and Ni). The catalytic conversion process was carried out at 350 °C and a space velocity of 12 h⁻¹. The result of the pure and metal-doped HZSM-5 showed the presence of metal species (with increased metal doping) within the catalyst matrix, while their MFI structures were not altered after the modification. The introduction of transition metal also influenced the surface area, morphology, particle size and acidity of the catalyst, as shown by BET, SEM-EDS, PSD and NH₃-TPD results. The catalytic tests demonstrated that several processes facilitated ethanol conversion, including dehydration, oligomerization, and aromatization. The ZSM-5 catalysts doped with Co, Fe, and Ni exhibited improved catalytic performance, showing high selectivity towards aromatics such as benzene and a wider product distribution than the unmodified catalyst. While the low metal-doped catalysts exhibited optimal catalytic activity, high metal doping increased coke deposition and catalyst deactivation due to increased strong acid site concentration. The catalytic results underline the suitability of metal-reinforced ZSM-5 for use in hydrocarbon reactions.

Keywords: Catalyst, Ethanol, Transition metals, Zeolite, ZSM-

Graphical Abstract



4.1 Introduction

One of the most often used zeolite solid acid catalysts is ZSM-5. This catalyst has a variety of applications in the petrochemical industry, including the improvement of fuel properties and the production of petrochemicals. ZSM-5 may achieve significant recognition in catalysis processes due to the substantial acid sites accessible on the material. In addition to this, its overlapping 10-member ring micropores ($5.5 \text{ \AA} \times 5.1 \text{ \AA}$; $5.3 \text{ \AA} \times 5.6 \text{ \AA}$) justify its acceptable specificity and coke-resistant strength (Li et al., 2008). Crystalline networks of SiO_4 and AlO_4 constituents, organized in a three-dimensional structure using tetrahedral geometry, are the building blocks of these zeolites. In further detail, elliptical and straight pores are present in each cross-section of ZSM-5 structures, and these pores overlap in a zigzag arrangement at the right angle (Fathi et al., 2014, Louis and Kiwi-Minsker, 2004). After applying ZSM-5 in some processes, a charge imbalance occurs between the ions in the structures, namely between the Si and Al ions (Jacobs et al., 2001). The characteristics of ZSM-5 are significantly affected by several variables, including alkalinity, the chemical content of the fabrication gel, the template, the Si/Al ratio, the duration of crystallization, temperature, the zeolite fabrication technique (stationary or rotational environments), metal incorporation and other operational variables that are common in the hydrothermal process. These parameters may significantly impact its durability, effectiveness, and specificity (Kumar et al., 2002). Zeolite catalysts are used in producing chemical feedstocks from petroleum and environmental remediation, including wastewater treatment. Zeolites are also considered promising as potential catalysts for the production of chemical compounds via the transformation of

biomass. Due to their ordered crystalline framework, chemical and thermal durability, and pores aligned with the molecule sizes in the reaction medium, zeolites have a wide range of utilization as adsorbents, molecular sieves, and catalysts (Kuz'mina et al., 2010). These functions are directly associated with the characteristics of zeolites, which include adsorption in environmental remediation, ion exchange, and molecular selectivity.

Despite this, it is essential to highlight that carbon accumulation across the ZSM-5 surface reduces catalysts' stability and performance attributed to incorporating promoters, including transition metals. This is the most significant challenge that ZSM-5 zeolites provide for use in commercial processes. The performance of the catalysts can be improved by applying the appropriate introduction of metallic or non-metallic elements based on the target product. In addition, the catalyst can be made bifunctional by combining an acid zeolite with a component that catalyzes several hydrocarbon reactions, mainly a metallic element. It is necessary to use a suitable modification strategy to produce zeolites that have fundamental properties. Contrary to acid zeolites, basic zeolites, due to the fundamental nature of their characteristics, are unlikely to garner considerable interest in industrial catalysis. In addition, the world is in desperate demand of both practical and capable catalysts that increase the catalytic activity while reducing the deactivation and quantity of coke produced during operations. Consequently, suitable zeolites and modification in the catalytic process is necessary. These zeolites can alter the properties of products in accordance with the preferences of the target product (Sharifi et al., 2020).

There have been several studies on the influence of metal doping on the catalytic activity of ZSM-5. According to Li et al. (2020b), a decrease in bio-oil productivity was recorded due to metal doping on ZSM-5. However, the authors claimed that monoaromatic hydrocarbons (MAH) yield was higher with Fe and Co metal doping. The study also found that Fe doping drastically reduced the amount of coke (Li et al., 2020b). Zheng et al. (2017) reported that doping ZSM-5 with Ga, Zn, Ni, Co, Mg, or Cu increased the gas yield while the liquid yield decreased; for Ga-ZSM-5 between metal-modified catalysts, they were able to achieve maximum hydrocarbon yield and minimum coke formation, which were 26.1% and 22.0%, respectively. The study concluded that a Ni- and Co-based catalyst increased benzene and indene production, respectively (Zheng et al., 2017). According to Du et al. (2013), doping a catalyst with Cu and Ga in an appropriate ratio improved aromatics yield. However, other studies in the literature take an opposite view on the effects of metal modification. For instance,

Persson et al. (2019a) found that loading Fe or Ni onto ZSM-5 caused noticeable coke deposition on the catalyst. They found that incorporating Ni or Fe on ZSM-5 improved the yield of MAH. Ni/ZSM-5 was active in the production of naphthalene (Persson et al., 2019a). Although these studies investigated the effects of metal doping on ZSM-5 catalysts, some studies used commercially available catalysts, while others did not investigate ethanol conversion at high metal loading (> 5 wt%) and did not study the effects of the various metals on ZSM-5 catalyst properties and product distribution specifically in ethanol conversion into liquid hydrocarbons.

Therefore, this study aims to investigate the effects of selected transition metals on ZSM-5 catalyst properties (including crystallinity, functional groups, textural features – surface area, total pore volume, pore diameter and distribution) and catalytic performance in hydrocarbon reaction. This involves the synthesis, characterization, promotion, and evaluation of newly fabricated ZSM-5 catalysts. Based on experimental and secondary data from the literature, this study systematically evaluated the changes in the characteristic features of ZSM-5 catalysts before and after (low and high) metal modification (0.5 and 10 wt.%). In addition, the doping effect of the catalyst in ethanol conversion into hydrocarbons was discussed, which allows appropriate conclusions to be drawn about how the properties and activities of the ZSM-5 in catalytic processes are affected by the presence of different transition metal promoters. This study provides researchers and petrochemical industries with useful background on the detailed effects of metals on catalyst properties, performance, and product distribution, enabling the synthesis and effective modification of the required catalyst for the selective production of the target product.

4.2 Materials and Methods

Materials used for this study includes $\text{Na}_2\text{OsiO}_2\cdot\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$, $\text{C}_{12}\text{H}_{28}\text{BrN}$, NaOH (97%), H_2SO_4 (98%), NH_4NO_3 , $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2\cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH}$. All chemicals were analytical grade obtained from Sigma Aldrich. A stainless-steel hydrothermal reactor (HTR) with a Teflon lining of 200 ml with 150 ml working volume was used for catalyst evaluation. Catalysts were synthesised, characterised and evaluated according to the method described in *Section 3.2.2*.

Thermo Gravimetric-Differential Thermal Analysis (TG-DTA) was conducted using the TA Instruments Q50 equipment (USA) to determine the extent of coke deposition. The catalyst

samples were gradually heated in an N₂ stream from room temperature to 200 °C at 15 °C/min, with a flowrate of 50 ml/min. This heating process aimed to remove moisture and volatile components from the catalyst. Afterwards, the nitrogen gas was replaced with airflow, and the temperature was raised to 800 °C while maintaining the same flow rate.

4.3 Results and Discussion

4.3.1 Effect of Transition Metal Modification on the Crystallinity of ZSM-5

All the XRD patterns of synthesised materials showed the characteristic peak of the standard ZSM-5 catalyst. The XRD result revealed that the characteristic peaks were observed for the original and the transition metal-doped catalyst at $2\theta = 7-9^\circ$ and $23-25^\circ$. Distinctive diffraction peaks were observed at 7.97° , 8.88° , 14.81° , 23.14° , 23.32° , and 24.00° assigned to reflective planes (101), (020), (301), (501), (303) and (133) of the MFI framework of the ZSM-5 catalyst (Figure 4.1) (ICDD PDF No. 96-154-02468). The fact that the XRD patterns do not contain any other unexplained peaks is evidence that amorphous SiO₂ did not form simultaneously with ZSM-5. The absence of promoter-related peaks in the XRD patterns of some promoted catalysts is due to the presence of transition metal promoter in a small amount (0.5 wt% of Co, Fe and Ni), which denotes homogeneous dispersion of metal species during the doping process (Rahimi et al., 2021). The height of the peak ratio at $2\theta = 22.5-25.0^\circ$ compared to the peak area of the pure catalyst is the definition of relative crystallinity, determined according to ASTM (2015). Since the increased loading of transition metals lowers both the intensity and peak area, the impregnated HZSM-5 catalysts exhibit lower relative crystallinity, with a loading of 10 wt.% Co, Fe, and Ni compared to a loading of 0.5 wt% and an unmodified catalyst. The peaks of metal oxides were prominent in high metal loading. The peak at 37.2° , 43.3° and 62.9° corresponds to NiO assigned to ICDD PDF No. 96-432-9324, and the peaks at 33.2° and 35.8° and 49.2° are attributed to Fe₂O₃ (ICDD PDF No. 00-024-0072), while Co₃O₄ corresponds to the peaks at 31.7° , 36.9° and 65.4° (Figure 4.2) which corresponds to ICDD PDF No. 96-153-8532. Both before and after the modification, all the catalysts had MFI framework and showed diffraction peaks of ZSM-5 (Ji et al., 2018). Thus, the framework of ZSM-5 was successfully preserved despite introducing transition metals. This is evidence that the catalyst in question has a ZSM-5 zeolite framework. However, a reduction in percentage crystallinity was recorded with the modification of transition metals and a further decrease in the characteristic peak with increased percentage doping (Ji et al., 2018). In addition, Hajimirzaee et al. (2020) noted that metal incorporation into the ZSM-5 shows that the peaks of the metal-doped zeolite correlate

with those of the reference standard for calcined high-purity HZMS-5 catalyst. The findings of the XRD characterization of relative degrees of crystallization of different transition metal-doped ZSM-5 catalysts were computed and presented in Table 4.1 using the four significantly stronger diffraction peaks of unmodified HZSM-5 at $2\theta = 7^\circ$ - 9° and 23° - 25° as reference points.

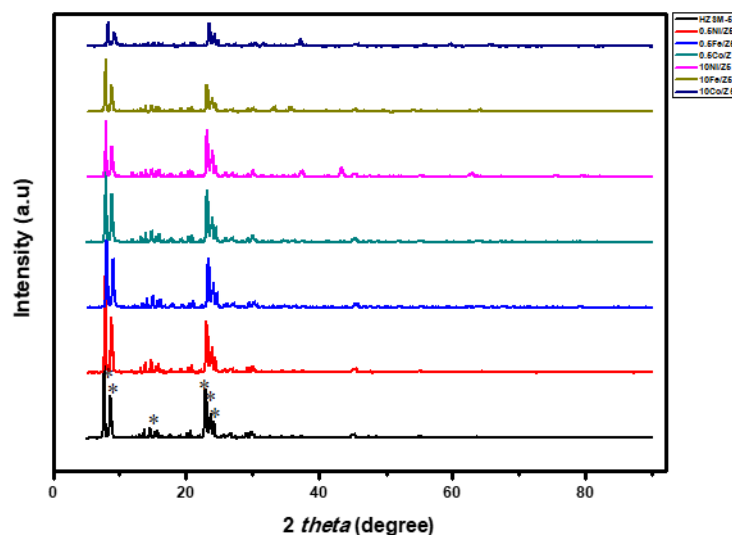


Figure 4-1. XRD patterns of pure and transition metal-modified HZSM-5 catalysts

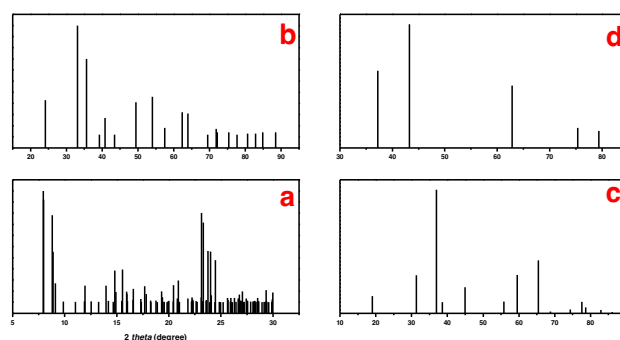


Figure 4-2. XRD peaks of (a) HZSM-5 and metal oxides: (b) Fe/Z5 (Fe_2O_3) (c) Co/Z5 (Co_3O_4) (d) Ni/Z5 (NiO)

Notably, the percentage relative degree of crystallization (RDC) of each doped catalyst either increased or decreased due to the modification process. According to Machado et al. (2005) the RDC of the (4.8 wt%)Fe/ZSM-5 catalyst reduced drastically to 60%, while the RDC of the

(0.25 wt%)Fe/HZSM-5 catalyst increased slightly to 114%, attributed to high and low metal-doping, respectively (Machado et al., 2005). It can be deduced that the type of transition metal and increased loading leads to a loss in structural orderliness, as seen by the lower relative degree of crystallization. Ji et al. (2018) noted that compared to the spectrum of HZSM-5, the metal-doped spectrum does not contain any of the distinctive diffraction peaks of transition metal species. Hence, incorporating transition metal did not result in any discernible alteration to the crystal framework or crystallinity of the ZSM-5 especially for 0.5 wt% metal-doping. In agreement with these findings, the XRD findings by Hajimirzaee et al. (2020) suggest that modification of Zn and Ga (0.2-1 wt%) does not affect the crystallinity or framework of the zeolite. In contrast to low metal loading, a careful examination revealed the presence of metal oxide peaks when the catalyst was subjected to a high metal doping of 10 wt%. These peaks provided evidence that metal-doped samples had undergone the production of transition metal oxides. It can be inferred that the absence of noticeable peaks within the angles examined may indicate the absence of metal oxide or the presence of doped metal in small amounts (Zheng et al., 2017).

Contrary to the observations by Hajimirzaee et al. (2020), but in agreement with the present study, Li et al. (2018b) reported from the XRD of the metal-doped (5-10 wt%) samples the presence of metal oxide was discovered after careful inspection of the patterns (peaks) in the range of $2\theta = 35.6^\circ$ and 38.7° for CuO (Huo et al., 2014); $2\theta = 37.2^\circ$ and 43.3° for NiO and $2\theta = 33.6^\circ$, 36.1° and 41.5° for Cr_2O_3 (Wu et al., 2016). The peaks in these samples indicated the formation of transition metal oxides. With respect to YZM, it was found that there were no conspicuous peaks within the studied angles, suggesting either the absence of yttrium oxide or an exceptionally uniform distribution of Y metal species (Mimura et al., 2002). Considering that there was no significant shift in the intensity of the diffraction peaks between the several molecular sieves, it was concluded that the framework of the ZSM-5 molecular sieve was not affected. In addition, the alteration of the metal impregnation results in a highly distributed state of the metal oxide on the catalyst's surface. The low-angle diffraction-peak intensity of some metal-doped molecular sieves demonstrates that the transition metal element could easily pass through the inner part of the molecular sieve pore (Zheng et al., 2017). However, in a more recent study by Tong et al. (2022) using similar transition metals (Ni and Co), no specific diffraction peaks of NiO and Co_3O_4 were detected in the metal-doped HZSM-5, suggesting that the metal oxide species were incorporated in small quantities and homogeneously dispersed on the HZSM-5 support. In addition, the metal loading caused a drop in the absorption peak of

HZSM-5. This suggests that the loading of Co or Ni led to a reduction in the catalyst crystallinity (Tong et al., 2022).

In agreement with the present study and Tong et al. (2022), Saeidi and Hamidzadeh (2017) reported a low relative crystallinity with co-doping of transition metals. The low crystallinity was attributed to the synergy between Cu (in Mn-Cu/ZSM-5) and pure ZSM-5, facilitating a stronger metal-support relationship than Cr and ZSM-5. The dispersion of copper in Mn-Cu/ZSM-5 is substantially greater than in Mn-Cr/Z. This may be the primary cause of the Mn-Cu/ZSM-5 catalyst's significantly increased activity compared to Mn-Cr/ZSM-5 (Aboul-Gheit et al., 2011). However, Calsavara et al. (2008b) noted that certain samples had multiple crystalline phases after being enriched with a transition metal. The XRD pattern of these samples exhibits a high peak at $2\theta = 26.5^\circ$ and an increase in 21° peak, confirming the formation of α -quartz (Baerlocher et al., 1996). Only samples 4.8 and 5 wt% Fe showed accumulation of oxide particles after calcination, which depicts the presence of Fe oxide ($2\theta = 33.2^\circ$ and 35.7°). These peaks were not detected in the catalyst prepared by direct method. It should be noted that the differences in crystallinity can also be attributed to the synthesis method and post-treatment techniques applied to these catalysts (Calsavara et al., 2008b).

Table 4-1. Comparing the sum of intensities of transition metal doped HZSM-5 with that of pure HZSM-5

Catalysts	% Metal loading	Relative crystallization (XRD) %	Ref.
HZSM-5 (Si/Al = 40)	0	100	Present Study
0.5Co/Z5	0.5	85.7	
0.5Fe/Z5	0.5	85.6	
0.5Ni/Z5	0.5	99.9	
10Co/Z5	10	43.7	
10Fe/Z5	10	57.1	
10Ni/Z5	10	71.4	
HZSM-5	0	100	(Machado et al., 2005)
Fe/Z5	0.25	114	
Fe/Z5	0.25	108	
Fe/Z5	0.33	108	
Fe/Z5	0.33	105	

Fe/Z5	4.8	60	
Fe/Z5	4.7	80	
Fe/Z5	5.0	80	
HZSM-5	0	100	(Ji et al., 2018)
Cu/Z5	3	88.4	
La/Z5	3	77.9	
Zn/Z5	3	48.6	
ZSM-5	0	90	(Saeidi and Hamidzadeh, 2017)
Mn/Z5	Mn (4)	67.5	
Mn-Cr/Z5	Mn-Cr (4-0.93)	79.2	
Mn-Mn/Z5	Mn-Mn (4-0.98)	70.2	
Mn-Fe/Z5	Mn-Fe (4-1)	56.7	
Mn-Co/Z5	Mn-Co (4-1.05)	56.7	
Mn-Ni/Z5	Mn-Ni (4-1.05)	73.8	
Mn-Cu/Z5	Mn-Cu (4-1.14)	50.4	
Mn-Zn/Z5	Mn-Zn (4-1.17)	57.6	
Ga/Z5	5%Ga	100	(Seemala and Wyman, 2022)
Ga/Z5 _{0.2M}	5%Ga0.2%NaOH	94.7	
Ga/Z5 _{0.6M}	5%Ga0.6%NaOH	90.3	
Ga/Z5 _{0.8M}	5%Ga0.8%NaOH	82.4	
Ga/Z5 _{1.0M}	5%Ga1.0%NaOH	72.9	
ZSM-5 (Si/Al=20)	0	100	
Fe/Z5	0.5	89	
Fe/Z5	0.25	90	(Calsavara et al., 2008b)
Fe/Z5	4.8	95	
Fe/Z5	1.82	97	
Fe/Z5	5	98	

4.3.2 Effect of Transition Metal Modification on the Functional Groups of ZSM-5 Catalyst

The FTIR analysis is usually performed in the 400-4000 cm⁻¹ range to identify functional groups in the synthesised materials, such as the ZSM-5 zeolite catalyst. The FTIR result shows

that the pure and transition metal-doped ZSM-5 exhibit characteristic peaks of the functional groups of ZSM-5 represented by different bands (Figure 4.3). However, increased metal doping from 0.5 wt.% to 10 wt.% Co, Fe and Ni resulted in decreased intensity, and different peaks represented the presence of metal oxides at high loading. The decrease in peak intensity at high loading (10 wt.%) follows the pattern: $\text{Co} < \text{Fe} < \text{Ni}$. The crystalline framework of the zeolite is revealed by the strength of the bond at ~ 400 and 500 cm^{-1} . The band at 440 cm^{-1} corresponds to the stretching of T-O bonding of the internal tetrahedral of SiO_4 and AlO_4 units, while the pattern of peaks at $\sim 543\text{ cm}^{-1}$ depicts the vibrational intensity of the double five-member ring in the MFI framework of the ZSM-5 catalyst (Rahimi et al., 2021). The intense peak in the region of $791 - 1064\text{ cm}^{-1}$ is due to the internal asymmetrical stretching vibration between the Si-O-Si bonds (Tong et al., 2022), which depends on the Si/Al ratio; a decrease in the ratio of this peak results in a shift to lower values while the peak at 1218 cm^{-1} is attributed to external asymmetrical stretching. A peak denotes the adsorbed H_2O on the catalyst surface at 1633 cm^{-1} (Rahimi et al., 2021). The IR spectrum in the range of $3000\text{-}3900\text{ cm}^{-1}$ corresponds to the vibration and elasticity of the O-H bonds (Kazemi Hakki et al., 2021). However, the bands at about 3646 cm^{-1} identify the hydroxyl groups on extra framework Al and strong Brønsted acid sites (Si-Al-OH) (Rahimi et al., 2021). The metal oxides (for 10 wt% metal species) are attributed to the 661, 545, and 670 cm^{-1} peaks, representing Co_3O_4 , Fe_2O_3 and NiO , respectively (Ba Mohammed et al., 2020, Zhu et al., 2013, Shams-Ghahfarokhi and Nezamzadeh-Ejhieh, 2015). It can also be seen from Figure 4.3 that the loading of 10wt% Ni on the ZSM-5 causes the most absorption bands in the region of $400 - 4000\text{ cm}^{-1}$ to drop drastically and nearly completely disappear. Owing to the small concentration of 0.5 wt% metal doping, the FTIR results on these samples did not show any clear peaks of the oxide (Li et al., 2018b).

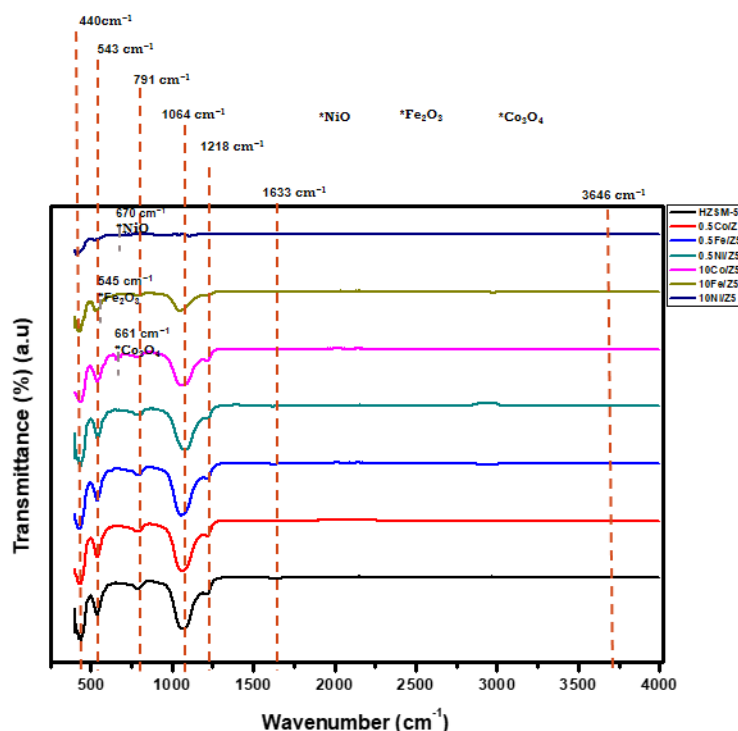


Figure 4-3. FTIR spectra of pure and transition metal-doped HZSM-5 catalysts

Table 4.2 shows the absorbance at wavelengths 540 and 450 cm^{-1} and illustrates that modification of the transition metals can lead to a decrease or increase in FTIR crystallinity at these peaks, depending on the metal type and concentration. Except for 0.5 wt% Fe, loading with other transition metals reduced the intensity of 450 and 540 cm^{-1} peaks, with higher loading (10 wt%) resulting in a significant decrease in these peaks. The present study agrees with the study by Calsavara et al. (2008b), who found a decrease in the absorbance at 540 and 450 cm^{-1} wavelengths with the introduction of transition metals. However, Saeidi and Hamidzadeh (2017) noted that the strength of the peak was increased by incorporating Mn and co-doped metals, confirming that the number of Brønsted acid sites was increased (Saeidi and Hamidzadeh, 2017). Consequently, the intensity ratio (also known as IR crystallinity) of the peaks at 540 and 450 cm^{-1} is due to the evolution of the MFI zeolite. This ratio ranged from 0.96 for Mn-Cu/Z5 to 0.88 for Mn-Cr/Z5 catalyst. This depicts the varying effect of transition metals with regard to a decrease in IR crystallinity. However, Cundy and Cox (2005) found that the correlation between IR crystallinity and typical XRD crystallinity is uncertain. With the metal doping in ZSM-5, and similar to the present study, Kazemi Hakki et al. (2021) reported a reduction of the peak at $\sim 3622 \text{ cm}^{-1}$ which shows the presence of Fe ions in the catalyst structure of Fe-doped catalyst. The intensity of the iron peaks was reduced in the FTIR

as the calcination temperature was increased. Tong et al. (2022) reported that the mixed phase of Mo and MoO₃ (doped) in the ZSM-5 nanocatalyst is responsible for the bands at 594 and 878 cm⁻¹ while Li et al. (2018b) noted that the stretching vibration of the Cr–O bond was corresponding to the peak that was found in CrZM at a wavelength of 625 cm⁻¹.

Table 4-2. Comparing the absorbance/transmittance at 550 and 450 cm⁻¹ of transition metal-doped with that of pure ZSM-5

Sample	Transition content (%)	metal	Peak Intensity, FTIR (%) <i>I</i> ₄₅₀	Peak Intensity, FTIR (%) <i>I</i> ₅₄₀	<i>I</i> ₄₅₀ / <i>I</i> ₅₄₀	Ref.
HZSM-5	0		100	100	1.00	Present study
0.5Co/Z5	0.5		99.1	98.5	0.994	
0.5Fe/Z5	0.5		102.7	101.5	0.989	
0.5Ni/Z5	0.5		93.8	90.9	0.970	
10Co/Z5	10		83.9	86.4	1.029	
10Fe/Z5	10		60.7	53.0	0.873	
10Ni/Z5	10		29.4	15.2	0.514	
Mn/ZSM-5			67.0	62	0.925	(Saeidi and Hamidzadeh, 2017)
	Mn (4)					
Mn–Cr/ZSM-5	Mn–Cr (4–0.93)		57	50	0.877	
Mn–Mn/ZSM-5	Mn–Mn (4–0.98)		72	66	0.917	
Mn–Fe/ZSM-5	Mn–Fe (4–1)		62	57	0.919	
Mn–Co/ZSM-5	Mn–Co (4–1.05)		70	66	0.942	
Mn–Ni/ZSM-5	Mn–Ni (4–1.05)		76	72	0.947	
Mn–Cu/ZSM-5	Mn–Cu (4–1.14)		68	65	0.956	
Mn–Zn/ZSM-5	Mn–Zn (4–1.17)		72	66	0.917	
Fe/Z5	0.02		100			(Calsavara et al., 2008b)
Fe/Z5	4.7		95			
Fe/Z5	5.0		98			
Fe/Z5	0.25		95			
Fe/Z5	0.25		90			
Fe/Z5	0.33		90			
Fe/Z5	0.33		97			
Fe/Z5	4.8		91			
Fe/Z5	4.8		95			

4.3.3 Effect of Transition Metal Modification on Morphology and Particle Size of HZSM-5 Catalyst

Images from SEM analysis show a spherical aggregate largely homogeneous for both parent catalysts and catalysts doped with transition metals (Figure 4.4a). Images with a high-resolution scanning electron microscope show nanoscale crystals aggregating into microspheres. Due to the higher nucleation density, delayed crystallization, and aggregation after nucleation, smaller particles may be visible on the microspheres (Tong et al., 2022, Zheng et al., 2020). The SEM result showed that the catalyst consists of prismatic crystals of MFI structure, which agrees with the result obtained from the XRD pattern (Feng et al., 2018). After impregnation, the morphology of the crystal showed no signs of significant changes. Also, the Si/Al ratio did not change during the impregnation process, which is further evidence that the impregnation process did not affect the overall composition of the zeolite framework (Hajimirzaee et al., 2020). When the metal promotion was performed at a concentration of 10 wt%, an unusual side effect occurred: some of the promoters precipitated on the catalyst surface, which could be observed in the EDS analysis (Fig. 3b). This precipitation is also visible on the SEM images of 10 wt% metal loading, which result in a change in catalyst particle size. However, the particle size distribution (PSD) result shows that doping with transition metals increases the particle size. The particle size of the doped HZSM-5 tends to increase (with reference to the particle size of parent HZSM-5, 4.55 μm) with an increase in metal doping from 0.5 to 10 wt%. Transition metal doped catalysts 0.5Fe and 10Fe increase by 1.19 and 6.93 μm ; 0.5Ni and 10Ni increase by 1.78 and 8.67 μm ; 0.5Co decreases by 0.23 while 10Co increases by 4.31 μm . These results correspond to the findings of other studies (Hajimirzaee et al., 2020, Tong et al., 2022, Zheng et al., 2020). The EDS spectrum showed the presence of transition metals (Co, Fe and Ni) at 10wt% in the modified catalysts (Figure 4.4b).

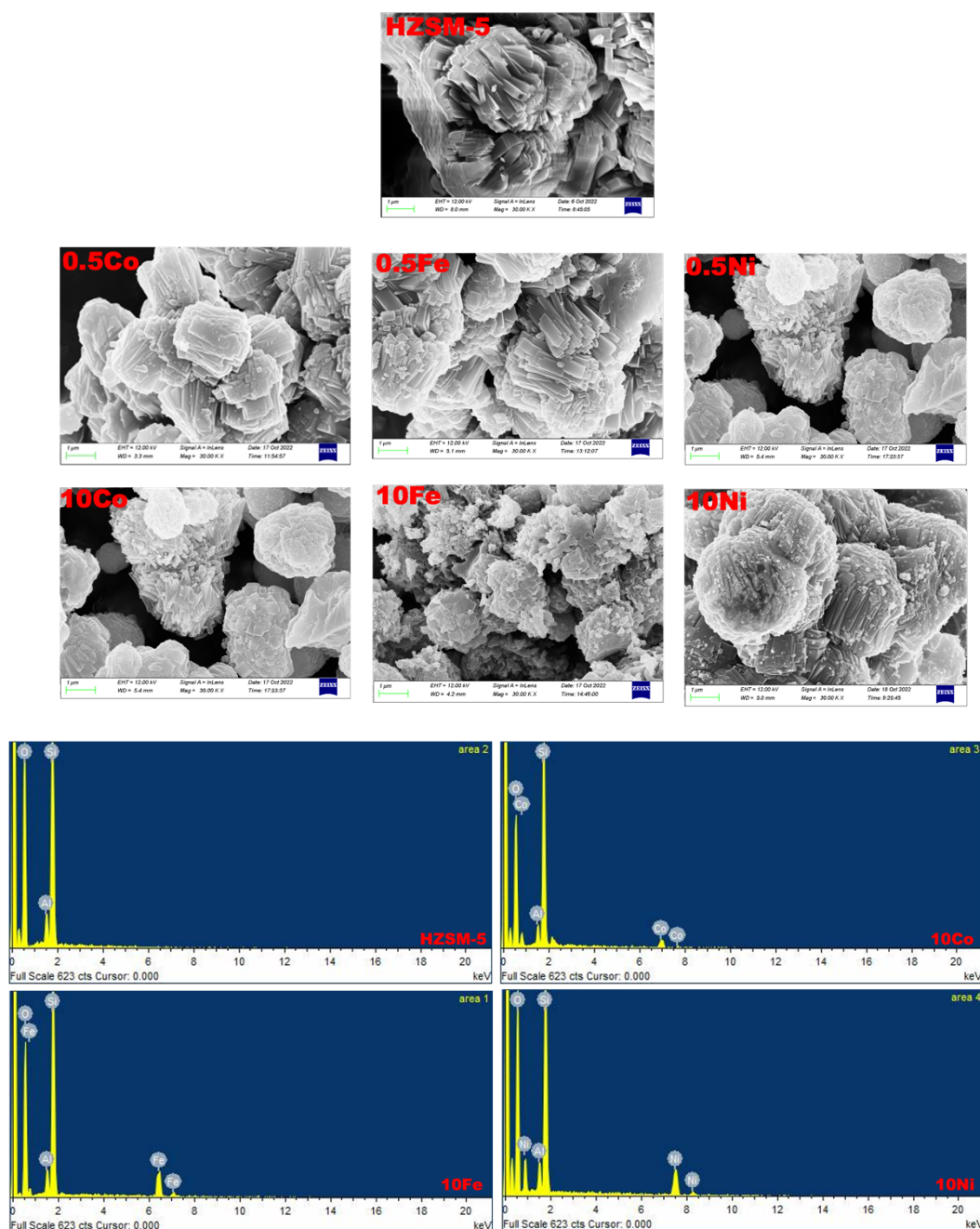


Figure 4-4 (a) SEM images of pure and transition metal-doped HZSM-5 (b) EDS spectrum of pure and transition metal-doped HZSM-5 at 10wt%

4.3.4 Effect of Transition Metal Modification on the Surface Area and Porosity of ZSM-5

The catalyst's specific surface area (SBET) is another vital factor in catalytic activity. The surface area and pore distribution of the heterogeneous catalyst, ZSM-5 samples, is usually determined by BET analysis. Table 3 presents the results of different BET analyses from the

present and other studies on ZSM-5 to show the surface area, pore volume and pore size distribution. It can be inferred from Table 3 that the modification of transition metals reduces the surface area and total pore volume of the modified catalysts. The surface area of the synthesised material in the present study was observed to decrease from 397.5 (for pure ZSM-5) to 362.6, 387.2 and 381.6 m^2g^{-1} for 0.5 wt% and 319.3, 348.0 and 306.2 m^2g^{-1} for 10 wt% Co, Fe and Ni, respectively. The increased doping of 10 wt% of transition metals further decreases the modified catalysts' respective surface areas (S_{BET}). It can be noted that the synthesised ZSM-5 in the present study has a significant surface area (397.5 m^2g^{-1}) compared to other studies examined, as shown in table 3. Similarly, the total pore volume decreases with metal doping from 0.71 (of the starting pure ZSM-5) to 0.46, 0.45, 0.59 cm^3g^{-1} for 0.5 wt% and 0.42, 0.70 and 0.66 cm^3g^{-1} for 10 wt% Co, Fe and Ni loading, respectively. However, the average pore diameter decreased with 0.5 wt% loadings and increased with 10 wt% metal loading. It is evident from Table 3 that an increase in transition metal loading results in a decrease in the S_{BET} and total pore volume of the ZSM-5 support catalyst. The decrease in S_{BET} and pore volumes is due to transition metals (Co, Fe and Ni) species covering the surface of ZSM-5 and partly blocking zeolite channels. The metal oxide was formed during the transition metal modification process, resulting in synthesising a metal-doped zeolite with a reduced surface area (Li et al., 2019b). The minor change in mesoporous volume, determined using the BJH approach, revealed that the drop in overall pore volume was caused mainly by the decrease in macropore volume. The substantial reduction in the volume of the mesopores that ranged in size from 10 to 50 nm was the cause of the decline in the total pore volume determined using BJH method. The impact that metal doping had on the size of the pores in the region of 1–5 nm varied depending on the metal and amount of metal content as 10 wt% Ni, followed by Fe and then Co showed larger pore size compared to 0.5 wt% loading of these metals.

The findings of this study are similar to those of previous works. Li et al. (2019b) showed that the BET surface area for Cr/Z5, Cu/Z5, Ni/Z5, and Y/Z5 all dropped from 373 m^2g^{-1} to 286, 297, 317, and 293 m^2g^{-1} , respectively. In a manner analogous to this, the pore volume decreased from 0.300 to 0.219, 0.202, 0.217, and 0.208 cm^3g^{-1} for Cr/Z5, Cu/Z5, and Ni/Z5, respectively. The Cu/Z5 and Y/Z5 were reported to show lower peak intensities in the region of 1–5 nm. Conversely, Cr/Z5 and Ni/Z5 produced larger peak intensities due to the formation of Cr and Ni oxide, the significant mesopores in this range. Hence metal type affects the size of the pores (Li et al., 2019b). Similarly, Zheng et al. (2017) reported that the S_{BET} of the

unmodified H-ZSM-5 is considerably high ($338.44 \text{ m}^2\text{g}^{-1}$) compared with that of the improved ZSM-5, which reduces, ranging from $293 - 287 \text{ m}^2\text{g}^{-1}$. The pore volume reduced, and the average pore size increased, although the change was minimal, which was probably due to the deposition of metal species at the molecular sieve opening or deep inside the channel, which clogged the interior of the zeolite channel and resulted in a decreased pore volume (Long et al., 2013). In addition, the blockage in the mesoporous pore sizes triggers an increase in overall pore size, which demonstrates that the metal ions were distributed evenly on the ZSM-5 surface. These findings were comparable to those of Schultz et al. (2017). Moreover, Cu/Z5 catalyst recorded the most significant reduction in pore volume, possibly due to increasing Cu species reaching the channel and causing blockages (Zheng et al., 2017). However, the study by Ji et al. (2018) reported that the S_{BET} of $342.9 \text{ m}^2\text{g}^{-1}$, pore volume of $0.457 \text{ cm}^3\text{g}^{-1}$, and average pore diameter of 5.9 nm of HZSM-5 catalyst were affected by transition metal modifications. The average pore width remains the same, while the S_{BET} of the modified catalysts decreases slightly between $320 - 330 \text{ m}^2\text{g}^{-1}$ and the pore volume decreases slightly. It can be noted that although part of the zeolite surface is covered and the modifications block some pores, the material's structural integrity has not changed (Ji et al., 2018).

Figure 4.5 displays the N_2 adsorption–desorption isotherms of the examined materials of the present study. The unmodified ZSM-5 demonstrated a greater N_2 adsorption than the other metal-doped zeolites. The comparable pressure ranged from 0.05 to 1.0 for all the samples, and these catalysts demonstrated type IV isotherms with hysteresis loops of varying diameters. This is agreed with the study by Ji et al. (2018). In addition to the inherent zeolite channels, the various peaks observed for all samples indicated that the ZSM-5 catalyst has a hierarchical macro-mesoporous structure (Li et al., 2019b). The isotherms of the HZSM-5 and the modified catalyst samples showed a hysteresis branch corresponding to adsorption-desorption in the mesopores. Furthermore, the adsorbed volume increased continuously with P/P_0 as the samples were examined. Following the addition of transition metals by the impregnation synthesis approach, the isotherms displayed a clear hysteresis loop at increased pressure, especially for 10 wt% Fe and Ni, caused by the mesoporous framework. It can be inferred that after the incorporation of the metal species framework, a fewer mesoporous structures were destroyed, and a fewer macroporous structures were produced.

Table 4-3. Review of results of different BET analyses on the effect of transition metal modification on the surface area, pore volume and pore size distribution of the ZSM-5 zeolite catalyst

Catalysts (Si/Al)	S _{BET} (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	S _{ext} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	Avg pore dia. (nm)	Metal (wt%)	Ref.
HZSM-5 ₍₄₀₎	397.5	335.2		0.706	0.678	0.0285	2.224	0	Present study
0.5Co/Z5	362.6	312.4		0.461	0.456	0.0057	2.008	0.5	
0.5Fe/Z5	387.2	331.4		0.449	0.448	0.0006	1.999	0.5	
0.5Ni/Z5	381.4	318.9		0.710	0.709	0.0001	2.024	0.5	
10Co/Z5	319.3	261.3		0.420	0.405	0.0147	1.919	10	
10Fe/Z5	348.0	289.8		0.701	0.668	0.0325	2.497	10	
10Ni/Z5	306.2	250.0		0.663	0.663	0.0002	2.681	10	
ZSM-5_M	373	214	159	0.300	0.100	0.200		–	(Li et al., 2019b)
Cr/Z5	286	180	106	0.219	0.090	0.129		11.62	
Cu/Z5	297	197	100	0.202	0.096	0.106		9.56	
Ga/Z5	318	197	121	0.213	0.096	0.117		10.31	
La/Z5	335	215	120	0.234	0.105	0.129		8.95	
Mg/Z5	229	178	51	0.177	0.087	0.090		8.64	
Y/Z5	293	185	108	0.208	0.090	0.118		10.34	
Ni/Z5	317	195	122	0.217	0.095	0.122		11.05	
Zn/Z5	285	185	100	0.227	0.090	0.137		11.34	
HZSM-5	342.9			0.457			5.9	3	(Ji et al., 2018)
Cu/Z5	328.2			0.440			6.0	3	
La/Z5	325.3			0.438			6.0	3	
Zn/Z5	326.2			0.437			6.0	3	
ZSM-5 ₍₂₀₎	386			0.25	0.16	0.09	2.41	0	(Rahimi et al., 2021)
Mo/Z5	259			0.18	0.10	0.08	2.40	25	
HZSM-5 ₍₂₅₎	338.4	195.6	142.8	0.2861	0.1016	0.1845	3.38	0	(Zheng et al., 2017)
Ga/Z5	293.5	163.6	129.9	0.2467	0.08499	0.1617	3.39	5	
Ni/Z5	291.4	162.9	128.4	0.2488	0.08472	0.1641	3.45	5	
Mg/Z5	282.1	167.7	114.4	0.2448	0.08626	0.1585	3.42	5	
Co/Z5	288.9	161.0	127.9	0.2460	0.08376	0.1622	3.44	5	
Zn/Z5	288.2	167.6	120.6	0.2483	0.08738	0.1609	3.38	5	
Cu/Z5	287.5	166.0	121.6	0.2387	0.08708	0.1516	3.41	5	
Ga/Z5	338		60.1		0.064			(Si/Ga) 5.4	(Seemal a and Wyman, 2022)
Ga/Z5 _{0.2M}	334		64.6		0.092			6	
Ga/Z5 _{0.6M}	366		106.7		0.156			14	
Ga/Z5 _{0.8M}	393		134.2		0.238			13.5	
Ga/Z5 _{1.0M}	421		170.6		0.457			12.5	
ZSM-5 ₍₂₀₀₎	321.11	281.71	39.40	0.19	0.13	0.06		0.5	(Rostam izadeh et

								al., 2018a)
Ag/Z5	315.14	276.41	38.73	0.18	0.12	0.06	0.5	
Ir/ Z5	327.35	288.13	39.22	0.19	0.12	0.07	0.5	
Ni/Z5	314.67	272.85	41.82	0.19	0.12	0.07	0.5	

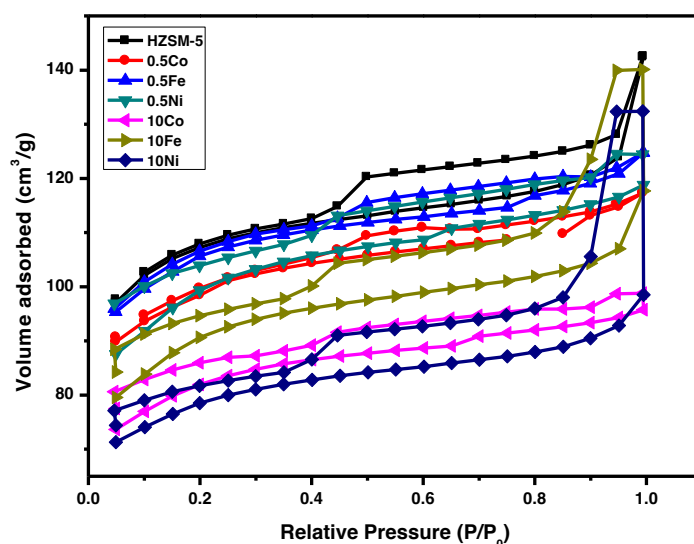


Figure 4-5. N₂ adsorption-desorption isotherm results for the pure and transition metal-doped HZSM-5 catalysts

4.3.5 Effect of Transition Metals on the Acidity of ZSM-5

The strength and concentration of acidic sites in ZSM-5 catalysts can be determined using the NH₃-TPD assay. Table 1 shows the results of ammonia temperature-programmed desorption (TPD) for pure HZSM-5 and metal-modified HZSM-5 catalysts. The TPD analysis revealed three distinct desorption bands observed at different temperature ranges: 180-200 °C, 400-450 °C and 650-700 °C, corresponding to weak acid, moderate acid, and strong acid sites, respectively. The desorption band in the 180-200 °C range can be attributed to physically and weakly chemically adsorbed ammonia, while the band in the 400-450 °C range indicates NH₃ adsorbed on the hydroxyl group of zeolite. The 650-700 °C desorption band is associated with dehydroxylation and desorption of NH₃ from the strong Brønsted acid or Lewis acid sites (Saini et al., 2022, Deka, 1998). Introducing metal species into HZSM-5 results in a noticeable shift in acidic properties, leading to a discernible change in the distribution of acidic sites. In particular, this modification increases the number of weak acid sites with a simultaneous decrease in the number of moderate and strong acid sites within the material. These changes in acidity are accompanied by a shift in peak temperatures, which can be attributed to the

interaction between the zeolite framework and the metal species. The weak acid sites showed an increase of 9.5 %, 5.9 % and 10.4 % at peak temperatures of 189 °C, 194 °C and 190 °C, respectively, for 0.5wt% Co-, Fe- and Ni-doped catalysts compared to the unmodified HZSM-5 catalyst with 0.95 mmol/g at 198 °C. Among the metal-doped catalysts, the Ni-doped catalyst exhibited the highest increase in weak acid sites. Substantial increase (10 wt%) in metal doping resulted in a 46.3, 37.9, and 28.4 % decreased in Co, Fe and Ni-doped catalysts. The number of moderate acid sites increased slightly by 6.3 % at a peak temperature of 436 °C for the Fe-doped catalyst, while Co- and Ni-doped catalysts decreased by 6.8 % within this temperature range. While 10 wt% Co and Fe-doped catalysts recorded a decrease (5.4 and 48.6 %) in moderate acid, 10wt% Ni increased these acid sites by 56.7 %. A significant decrease in the strongly acid sites was observed for all metal-doped catalysts, resulting in decreases of 27.5 %, 29.2 % and 41.7 % for 0.5 wt% catalysts with reference to the unmodified HZSM-5 catalyst except 10 wt% which led to an increase in strong acid sites. However, despite the decline in strong acid sites for low metal-doped catalysts, the modification of transition metals led to an overall increase in the total acidity of the respective catalysts.

The present study's findings are consistent with previous research indicating that incorporating transition metals (Co, Fe, and Ni) can alter the concentration of acid sites within the catalyst (De Lucas et al., 2005, Deka, 1998, Saeidi and Hamidzadeh, 2017, Iliopoulou et al., 2012, Li et al., 2019b). This effect is primarily due to the electronic interactions between the metal species and the framework of the ZSM-5 zeolite. The tetrahedral units of Si and Al in the ZSM-5 zeolite are negatively charged and balanced by positively charged cations, such as protons (H^+). The protons attached to the oxygen atoms in the zeolite framework act as strong acid sites responsible for the acidity and catalytic activity of the catalyst. When metal species are doped into the ZSM-5 catalyst, they can replace some protons and occupy the cationic positions within the zeolite framework. The doped species are typically Co^{2+} , Fe^{3+} , Ni^{2+} ions. These ions have lower positive charge density than protons, resulting in weaker electrostatic interaction with the oxygen atoms of the framework. As a result, the metal-doped ZSM-5 catalyst exhibits reduced strong acidity as the less acidic metal ions replace the strongly acidic sites (protons). The weaker acid sites the metal species provide decrease strong acidity with a concomitant increase in weak acid sites (Wei et al., 2017;). It should be noted, however, that the decrease in strong acid sites is not always desirable because the catalytic performance of ZSM-5 may depend on the presence of these strong acid sites for some catalytic reactions. For the present

study, the deliberate incorporation of metal species aims to modify the catalytic behaviour of ZSM-5 and facilitate alternative reactions or selectivities that do not depend solely on strong acid sites.

The study by Rostamizadeh et al. (2018a) showed that the original and metal-doped nanocatalysts have profiles that are very similar to each other, while the density and strength of the acid sites are different. According to the study, the peak temperature corresponds to the strength, while the peak area denotes the concentration of the acid sites. The presence of weak and strong acid sites is indicated by the two distinct desorption peaks at temperatures ranging from 140 to 300 °C and 300 to 500 °C, respectively (Rostamizadeh et al., 2018a). A high concentration of moderate acid and a high concentration of strong acid was found in the initial nanocatalyst. The doping of Ag decreases the number of both acid sites (Table 4.4). The interaction of the metal specie with the nanocatalyst framework, which includes the neutralization of the acid sites on the surface, may explain this behaviour. Due to the tiny size of the Ag species (the pore size of ZSM-5 is 0.55 nm), diffusion of the metal species into the pores occurs, eliminating the acid sites on the inner surface (Sun et al., 2008, Vitale et al., 2013).

Similarly, Rostamizadeh and Yaripour (2016) reported that introducing Fe into the ZSM-5 structure reduces both forms of acid sites comparably, ultimately resulting in a slightly reduced ratio of strong to weak acids. In addition, the peak positions for the bifunctional nanocatalysts shift downward with decreasing temperature. The isomorphous replacement of the Al structure (strongly acidic sites) by Fe atoms may explain this phenomenon. The FT-IR band can identify the hydroxyl group in the Si(OH)Al groups at 3610 cm^{-1} , which is less intense in Fe-ZSM-5. Therefore, the results of FT-IR analysis are comparable to the decrease in density of the strong acid sites found in the bifunctional nanocatalyst. Moreover, the study by Yuan et al. (2002) showed that the Brønsted acidity of Fe OH Si was lower than that of Al OH Si. To further buttress this point, the acidity of [T]-ZSM-5 zeolite (T = B, Al, GA and Fe) was studied by Stave and Nicholas (1995) using local density functional theory. The study reported increased acidity in the order: $\text{B/Z5} < \text{Fe/Z5} < \text{Ga/Z5} < \text{Al/Z5}$. However, due to the relationship between Fe and the ZSM-5 structure during the doping of the parent catalyst, the acidity is reduced, confirming the results of Rostamizadeh

and Yaripour (2016). The reduction in acidity can be attributed to the blockage of the pores and the promoter's neutralization of the acidic surface sites (Sun et al., 2008). Since the effective ionic radius of the Fe ion is about 0.77 (Kustov et al., 1987), the promoter can penetrate the interior of the zeolite channels, which have a diameter of 5.5, and interact with the internal acid sites (Rostamizadeh and Yaripour, 2016).

Conversely, Ding et al. (2020) reported the total acidity does not change for unmodified and reduced 21 wt%Ni/Z5, respectively. However, when impregnated with Ni species, the total Brønsted acid reduced (from 451 to 243 mol.g⁻¹), while the total Lewis acid increased (168 to 345 mol.g⁻¹). The total Brønsted and Lewis acid variations were due to exchangeable cations, particularly Ni²⁺, replacing protons at Brønsted sites. This explains the variation in total Brønsted acidity (Huynh et al., 2014). After high-temperature treatment during the calcination or reduction process, Lewis acid could result from the dehydration of a protonated oxide bridge (Van Hooff and Roelofsen, 1991). Since the total area of desorption peaks increased for each catalyst after metal doping, the metals may be able to increase the total amount of acid.

Table 4-4. Effects of transition metals modification on strong and weak acid concentration

Catalysts	Peak			Acidity conc. (mmol NH ₃ /g)					REF
	Temp (°C)		H.T.	Total				SA/WA	
	L.T.	M.T.		Weak	Moderate	Strong	acidity		
HZSM-5	198	419	686	0.950	0.74	0.024	1.714	0.025	Present Study
0.5Co	189	425	667	1.050	0.690	0.015	1.755	0.014	
0.5Fe	194	436	678	1.010	0.790	0.017	1.817	0.017	
0.5Ni	190	435	688	1.060	0.690	0.014	1.764	0.013	
10Co	172	438	623	0.510	0.700	0.030	1.214	0.059	
10Fe	168	418	612	0.590	0.380	0.038	1.008	0.064	
10Ni	178	427	617	0.680	1.710	0.060	2.45	0.088	
ZSM-5	182	233	379	0.011	0.039	0.050	0.10	4.58	(Che et al., 2019d)
Zn/ZSM-5	194	255	365	0.023	0.024	0.053	0.10	2.29	
Fe/ZSM-5	182	236	385	0.011	0.039	0.050	0.10	4.40	
Ca/ZSM-5	193	254	341	0.021	0.051	0.029	0.10	1.41	
Ce/ZSM-5	193	252	383	0.024	0.035	0.041	0.10	1.68	
La/ZSM-5	220	304	444	0.023	0.054	0.023	0.10	1.03	
ZSM-5	207		394	0.42		0.20	0.61	0.50	

Cr/Z5	205	371	0.32	0.14	0.43	0.33	(Li et al., 2019b)
Cu/Z5	297	459	0.61	0.20	0.81	0.33	
Ga/Z5	207	364	0.43	0.21	0.62	0.50	
La/Z5	209	375	0.42	0.07	0.52	0.18	
Y/Z5	208	364	0.51	0.07	0.61	0.14	
Zn/Z5	213	375	0.53	0.06	0.61	0.12	
ZSM-5	207	394	0.40	0.16	0.56	0.40	
Ni/Z5	216	376	0.55	0.13	0.68	0.24	(Li et al., 2018b)
Y/Z5	208	385	0.52	0.07	0.59	0.13	
ZSM-5			0.53	0.53	1.06	1.00	
Fe/Z5			0.22	0.21	0.43	0.95	(Rostamizadeh and Yaripour, 2016)
0.1Fe/Z5			0.43	0.53	0.96	1.23	
0.5Fe/Z5			0.44	0.53	0.97	1.20	
1.0Fe/Z5			0.49	0.53	1.03	1.09	
HZSM-5 (Si/Al=200)			0.51	0.57	1.08	1.11	
Ag/Z5			0.43	0.53	0.96	1.23	(Rostamizadeh et al., 2018a)
Ir/Z5			0.52	0.69	1.21	1.32	
Ni/Z5			0.52	0.51	1.03	0.98	

LT – Low temperature; MT – Medium temperature; HT – High temperature; SA/WA – Strong acid/Weak acid

4.3.6 Effect of Transition Metal Modification on Catalytic Performance of ZSM-5 in Hydrocarbon Reaction

4.3.6.1 Effect of Transition Metal Modification on Ethanol Conversion

In the present study, ethanol conversion over HZSM-5 and metal-doped catalysts at T=350 °C and WHSV=12 h⁻¹ recorded >97 % conversion for all catalysts studied (Figure 4.6). Different types of hydrocarbons (HCs) are present in the products of the ZSM-5 before and after doping with transition metals. All catalysts showed a varying product distribution, including C₁-C₄, C₅-C₈, C₉-C₁₂, C₁₂+ and aromatics (benzene). Due to the reaction conditions employed, more liquid than gaseous products is found in the product distribution. This can be explained by the WHSV, which determines the duration of contact with the catalyst; for example, a higher

WHSV means a higher flow rate and, consequently, a shorter duration of contact with the catalyst. The less contact the hydrocarbon has with the catalyst, the fewer side reactions occur, ultimately leading to higher chain hydrocarbon selectivity (Arjah et al., 2017, Busto et al., 2011). However, while the unmodified catalyst did not show C₉-C₁₂ hydrocarbons in the product distribution, modified catalysts (mostly 0.5 wt% Co and Fe) showed appreciable amounts that decreased with increased metal concentration (from 0.5 to 10 wt%). The 0.5 wt%Fe catalysts recorded the lowest gaseous products (C₁-C₄), which can be attributed to the conversion of these products into liquid HCs (mainly C₉-C₁₂). Moreover, 0.5 wt%Fe was the most selective for C₉-C₁₂ HCs compared to the other catalysts, we attribute this to the large surface area that allows for better reaction and product distribution. The transition metal-doped (0.5 wt% Ni and 10 wt% Co and Fe) ZSM-5 favoured benzene production compared to other catalysts. The enhanced activity of modified catalysts can be due to the weak crystal framework of transition metal oxides, which can increase oxygen vacancy, leading to improved catalytic activity (Thirupathi and Smirniotis, 2011, Trinh et al., 2015). This agrees with the study by Persson et al. (2019b), which showed that metal modification improved the amount of aromatic HCs in the liquid product, especially monoaromatic HCs (MAH) and naphthalenes, from 59 to 83%. While Ni also favoured naphthalenes, Fe primarily improved the specificity of MAHs compared to unmodified ZSM-5 (Persson et al., 2019b). To further bolster the effect of transition metal, Huang et al. (2007) reported that adding Ni, Fe, or Co has little effect on catalytic performance but alters the product distribution. Despite an increase in ethylbenzene, the content of non-aromatics and aromatics increased relative to Fe/HZSM while Ni increased especially the aromatic content.

Among the catalysts doped with 0.5 wt%, Ni/HZSM-5 exhibited the highest selectivity for aromatics compared to the other catalysts. This can be attributed to modifying the acid sites by incorporating Ni metal species, which significantly increased the concentration of weak acid and total acid sites. This increased concentration of weak acid sites in the Ni-doped catalyst enhances the selective formation of aromatics through the formation of active sites that favour aromatisation reactions, resulting in higher aromatic selectivity compared to Co and Fe-doped catalysts that favour C₉-C₁₂ HCs. Increased total and weak acid sites promote aromatic formation by aiding aromatisation during the conversion of lower alcohols to hydrocarbons (Yang et al., 2019, Li et al., 2020a). However, a decrease in aromatic selectivity was recorded with the high (10 wt%) Ni loading. This is due to the significant presence of strong acid sites

in the catalyst and the small number of weak acid sites. Strong acid sites promote undesirable side reactions such as cracking and shortening the hydrocarbon chain, which competes with aromatics formation. The increase in aromatics selectivity observed with 10 wt% Co- and Fe-doped HZSM-5 catalysts can be attributed to a slight increase in the moderate and strong acid sites compared to Ni/HZSM-5, which has a significant increase in these acid sites. Compared to the unmodified catalysts, the appreciable total acid sites in the Co- and Fe-doped catalysts provide more active sites for converting oxygenated intermediates to olefins, followed by cyclisation and aromatisation to produce aromatics. A similar trend has already been reported (Yang et al., 2019, Wang et al., 2019a). Hence, the presence of metal dopants enhances the catalytic activity of the zeolite, resulting in higher yields of aromatics.

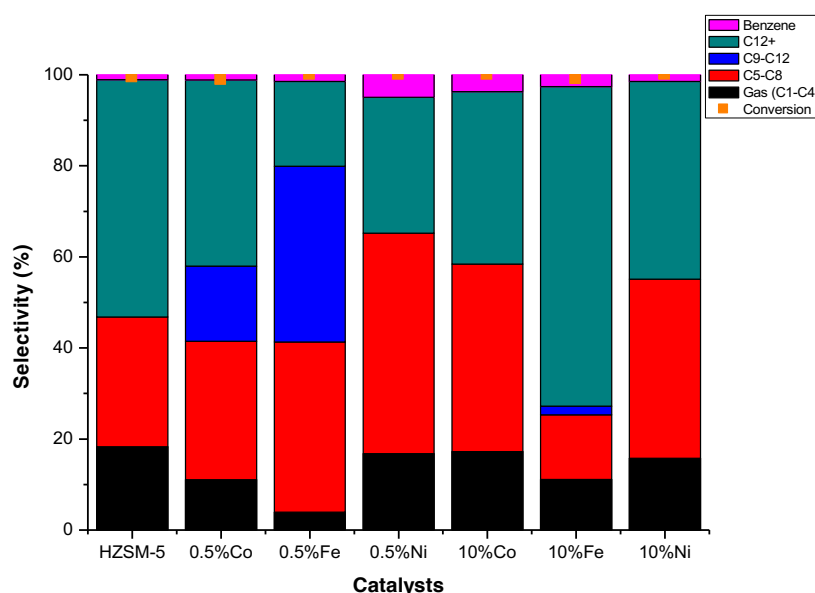


Figure 4-6. Product distribution over pure and modified HZSM-5 for ethanol-to-hydrocarbon (ETH) reaction. Reaction conditions: 350 °C; WHSV=12 h⁻¹

For metal-doped ZSM-5 catalysts, the improved performance of the doped catalysts can be attributed to the presence of metal species that actively participate in the hydrocarbon (HC) reaction. When metal species are introduced into the ZSM-5 framework, they alter the properties of the catalyst, as described in the previous sections, and the catalytic performance. The interaction between the metal species and the zeolite framework leads to synergistic effects, where the combined properties of the metal and zeolite result in improved catalytic performance, as evident in product distribution (Figure 4.6). Compared

to unmodified catalysts, the metal species (Co^{2+} , Fe^{3+} , and Ni^{2+}) present in the metal-doped catalysts play a crucial role in promoting the formation of intermediates. These intermediates act as Lewis acid sites during the HC reaction. The metal species actively enhance these Lewis acid sites to improve the dehydration of ethanol, leading to increased ethylene production. The availability of more ethylene, in turn, promotes secondary reactions, leading to a broader production distribution. In contrast to the parent catalyst, metal doping tends to change the parent catalyst's acid-base properties, increasing the selectivity of liquid hydrocarbon and decreasing the yield of gaseous hydrocarbon, especially for the catalysts doped with 0.5 wt% metal. While the yield of aromatics and C_9 - C_{12} was very low with the unmodified catalyst, metal species provided additional sites for hydrocarbon activation, acting as hydrogenation/dehydrogenation catalysts and promoting hydrocarbon activation by breaking carbon-carbon or carbon-hydrogen bonds. This leads to increased reactivity and the formation of the desired products, including aromatics and C_9 - C_{12} hydrocarbons. However, it should be noted that metal doping can also increase the likelihood of coke deposition and subsequent catalyst deactivation. The formation of coke is primarily caused by processes such as oligomerisation, dehydrogenation, aromatisation, and hydrogen transfer, all of which are mainly connected to the strength and quantity of acid sites on the catalyst's surface (Akhoundzadeh et al., 2018).

The particle size of metal-doped ZSM-5 catalysts plays a crucial role in shaping the product distribution during ethanol conversion. This influence arises from its effect on several critical factors, including catalyst surface area, acidity, metal dispersion, and reactant accessibility. Upon examining the catalyst evaluation results, it is clear that smaller particles can favour greater surface area, better accessibility to active sites, and cracking of hydrocarbons. These conditions favour the production of lighter hydrocarbons in the range of C_1 - C_4 and aromatics. Conversely, as particle size increases (from 4.85 to 5.74 and further to 6.33 μm), as observed with 0.5 wt% metal-doped catalysts (Co, Fe, and Ni), the propensity to form lighter hydrocarbons decreases. In contrast, larger particles tend to promote the formation of heavier hydrocarbon compounds. This effect is evident when 10 wt% Co-, Ni, and Fe-doped catalysts are studied, which yield substantial amounts of long-chain hydrocarbons compared to 0.5 wt% metal-doped catalysts with smaller particle sizes. Consistent with the result of this study, Kumagai et al. (2014) reported a corresponding increase in benzene and liquid hydrocarbon

production with decreasing particle size, suggesting that smaller particle size is beneficial for this process in three size ranges: $> 250\ \mu\text{m}$, $150 - 250\ \mu\text{m}$, and $< 150\ \mu\text{m}$. In the study by Rioux et al. (2008), small particles were found to have higher activity in the dehydrogenation process and lower apparent activation energies compared to their larger counterparts. The ability to regulate selectivity is related to the change in particle size, a phenomenon due to the structural sensitivity of both reactions occurring simultaneously in the temperature range favourable for hydrogenation and dehydrogenation. It's worth emphasizing that the specific outcomes can vary depending on factors such as the catalyst composition, reaction conditions, and the nature of metal doping.

The mechanism for converting ETH conversion is very similar to the process for transforming methanol-to-hydrocarbons. However, the direct dehydration of ethanol to produce ethylene eliminates the need for an indirect carbon–carbon coupling pathway, including the hydrocarbon pool mechanism. In the present study, based on the product distribution, it is believed that ethanol was first dehydrated to generate ethylene and diethyl ether (DEE) by a concerted mechanism. DEE can be further cracked to produce ethylene, providing an alternative reaction pathway. Ethylene can undergo dehydrogenation to form ethyl radicals participating in secondary reaction pathways. Aromatisation reactions involve the cyclisation of carbocation intermediates, forming aromatic hydrocarbons such as benzene. ZSM-5 catalysts also facilitate the formation of long-chain hydrocarbons (C_5^+) through oligomerization reactions. These HCs are usually formed through secondary carbocation reactions or additional transformations of the intermediates generated during aromatisation (Sun and Wang, 2014, Kwak et al., 2011, Roy et al., 2012, Janik et al., 2009). The incorporation of metal species (Co^{2+} , Fe^{3+} and Ni^{2+}) enhanced catalytic performance by promoting the formation of intermediates and acting as Lewis acid sites during the reaction, leading to increased ethylene synthesis and broader product distribution. The study by Niu et al. (2020b) also reported a similar pathway. These processes can trigger coke formation on the catalyst's surface and lead to its deactivation. The generation of coke is primarily caused by processes such as oligomerization, dehydrogenation, aromatization, and hydrogen transfer, all of which are mainly connected to the strength and quantity of acid sites on the catalyst's surface (Akhoundzadeh et al., 2018).

The study by Ji et al. (2018) showed that the aromatization products using HZSM-5 as a catalyst comprise 40% non-aromatic HCs, while the synthesis of benzene, toluene and xylene (BTX) increases in turn as 2%, 13% and 21% respectively. However, the products from La and Cu-

doped HZSM-5 had up to 6% and 1% higher content of non-aromatic hydrocarbons than the original catalyst. In comparison, the components of BTX are 1%, 7%, and 3% higher than the unmodified catalyst, respectively, and the aromatic heavier than C₉ is slightly less than that of HZSM-5. In addition, the toluene content of Cu/ZSM-5 is only 0.9% lower, while the non-aromatic HCs in the products of the Zn/ZSM-5 are 12% lower than that of HZSM-5 and the other constituents are identical to those of the original catalyst. The studies by Li et al. (2019b) and Conte et al. (2012) on methanol conversion also showed that transition metals modified ZSM-5 improved the catalytic activity, which increased paraffin production compared to unmodified catalyst. However, there is no significant changes in BTX production and methanol conversion efficiency with the introduction of transition metals. Conversely, ethanol conversion showed that transition metal modification decreased paraffin synthesis while Cu- and Co-doped catalysts had the lowest BTX products, as reported by Liu et al. (2020a). Moreover, all catalysts showed significant ethanol conversion. The result showed that loading ZSM-5 with transition metals improved the product selectivity, HC yield and overall catalyst performance (Ji et al., 2018). However, the performance of ZSM-5 catalysts modified with transition metals depends on the nature and concentration of the transition metal in the ZSM-5 catalyst support and the operating conditions used for the reaction, which affect product selectivity and distribution.

4.3.6.2 *Effect of Transition Metal Modification on Stability, Coking and Deactivation of ZSM-5*

A well-known method for promoting the synthesis and performance of certain catalysts is using metal-doped zeolites in catalytic processes. Rapid deactivation of such catalysts by coke formation is among their significant technical problems. The thermal stability of the catalyst used in this study was evaluated after ethanol conversion. The initial weight loss under nitrogen flow (from T=0-200 °C) was not considered in the coke calculation because the weight loss at this stage was attributed to the removal of absorbed water and other volatile compounds in the spent catalysts (Ahmed et al., 2011, Wang and Manos, 2007). The pure (unused) HZSM-5 and the used HZSM-5 are denoted as HZSM-5 (pure) and HZSM-5 (spent). From T=200-800°C, the gas flow was switched to air while maintaining the same flow rate. The weight loss at this stage is due to the decoking process (Figure 4.7), and three stages of decoking were identified: stage one involves the burning of soft coke at T=200-400 °C, which is a slow process. The weight loss at this stage showed that 0.5% doped catalysts had the lowest percentage weight

loss at 0.88, 0.59, and 1.07 wt% for 0.5% Fe, Ni, and Co, respectively, compared to 10% metal loaded HZSM-5 catalyst, which had a weight loss >of 1.4 wt% at this temperature. A temperature rise of 400-600 °C triggers the second stage of coke decomposition, which consists of burning hard coke. Significant weight loss is observed in this stage due to the higher reaction rate, with 0.5% Ni and Co showing the lowest weight loss at 2.8 wt% and 2.3 wt%, respectively, compared to 0.5% Fe (4.12 wt%) and the unmodified catalyst (3.50 wt%). At a higher metal doping of 10%, a high weight loss was observed, especially for catalysts doped with Fe (8.70 wt%) and Ni (6.33 wt%), in contrast to Co (3.86 wt%), which showed appreciable stability with the lowest coke amount at this stage. A decrease in the amount of coke was observed in stage 3 from 600-800 °C, which may be attributed to the non-volatile or laid coke (Ahmed et al., 2011). The catalyst loaded with 10 % metal showed the lowest weight loss in this stage. It is obvious that the pure catalyst had the lowest weight loss (1.62 wt%) since it was not subjected to any reaction, so no coke was deposited, and the weight loss can be attributed to the impurities or other organic compounds. The increase in total coke deposition is in the order HZSM-5 (pure) (1.62) < 0.5Co (4.56) < 0.5Ni (4.59) < 10Co (6.20) < HZSM-5 (spent) (6.74) < 0.5Fe (6.77) < 10Ni (8.57) < 10Fe (12.06) wt% and results show that metal loading increasing coke deposition which increases with increased concentration. Coke deposition is closely related to the acidity of the catalyst, as shown by the observation that higher metal doping, leading to increased strong acid sites, is associated with greater coke deposition. This trend is particularly evident for catalysts modified with 10 wt% (Co, Fe, and Ni), which recorded a significant coke formation. In contrast, catalysts with lower metal doping (0.5 wt%), have a lower level of strong acid sites, resulting in reduced coke deposition. This is consistent with previous studies (Persson et al., 2019b, Masiero et al., 2009, Zhou et al., 2017).

In agreement with the present study, Xu et al. (2012) reported that Fe influences the ZSM-5 by forming carbonaceous deposits. However, the amounts of coke discovered by TGA increase with an increase in metal (Fe) concentration, do not confirm the earlier result by Weckhuysen et al. (1998) that coke formation is prevented by metal introduction. Although the amount of coke formed in the subsequently consumed metal-doped sample is much greater than that produced with the unmodified catalyst (5 wt%Mo/Z5), the catalyst doped with 1.0 wt% Fe shows the best consistent performance in the synthesis of benzene over the limited time. The catalysts with 0.3 wt% and 0.5 wt% Fe/(5 wt%Mo/Z5) demonstrated better performance and stability than the pure catalyst and showed that the coke generation is not reduced by adding

Fe Xu et al. (2012). The study by Persson et al. (2019b) revealed that metal modification promotes coke formation, primarily due to increased concentration of strong acid sites. In addition, the strength of the acid sites affects how much coking occurs. The coke deposition increased from 4 wt% for HZSM-5 to a maximum of 7 wt% for Fe/ZSM-5. While metal modification increases the catalyst's susceptibility to coking, it also accelerates coke oxidation while lowering the catalyst's regeneration temperature. Unfortunately, "hot spots", i.e., localized areas of elevated temperature, can cause the catalyst to be permanently damaged by processes such as sintering and dealumination during regeneration (Satyanarayana et al., 2016, Cerqueira et al., 2008). The type and amount of coke affect the regeneration parameters and, consequently, the degree of permanent catalyst deactivation (Shao et al., 2017, Guisnet and Magnoux, 2001). Previous studies have shown conflicting results on the effect of Ni on coke deposition in the case of Ni doping (Iliopoulou et al., 2012, Jiang et al., 2018). Therefore, further studies are needed to evaluate and compare these properties.

According to the thermogravimetric analysis (TGA) studies by Persson et al. (2019b), the amount of coke formed on the catalysts coincides with the strength of the acid sites. Thus, the findings revealed that coke production increases with the strength of the acid sites. This could be due to more Brønsted acid sites, which increase the cracking processes within the catalysts and the coke formation rate (Iliopoulou et al., 2012, Jiang et al., 2018, Foster et al., 2012). However, compared to Fe/ZSM-5, the co-modified catalyst has a lesser coke formation. In addition, no patterns were observed between promoting certain chemicals and coke production (Persson et al., 2019b).

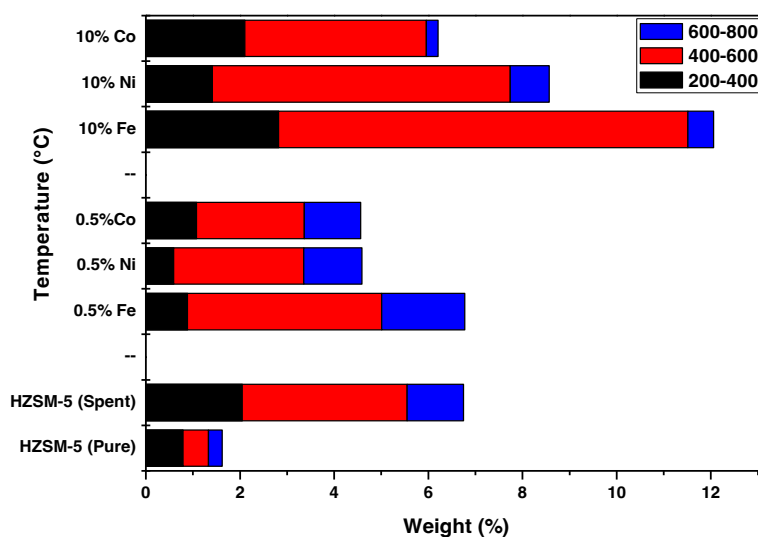


Figure 4-7. Coke deposition on spent catalysts: *Effect of transition metal concentration on coke formation*

4.4 Conclusion and Outlook

Zeolites are considered the preferred porous materials for heterogeneous catalysis because of Brønsted acid sites on their surfaces. Modifying transition metals on ZSM-5 has been shown to alter the physicochemical properties and catalytic activities. The results of this study show that ZSM-5 modified with transition metals does not alter the characteristic peaks of the MFI framework of the ZSM-5 zeolite, but decreases the crystallinity of pure ZSM-5, as the presence of metal oxide peaks becomes visible at elevated metal concentration. The metal-modified ZSM-5 retained the characteristic functional groups of ZSM-5, but the vibrational bands decreased with increasing metal concentration. The particle size of the catalyst increases with increasing metal concentration while the prismatic crystal shape remains unaltered. Surface area, total pore size, and pore diameter decreased with increasing metal concentration. While some metals increase the acid sites of the catalyst, others reduce the number of acid sites. This can be attributed to the neutralization of some parts of the Brønsted sites by forming additional Lewis acid sites. Consequently, the distribution of metal elements and acid sites on the catalysts in hydrocarbon conversion processes determines the performance and specificity of the catalysts. When metallic transition components are introduced on top of zeolite structures, it promotes the function of zeolite as a bifunctional catalyst, which improves catalytic performance, product selectivity and distribution. Due to this development, the use of surface

groups in catalytic processes has gained considerable importance. Low metal doping (0.5 wt%) showed optimal catalytic performance with broader product distribution and low coke deposition compared to high metal-doped catalysts. While the Ni-doped catalyst favours aromatics and C₅-C₉, Fe and Co-doped catalysts preferred C₉-C₁₂ and C₁₂+ HCs, respectively.

The metal doping dramatically accelerates the coke yield due to increased acid sites, unlike HZSM-5. In the temperature range of 400-600°C, substantial weight loss occurs due to the burning of hard coke. Among the catalysts examined, those containing 0.5% Ni and Co result in minimal weight losses of 2.8 wt% and 2.3 wt%, respectively. In contrast, the 0.5% Fe catalyst and the unmodified catalyst demonstrate higher weight losses, registering at 4.12 wt% and 3.50 wt%, respectively. The acid site strength was found to affect the coke formation on the catalyst. However, the metal modification accelerates the oxidation of coke. It reduces the temperature at which regeneration occurs, potentially reducing the severity of irrevocable catalyst deactivation. The higher coke formation was not due to higher catalytic activity during the catalytic process. Rather, acid site strength and appropriate metal selection are required to reduce coke formation during catalytic processes. Coking is reversible, and the combustion of a coke can be used to replenish the catalyst. However, there is a paucity of information on how doping catalysts with metals affects coking properties, including formation rate, content, and regenerability. Therefore, coking is a crucial factor in developing industrial application catalysts. These catalysts should have sufficient capacity to achieve the desired result and have a lower deactivation rate. Engineers must understand the nature and electronic state of the metals and their distribution on zeolite surfaces to design catalysts that will produce the required products under the conditions prevailing in the industry. It should be noted that incorporating appropriate metal on catalysts can reduce secondary reactions and increase the selectivity of target products.

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CHAPTER 5

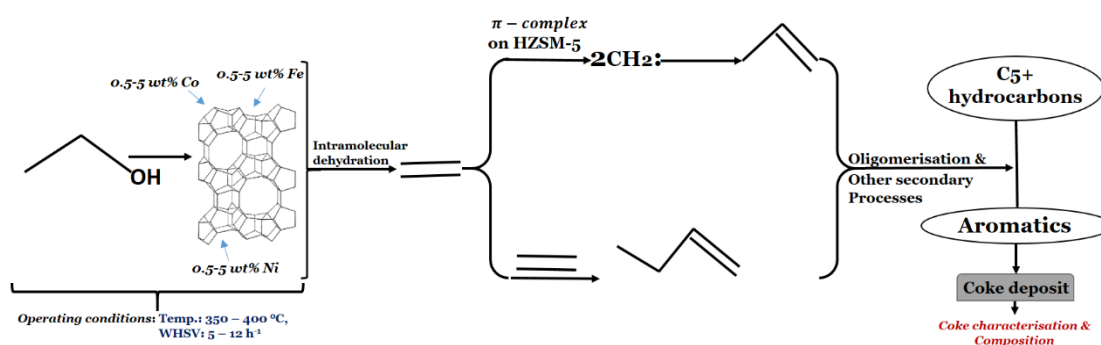
Ethanol Conversion to Liquid Hydrocarbons over Transition Metal-doped HZSM-5: Effect of Operating Conditions and Catalyst Modifications on Product Distribution and Coking

Abstract

This chapter investigates the effects of incorporating transition metals in ZSM-5 and operating conditions on the ethanol-to-hydrocarbon (ETH) conversion. The study involved the synthesis of HZSM-5 zeolite catalysts doped with different amounts (0.5-5 wt%) of cobalt, iron, and nickel. The effects of metal-doped HZSM-5 on hydrocarbon product selectivity were investigated with respect to ETH as a function of reaction temperature and weight hourly space velocity (WHSV). The results indicated that Co, Fe, and Ni-doped catalysts showed wider product distribution and increased selectivity to aromatics, C₅-C₈, and C₉-C₁₂ hydrocarbons compared to non-promoted catalysts. The thermogravimetric analysis of spent catalysis revealed that the concentration of metal species in the catalyst influenced coke deposition, which increased with increasing metal concentration. Carbon deposition also increased with higher reaction temperature and WHSV. The study concludes that the performance of the catalysts depends on specific operating parameters and the concentration of transition metals, emphasising the importance of careful catalyst formulation and process optimisation for specific applications.

Keywords: Catalyst, Coke deposition, Ethanol, HZSM-5, Transition metals

Graphical Abstract



5.1 Introduction

The increasing public awareness about environmental issues and the recent advancements in the utilisation of crude oil has resulted in the need to produce fuels and petrochemicals from

renewable sources (Mores et al., 2011). The synthesis of fuels and chemicals is expected to shift from fossil feedstock to sustainable procedures that use renewable energy sources. Biomass resources like lignocellulose have received significant interest due to their environmental friendliness, safety, and renewability (Yiin et al., 2018, Akhmedov et al., 2017). Recent technological advancements have greatly improved the process of producing ethanol from biomass (Yuan and Eden, 2016, Hu et al., 2020). According to the American Renewable Fuel Association (RFA), employing bioethanol as a feedstock to synthesise light olefins (ETO) can significantly reduce net greenhouse gas emissions. Bioethanol is expected to be synthesised on a large scale and commercially applied after 2025 (Liu et al., 2013b, Liu et al., 2015b, Liu et al., 2015c). As a result, a significant focus has been on the catalytic conversion of alcohol, which can easily provide valuable chemical building blocks, including ethylene and propylene (Mores et al., 2011).

Due to its exceptional shape-specificity, catalytic activity and adsorption function, HZSM-5 is commonly utilised in industrial catalysis (Fathi et al., 2014, Meng et al., 2020, Bi et al., 2011, Ramasamy and Wang, 2014, Van der Borgh et al., 2015b, Song et al., 2009b). In particular, the ETO reaction catalyst research focuses on HZSM-5 (Ramasamy and Wang, 2014, Liu, 2018). The acidic sites present in the ZSM-5 zeolite catalyst facilitate the bioethanol dehydration process. Initially, bioethanol undergoes dehydration to produce ethylene as the primary reaction. Subsequently, ethylene is further transformed through oligomerisation, leading to the formation of various other compounds. However, elevated steam temperatures can cause the dealumination of the zeolite's pore structure, resulting in its permanent deactivation and rapid activity loss during the reaction. Nonetheless, if ethylene goes through deep polymerisation due to strong acids, macromolecular alkanes or aromatics may be produced, which can ultimately lead to the deposition of coke that may clog the pores of the zeolite. Modifying HZSM-5 is a viable technique to enhance the catalyst's stability to prevent dealumination and coke formation during the ethanol-to-hydrocarbon (ETH) reaction. Non-metallic phosphorus and transition metal are potentially useful components for ZSM-5 modification, as they can enhance product selectivity and distribution (Furumoto et al., 2011, Huangfu et al., 2016, Takahashi et al., 2012a).

Numerous methods have been applied to improve the specificity towards desired products in ZSM-5 zeolites with the MFI structure. These include adjusting the acidity (Björger et al., 2008, Gayubo et al., 1996), reducing crystal size (Rownaghi and Hedlund, 2011, Jang et al.,

2012), modifying the pore structure (Rownaghi et al., 2012, Olsbye et al., 2012), and incorporating heteroatoms (Liu et al., 2015a, Kaarsholm et al., 2007) such as alkali metals (Lin et al., 1991), alkaline earth metals (Goto et al., 2010a), transition metals (Kaur et al., 2013), non-metals (mainly phosphorus) (Ramesh et al., 2010), and semi-metals (primarily boron) (Coudurier et al., 1987). The incorporation of heteroatoms into the zeolite framework can significantly alter the catalyst's acidity. ZSM-5 can also be post-treated by introducing protons and extra-framework cations (usually metal) to create acid/base or redox sites. Metal doping of zeolites is typically accomplished through ion-exchange or impregnation (Kinger et al., 2000). Many metals have been studied as promoters in ZSM-5 type zeolites for ethanol transformation to hydrocarbons. However, the impact of the promoter on product distribution varies depending on the metal used. Metals like chromium, palladium, and yttrium have also been added as promoters to MFI zeolites to manufacture light olefins (Lee et al., 2013, Liu et al., 2016, Lappas et al., 2002). Nevertheless, the synthesis of zeolite catalysts using these methods is challenging due to low micro-scale controllability and the sensitivity of zeolite crystals to cation solution pH.

Several studies, including those by Calsavara et al. (Calsavara et al., 2008b), Phung et al. (Phung et al., 2015d), Abdulrazzaq et al. (Abdulrazzaq and Schwartz, 2019), Dowson et al. (Dowson et al., 2013), Taifan et al. (Taifan et al., 2017), and Subramaniam et al. (Subramaniam et al., 2020), have reported on the catalytic conversion of ethanol. Additionally, the incorporation of metal promoters such as Pd, Ag, Mn, Fe, Cu, Sm, Ni, and Yb into the zeolite framework for improved catalytic performance has been studied (Taifan et al., 2017, Li et al., 2019b, Singh and Ekhe, 2015, Chen et al., 2016). While some of these studies utilised commercially available ZSM-5 catalysts to investigate the effect of operating parameters, others focused on synthesising specific products, including olefins (ethylene, butadiene, propylene) or aromatics from ethanol conversion. Moreover, while some studies considered only a single metal doping, others examined the effect of more than one metal without varying the content of these metals or the effect of different metal doping (and concentration) on coke formation.

This study aims to study the effect of operating parameters on ethanol conversion into hydrocarbons. Specifically, the study seeks to achieve the following objectives: to synthesise a novel HZSM-5 (Si/Al = 40) catalysts modified with varying concentrations of transition metals, Co, Fe, and Ni (0.5-5 wt%), characterise the catalysts, conduct catalyst evaluation tests

at different temperatures (350 °C and 400 °C) and weight hourly space velocities (WHSV) of 5-12 h⁻¹, and perform a thermal stability and coke deposition study on the spent catalyst. Through these objectives, the study hopes to provide insights into the performance of novel, non-commercial HZSM-5 zeolite catalysts doped with transition metals in converting ethanol into hydrocarbons.

5.2 Materials and Methods

The following chemicals were used for the synthesis of the parent zeolites used for this study: (Na₂O)SiO₂·H₂O, Al₂(SO₄)₃·18H₂O, C₁₂H₂₈BrN, NaOH (97%), H₂SO₄ (98% concentration), NH₄NO₃, and precursors of transition metals doping: Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O and Fe₂(NO₃)₂·18H₂O, while C₂H₅OH served as the conversion feedstock. Each of the compounds was of analytical grade and was obtained from Sigma-Aldrich. For catalyst synthesis, a hydrothermal reactor (HTR) made of stainless steel and lined with Teflon of 200 ml and a working volume of 150 ml was employed. Catalysts were synthesised and characterised according to *Section 3.2.2* while the TGA was conducted according to the method described in *Section 4.2*.

The catalytic activity of pure and modified catalysts was tested based on their efficiency and product distribution in ETH conversion. The study was conducted at two different temperatures, namely 350 and 400 °C, and weight hourly space velocities (WHSV) of 5-12 h⁻¹. Both glass beads and glass wool were used in the experiments to provide suitable structural support for the catalyst bed. Ethanol was utilised as feedstock, and after the catalyst was activated at 400 °C, an HPLC pump was used to introduce the low alcohols into the reactor. The product selectivity (S_i) and conversion (X) were determined as per Sun et al. (2020).

5.3 Results and Discussions

5.3.1 Catalytic Evaluation of Catalysts in Ethanol Conversion

The catalytic performance of the synthesised material as a catalyst for the conversion of ethanol to hydrocarbon (ETH) was evaluated at different temperatures and WHSV. To investigate the effects of operating conditions in ethanol conversion over HZSM-5 doped with transition metals (Ni, Fe and Co), the weight hourly space velocity (WHSV) was varied from 0.5-12 h⁻¹ at temperatures of 350 and 400 °C. The products obtained from ethanol conversion over the studied catalysts consist of gases (C₁-C₄), C₅-C₈, aromatics (benzene) and other hydrocarbons (HC) with higher carbon numbers (C₁₂+). Figure 5.1 shows the conversion of ethanol (XEOH)

and the hydrocarbon product (SHC) selectivity in product distribution as a function of the different catalysts tested. All samples showed substantial ethanol conversion of > 97% and a wide range of product distributions.

All Ni/HZSM-5 catalysts recorded > 97% ethanol conversion at all operating conditions studied and showed a broad product distribution consisting mainly of C₁-C₄, aromatics, higher carbon numbers (C₁₂⁺) and C₉-C₁₂ for some Ni-doped catalysts (Figures 5.1a & b). Ni-modified catalysts mainly promoted the production of gaseous hydrocarbons (C₁-C₄) at a (low) WHSV of 5 h⁻¹ and T=350 °C, with the unmodified catalyst showing the highest selectivity (85 %) for gaseous hydrocarbons compared to Ni-modified catalysts (70 %, average), which show low selectivity for aromatic (benzene). This can be attributed to the long reaction time (time-on-stream), favouring cracking (Liu et al., 2020b). However, the selectivity shifts to the liquid hydrocarbons with an increase in WHSV to 7 h⁻¹ at the same T=350 °C, triggering a decrease in C₁-C₄ selectivity to 65 % for the unmodified catalyst, which also recorded the highest (liquid HC) selectivity, particularly for the long-chain hydrocarbons, C₁₂⁺ (67.8 %). The low Ni doping, 0.5%Ni and 1%Ni showed the lowest selectivity for gaseous hydrocarbons with ~1% and ~25 % while promoting C₅⁺ products, mainly C₉-C₁₂, with 49.9 and 60.3% selectivity, respectively. Furthermore, 5%Ni showed considerable selectivity towards benzene (2.2 %) and C₅-C₈ (44.8 %) at 7h-1 and 350 °C compared to other Ni-catalysts. Further increasing the WHSV to 12 h⁻¹ resulted in a drastic decrease in selectivity for gaseous and C₉-C₁₂ HCs selectivity with a simultaneous increase in selectivity for benzene and long-chain hydrocarbons. Compared to unmodified catalysts, 5%Ni-doped catalysts showed considerable selectivity for C₅-C₈, C₉-C₁₂ and benzene with 61.7, 8.6 and 4.3%, respectively. While 0.5% Ni showed the highest selectivity (5%) for benzene, 1%Ni favoured the production of long-chain HCs (90.9%). This agrees with the study by Nekhaev and Maksimov (2021) which achieved the highest selectivity to aromatics with Ni-doped catalysts. However, increasing the temperature to 400 °C decreased selectivity to gaseous products, C₉-C₁₂ and C₁₂⁺ HCs at 5, 7 and 12 h⁻¹ respectively, this can be attributed to enhanced dehydration of ethanol and subsequent oligomerisation of ethylene into HCs (Kamsuwan et al., 2017, Sarve et al., 2022). The decrease in gaseous HC selectivity at 400°C can be attributed to a shift in the reaction pathway, leading to increased production of C₅-C₈ HCs, ranging from 20 % to 49 % and 51 % to 76 % at 5 and 12 h⁻¹ respectively. C₁₂⁺ HCs increased to 10-26 % for all catalysts at WHSV of 7 h⁻¹. While the 0.5% Ni catalyst showed considerable selectivity for the production of

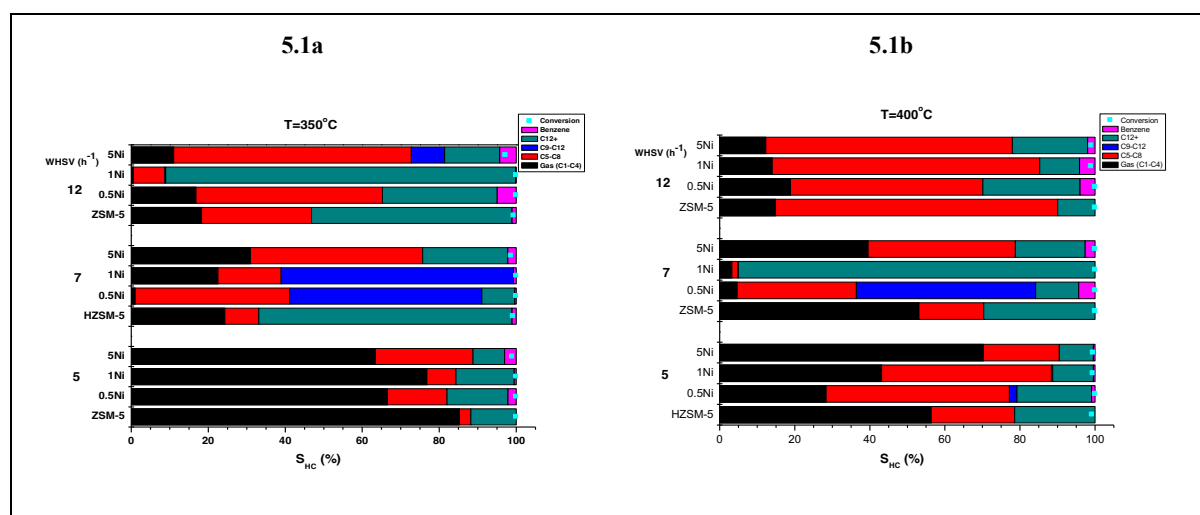
aromatic hydrocarbons (benzene) (4.4%) and C₉-C₁₂ (47.8%) at 7 h⁻¹, 1% Ni and 5% Ni favoured C₁₂⁺ (95.0%) and C₅-C₈ (39.2%) at 7 h⁻¹ compared to unmodified ZSM-5, which showed significant C₅-C₈ selectivity of 75.1% at 12 h⁻¹. Ni-doped catalysts showed appreciable selectivity towards aromatics and liquid HCs compared to parent HZSM-5 (Liu et al., 2020b, Kariim et al., 2022).

Fe-doped catalysts showed > 98% ethanol conversion for all reactions. The product distribution favoured gaseous products, with the unmodified catalyst exhibiting the highest (85.2%) C₁-C₄ selectivity compared to Fe-doped catalysts, while 0.5, 1 and 5% Fe showed 41.8%, 2.5%, 3.0% selectivity of C₅-C₈, C₉-C₁₂ and benzene, respectively, at 5 h⁻¹ and T=350 °C (Figures 5.1c & d). When the WSHV was increased to 7 h⁻¹ while maintaining the same temperature, a decrease in gaseous HC selectivity was observed, which was attributed to the high WHSV favouring the production of liquid HCs. This leads to increased selectivity towards C₅-C₈ (43.0%), C₉-C₁₂ (2.5%), benzene (5.0%) and long-chain hydrocarbons (C₁₂⁺) (65.8%) due to the performance of 5%Fe, 1%Fe, 0.5%Fe and HZSM-5, respectively. However, a further increase in WHSV at 350 °C favours the increase of liquid HCs, including C₅-C₈ and C₉-C₁₂, leading to a decrease in selectivity toward C₁-C₄ and C₁₂⁺ due to reduced time-on-stream, promoting C₅⁺ HCs. A similar trend was reported by (Liu et al., 2020b). Compared to the WHSV of 7 h⁻¹, 0.5% Fe showed increased C₉-C₁₂ selectivity from 0% to 33.6%, while benzene and C₅-C₈ HC production increased by 3.2 and 26.9% using 1% and 5% Fe/HZSM-5 catalysts, respectively, with a 13.7% decrease in C₁₂⁺ selectivity (for the unmodified catalyst) at 12 h⁻¹. It appears that increasing the reaction temperature to 400 °C resulted in a decline in gaseous and aromatic HC selectivity at a WHSV of 5 h⁻¹ but an increase in C₅-C₈ and C₁₂⁺ HC production, particularly for the Fe-doped catalysts due to the secondary oligomerisation reaction which promotes liquid HC synthesis (Sarve et al., 2022). However, there were no other significant changes observed at this WHSV. At higher WHSVs of 7 and 12 h⁻¹, the selectivity to C₅-C₈ and C₁₂⁺ was still maintained, with some minimal variation attributed to the increased selectivity to C₉-C₁₂. In addition, a WHSV of 7 h⁻¹ favoured benzene selectivity, resulting in an increase from 5% (at 350 °C) to 15.5% (at 400 °C) using the 0.5%Fe catalyst. The benzene production increased to 50.4% with the 1% Fe catalyst as the WHSV was increased to 12 h⁻¹. The product specificity changed significantly with the change in operating conditions. This can be attributed to deactivation by coke deposition and hydrothermal stability (Aguayo et al., 2002a).

The Co-doped catalyst showed a similar trend to its counterparts (Fe and Ni-doped catalysts) at a low WHSV of 5 h⁻¹, with considerable selectivity to gaseous HCs at 58-85% and 55-68% with unmodified and 5%Co catalysts recording the highest C1-C4 HCs at 350 and 400 °C respectively (Figures 5.1e & f). At a temperature of 350 °C and WHSV of 5 h⁻¹, product selectivity favours C₅-C₈ and long-chain hydrocarbons (C₁₂+), with considerable amounts recorded at 40.7% and 20.0%, respectively, for the 0.5% and 5% loadings, while 1%Co recorded a 4.5% benzene production. An increase in WHSV to 7 h⁻¹ at the same temperature shifted the selectivity to C₅-C₈, benzene, and long-chain hydrocarbons with a reduction in gaseous products. While unmodified HZSM-5 showed significant selectivity to C₁₂+ hydrocarbons (65.8%), catalysts loaded with Co facilitated the production of C₅-C₈ and benzene with 0.5%Co recording the highest selectivity, 59.3% and 3.3%, respectively. Further, an increase in WHSV to 12 h⁻¹ while maintaining the same temperature of 350 °C showed a drastic reduction in gaseous hydrocarbon production, promoting more liquid hydrocarbons. More aromatics are produced at this operating condition, increasing (1.1% - 5.7%) with increasing Co concentration, with the unmodified catalyst recording the lowest selectivity. 0.5%Co showed appreciable selectivity to C₉-C₁₂ compared to other doped catalysts, while 1%Co and unmodified ZSM-5 favour C₅-C₈ and C₁₂+ hydrocarbons. At a higher temperature of 400 °C and WHSV of 5 h⁻¹, a similar trend was observed at 350 °C, with product distribution shifting to C₅-C₈, while 1% Co maintained considerable benzene selectivity at 3.8%. In addition, 0.5%Co recorded the highest selectivity to C₅-C₈ and benzene (75% and 4.2%, respectively) at 7 h⁻¹, the same temperature, as 1%Co recorded C₉-C₁₂ and C₁₂+ hydrocarbons of 6.2% and 35.9%, respectively. Increased WHSV to 12 h⁻¹ at 400 °C showed significant selectivity towards C₅-C₈ for all catalysts, as benzene production increased with increasing Co doping, similar to the trend at 350 °C, 12 h⁻¹ operating condition. It can be noted that among all the catalysts tested, 5%Co recorded the highest benzene selectivity (46.9%) at this operating condition. A similar result was reported by Vichaphund et al. (2015), where the incorporation of Co into ZSM-5 improved the synthesis of monoaromatics HCs (BTEX: benzene, toluene, ethylbenzene and xylene).

The phase selectivity of various catalysts is illustrated in Figure 5.1g, revealing that as the concentration of transition metal increases, the selectivity of liquid hydrocarbons decreases for all doped catalysts (0.5% > 1% > 5%), while the selectivity of gaseous hydrocarbons follows the opposite trend. In comparison to unmodified catalysts, which exhibited the highest gaseous

and lowest liquid hydrocarbon selectivity (58.0%), Ni-, Fe-, and Co-doped catalysts showed 77.3%, 70.2%, and 69.1% liquid hydrocarbon selectivity, respectively. A low metal concentration in the catalysts favours liquid hydrocarbon production, whereas an increase in concentration (from 0.5-5 wt%) leads to a gradual shift from liquid to gaseous hydrocarbons and affects catalytic performance (Tursunov et al., 2019). Figure 5h summarises each metal-doped catalyst's performance concerning product distribution, phase selectivity, and conversion at varying temperatures, where all catalysts recorded ethanol conversion of approximately > 99% at 350 and 400 °C. The following trends were observed at both temperatures in terms of product distributions and liquid product selectivity: Ni > Fe > Co > ZSM-5; Co > Fe > Ni > ZSM-5; Ni > Co > Fe > ZSM-5; and ZSM-5 > Fe > Co > Ni for C₉-C₁₂, benzene, liquid, and gaseous hydrocarbons, respectively. Ni-doped catalysts demonstrated the highest selectivity to C₉-C₁₂ and liquid hydrocarbon production, while Co-doped and ZSM-5 catalysts preferred benzene and gaseous hydrocarbons, respectively. At 350 °C, ZSM-5 > Ni > Co > Fe and Co > Fe > Ni > ZSM-5 were the trends observed for C₅-C₈ and C₁₂+ hydrocarbons, while Co maintained the highest selectivity to C₉-C₁₂, and Ni-doped catalysts mostly favoured C₁₂+ hydrocarbons at 400 °C. Therefore, introducing transition metals into HZSM-5 catalysts improved catalytic performance and production distribution (Liu et al., 2020b, Kostyniuk et al., 2020, Li et al., 2019b, Saeidi and Hamidzadeh, 2017). The summary of average product distribution of all catalysts evaluated at different WHSV is presented in Table 5.1.



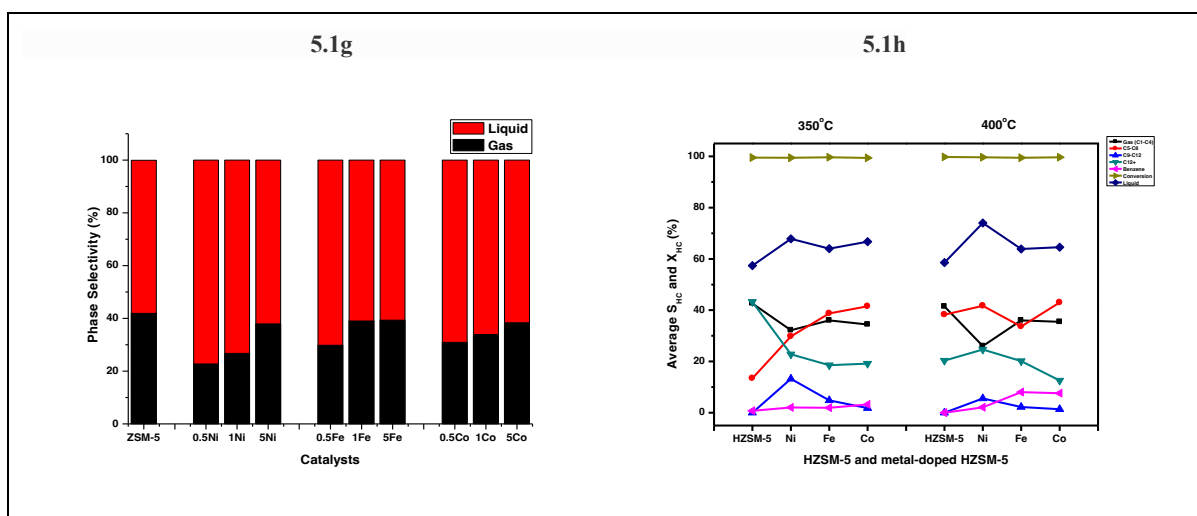
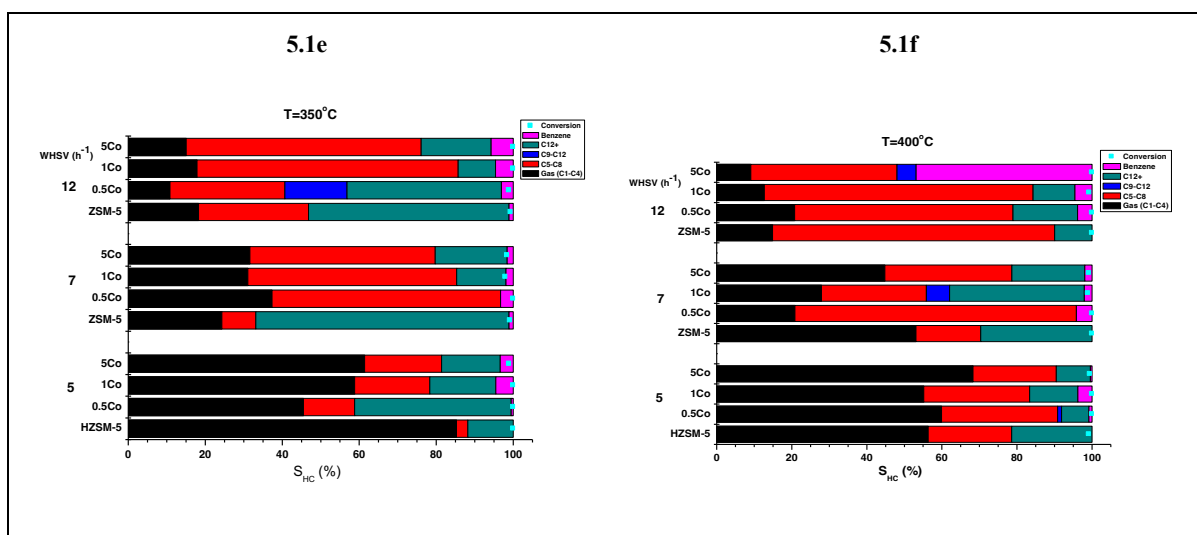
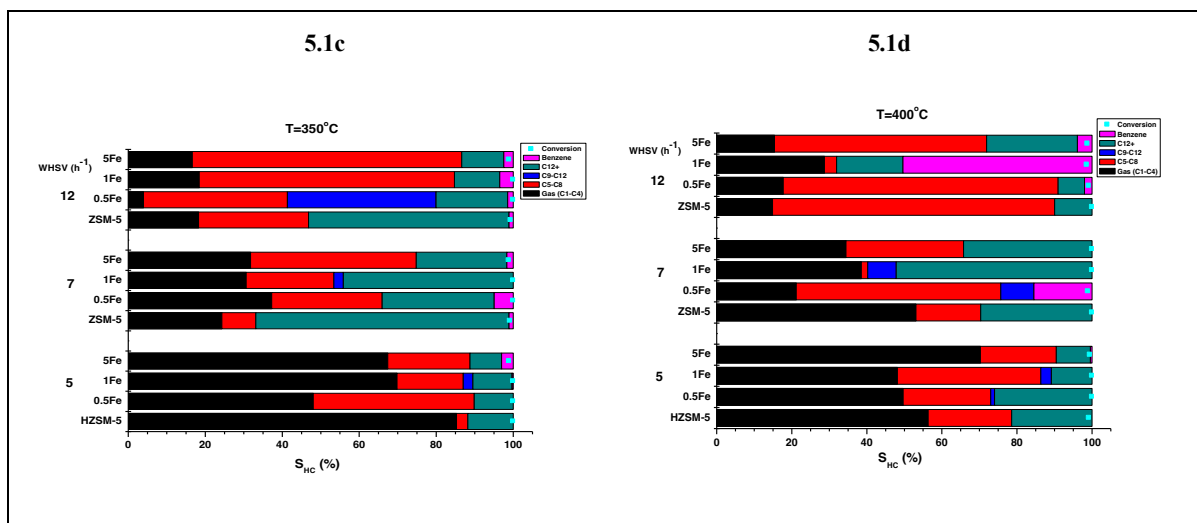


Figure 5-1. Product distribution of (0.5-5wt%) transition metal modified catalysts at WHSV=5-12 h⁻¹ for (a) Ni/HZSM-5 at 350 °C, (b) Ni/HZSM-5 at 400 °C, (c) Fe/HZSM-5 at 350 °C (d) Fe/HZSM-5 at 350 °C (e) Co/HZSM-5 at 350 °C, (f) Co/HZSM-5 at 400 °C, (g) summarised the average phase selectivity for all catalysts tested (h) summarised the performance of transition metal promoted catalysts in terms of product distribution (selectivity, S_{HC}) and conversion (X_{HC})

Table 5-1. Average HC product distribution of unmodified and metal-doped catalysts at Different WHSV

a. Ni-doped Catalysts								
	Gas							
Catalysts	(C ₁ -C ₄)	C ₅ -C ₈	C ₉ -C ₁₂	C ₁₂ +	Benzene	Conversion	Liquid	WHSV
HZSM-5	70.8	12.58	0	16.62	0	99.59	29.2	5
0.5Ni	47.46	32.14	1	17.86	1.54	100	52.54	
1Ni	59.97	26.38	0.17	13.01	0.47	99.7	40.03	
5Ni	66.82	22.8	0	8.66	1.72	99.18	33.18	
ZSM-5	38.68	13.04	0	47.73	0.55	99.58	61.32	7
0.5Ni	2.81	35.97	48.81	10.03	2.38	100	97.19	
1Ni	12.89	8.99	30.24	47.52	0.36	100	87.11	
5Ni	35.22	42	0	20.36	2.41	99.33	64.78	
ZSM-5	16.58	51.85	0	31.03	0.54	99.68	83.42	12
0.5Ni	17.83	49.85	0	27.85	4.47	100	82.17	
1Ni	7.27	39.71	0.13	50.74	2.15	99.46	92.6	
5Ni	11.66	63.7	4.31	17.21	3.12	98.11	88.34	
b. Fe-doped Catalysts								
	Gas							
Catalysts	(C ₁ -C ₄)	C ₅ -C ₈	C ₉ -C ₁₂	C ₁₂ +	Benzene	Conversion	Liquid	WHSV
HZSM-5	70.8	12.58	0	16.62	0	99.59	29.2	5
0.5Fe	48.86	32.57	0.51	18.06	0	100	51.14	
1Fe	58.97	27.73	2.64	10.51	0.16	100	41.03	
5Fe	68.82	20.8	0	8.66	1.72	99.18	31.18	
HZSM-5	38.68	13.04	0	47.73	0.55	99.58	61.32	7
0.5Fe	29.21	41.61	4.4	14.55	10.24	99.46	70.79	
1Fe	34.57	12.24	5.03	48.16	0	100	65.43	
5Fe	33.09	37.2	0	28.88	0.82	99.42	66.91	
HZSM-5	16.58	51.85	0	31.03	0.54	99.68	83.42	12
0.5Fe	10.83	55.3	19.31	12.81	1.75	99.57	88.64	

1Fe	23.57	34.77	0	14.73	26.93	99.3	76.43
5Fe	16.02	63.26	0	17.54	3.19	98.84	83.98

c. Co-doped Catalysts

Catalysts	Gas				Benzene	Conversion	Liquid	WHSV
	(C ₁ -C ₄)	C ₅ -C ₈	C ₉ -C ₁₂	C ₁₂ +				
HZSM-5	70.8	12.58	0	16.62	0	99.59	29.2	5
0.5Co	52.69	22.12	0.53	23.97	0.69	100	47.31	
1Co	56.97	23.88	0	15.01	4.14	100	43.03	
5Co	64.82	21.11	0	12.16	1.91	99.18	35.18	
HZSM-5	38.68	13.04	0	47.73	0.55	99.58	61.32	7
0.5Co	29.11	67.16	0	0	3.74	100	70.89	
1Co	29.48	41.11	3.09	24.34	1.98	98.44	70.52	
5Co	38.2	40.98	0	19.07	1.75	98.79	61.8	
HZSM-5	16.58	51.85	0	31.03	0.54	99.68	83.42	12
0.5Co	15.79	44	8.08	28.66	3.47	99.45	89.07	
1Co	15.27	69.73	0	10.42	4.58	99.63	84.73	
5Co	12.05	50.01	2.55	9.08	26.31	100	87.95	

This study focuses on the 350-400 °C temperature range and WHSV of 5-12 h⁻¹. The highest temperature studied was set at 400 °C to prevent irreversible deactivation of the HZSM-5 zeolite by dealumination (Sano et al., 1996). This factor influences the conversion of ethanol and the specificity of the different products. Besides the C₅+ HCs, special attention should be paid to the benzene aromatic component. With increasing temperature, the reaction course changes, forming additional aromatics in the metal-doped catalysts, with Co/HZSM-5 showing the highest benzene production. As reaction temperatures increase, gaseous products, including ethylene or diethyl ether, may be frequently incorporated into a chemisorbed ethanol molecule on the catalyst's surface, as Schulz and Bandermann (1994) reported. Hence, longer aliphatic chains may be formed, some of which may be rapidly converted into aromatic compounds depending on the operating conditions. The observed results support the assumption that the main products of ethanol transformation at the low WHSV and T < 350 °C are gaseous compounds such as ethylene and/or diethyl ether. Further reactions taking place at higher temperatures are expected to result in the synthesis of liquid HCs products. These liquid products will contain C₅+ and aromatic compounds. In accordance with this idea, Wu et al.

(2009) postulated that increasing the reaction temperature on TiO₂/zeolite catalysts is beneficial for the transformation of ethanol. When the reaction temperature was raised to a high value, e.g. in the range of 350-450 °C, the activity shifted to the synthesis of paraffin and aromatic compounds, which agrees with our observations.

In contrast, the unimpregnated HZSM-5 catalyst favours secondary reactions, suggesting that impregnation increases the specificity of this catalyst. Similar findings were reported by Madeira et al. (2010a), who suggested that secondary reactions and coke formation are reduced because impregnation favours the passivation of the strong Brønsted acid sites, limiting hydrogen transfer. Song et al. (2017) pointed out that although strong acid sites are necessary for the primary reactions, a significant proportion of strong acid sites favour secondary processes, including hydrogen transfer or cyclisation and subsequently increase coke deposition; similarly, weak acid sites favour the alkene methylation/cracking cycle. However, the specificity of the byproducts was different for metal-doped catalysts. In this case, impregnation resulted in the generation of more C₅⁺ and aromatic hydrocarbons compared to the unmodified HZSM-5 catalyst, and the production of these byproducts could only be reduced by metal impregnation (Gil-Horán et al., 2020). Accordingly, the variable that has the greatest effect on product selectivity is the acidity of the catalyst. However, impregnation with Co, Fe, and Ni specifically changed the nature and concentration of the available acid sites. The increased weak acid sites of the low metal-doped catalysts (0.5 and 1 wt%) may be responsible for the improved catalytic performance and product selectivity towards liquid HCs compared to 5 wt% metal-doped catalysts. As a result, these catalysts were more selective for C₅⁺, while others favoured aromatics and formed fewer byproducts than others (Gil-Horán et al., 2020).

The metal-doped catalysts show improved catalytic performance with a significant decrease in the selectivity of gaseous products with increasing WHSV and variation in the specificity of liquid products (Liu et al., 2020b). It was established by the BET analysis that metal oxide particles can block the mesopores of the zeolite, reducing the accessibility of active sites for reactant molecules, which can decrease the overall surface area. However, the decrease in surface area may not always be detrimental, as incorporating metal ions can also lead to forming new active sites, leading to improved catalytic activity and selectivity in some reactions. For instance, aromatisation is favoured by increased WHSV, which facilitates the production of aromatic products for metal-doped catalysts. This is because the longer WHSV

and reaction time enhance the development of longer aliphatic chains (Schulz and Bandermann, 1994, Bridgwater, 2012). Compared to unmodified catalysts, metal-doped HZSM-5 can produce more valuable aromatic and gasoline products at higher WHSV, suggesting that separation would be relatively easy (Liu et al., 2020b). The performance of metal-doped catalysts can also be due to the presence and uniform distribution of the metal species in the catalyst, which increases the selectivity for the liquid hydrocarbons. The metal species Co, Ni, and Fe were suggested to be dispersed throughout the Co, Ni, and Fe/HZSM-5 catalyst in the form of largely isolated framework and extraframework Fe^{3+} , Ni^{2+} , and Co^{3+} , as well as a minute amount of oligomeric clusters (Fe_xO_y , Ni_xO_y , and Co_xO_y) (Chen et al., 2016). On the other hand, the detection of significant metal species agglomerations or clusters was extremely rare. The dehydration of ethanol to ethylene was studied by Guan et al. (2007), who used a direct synthesis method to prepare FeSBA-15. The researchers showed results suggesting that isolated species (Fe^{3+}) served as active sites for ethylene synthesis, while Fe_xO_y clusters catalysed ethylene production and other products/reactions (Guan et al., 2007). As a result, the addition of metal species creates an interconnected network of mesopores that can improve the accessibility of active sites and enhance the diffusion of reactants. Moreover, the mesopores created by incorporating metals in ZSM-5 can also lead to enhanced mass transfer and reduced diffusion limitation, leading to a more significant improvement in catalytic activity. Thus, the improved catalytic activity of the metal-doped catalysts is related to a large number of isolated framework and extraframework species, as well as the low content of metal ion clusters and particles on the catalyst (Chen et al., 2016).

5.3.2 Analysis of Spent Catalysts

5.3.2.1 Thermal Stability Study - TGA-DTA

Thermogravimetric analysis/differential thermal analysis (TGA/DTA) was performed after ethanol transformation at 400 °C and 12 h⁻¹ to analyse the deactivated spent modified and unmodified HZSM-5 samples, referenced to the fresh one. The weight losses from 30 °C to 800 °C were recorded and presented in Figures 5.2a-f, which shows catalyst thermal stability with a focus on the effect of metal doping on catalysts coking and deactivation. The unused catalyst is considered the pure catalyst and was utilised as the reference sample for the TGA study. The initial weight loss under N₂ flow up to 200 °C was not considered during the coke calculations since this weight loss can be due to the removal of water and volatile compounds (Ahmed et al., 2011). The coke calculation starts from T=200 °C and above, with the gas switch

from N₂ to air. The weight loss during this period results from a decoking process which is distinctly categorised into three stages based on temperature: 200-400 °C, 400-600 °C and 600-800 °C, denoted (for this study) as stage one, two and three decoking processes respectively.

The TGA analysis revealed that all catalysts displayed weight loss from 30-200 °C at 1.9-2.7 %, 2.5-2.9 % and 2.0-3.7 % for Ni, Fe and Co-doped catalysts. The Fe-modified catalyst showed an increase in the burning of soft coke at the stage one decoking process with increasing metal doping from 0.5 to 5 % as 0.5 %Fe recorded the highest coke deposit attributed to 2.3 % wt loss compared to 0.5Ni (0.88%). A similar trend was observed with Ni-doped catalysts: the 5%Ni showed the highest coke deposit (1.8%), while 1%Ni showed a slightly lower wt loss (0.063 %) than 0.5Ni. However, 1%Co recorded the highest coke deposit with a 1.54 % wt loss, followed by 5%Co (1.3 %). The second stage decoking process, which involves the degradation of hard coke at 400-600 °C, recorded a significant weight loss accompanied by exothermic phenomena for all the catalysts tested attributed to the nature of coke. (Nie et al., 2021). As wt loss increases with increasing metal doping for Ni and Fe-doped catalysts, 1%Co exhibited more thermal stability than 0.5%Co with a 0.6 % difference in weight loss at this decoking stage. The final decoking process (600-800 °C), which promotes the degradation of non-volatile compounds, revealed a decreasing weight loss with increasing metal concentration for all metal-doped catalysts, which denotes the increased presence of non-volatile coke materials in catalysts with low metal loading. Ni and Fe-doped (1.5-2.2 % and 1.0-2.5 %) catalysts recorded a considerable amount of these coke materials compared to Co-based catalysts (0.3-2.1 %). Compared to metal-doped catalysts, the unmodified catalyst recorded the lowest weight loss during the decoking processes at 200-600 °C, while the pure catalyst showed the least wt loss at all decoking stages due to the absence of coke deposit. This showed that metal doping promotes coke deposition. The elevated temperature loss often resulted from the burning-off of the accumulated "hard" carbon species and non-volatile coke materials responsible for blocking the active centre and deactivating the zeolite during the ethanol conversion. It can also be inferred that the spent catalysts are mostly made up of hard coke (Odedairo and Al-Khattaf, 2010, Todorova et al., 2020, Dai et al., 2018, Bartholomew, 2001, Sanapur et al., 2019, Wang, 2006).

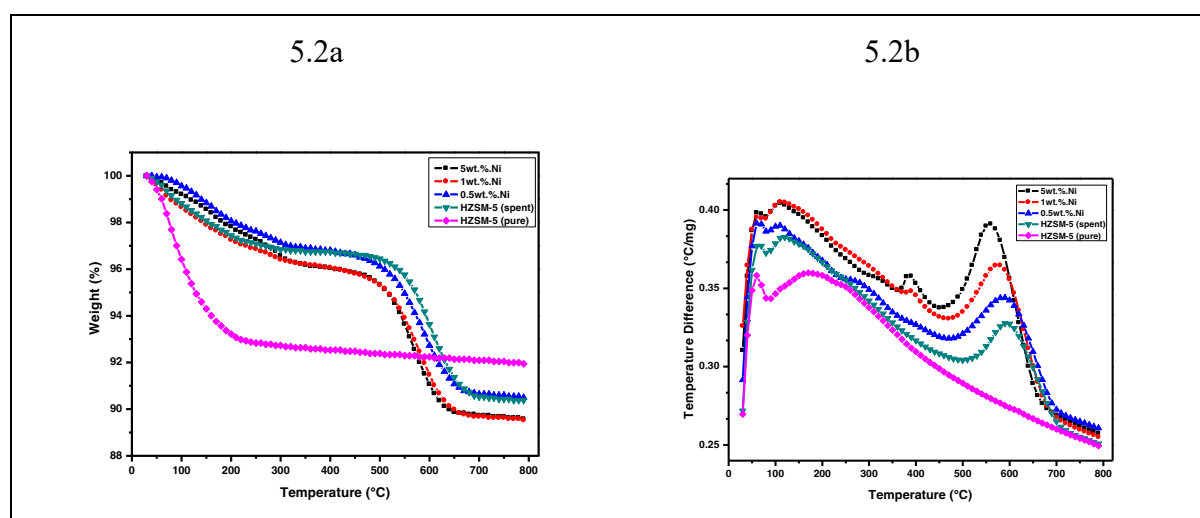
The effect of WHSV and temperature on catalyst coking was studied on spent catalysts (5%Ni) at WHSV=7 and 12 h⁻¹ and T=350 and 400 °C. Figure 5.2g shows that amount of coke increased by 0.27 % with increasing temperature from 350 to 400 °C at 12 h⁻¹ while the increase in WHSV

from 7 to 12 h⁻¹ at 350 °C resulted in 0.28 % increase in decoking from 200-800 °C. This showed that increased temperature and WHSV increased coke deposition attributed to the formation of long-chain HCs (as shown in Figures 5.1a & b above), which blocks the catalyst pores and subsequent deactivation. This agrees with the study by Mores et al. (2011), which reported that the conversion of small HCs species into larger compounds corresponded with blocking the straight pores of HZSM-5 crystals. Increased process temperatures finally result in coke deposition in the contact channel and the external zeolite surface (Mores et al., 2011). The nature or type of coke deposition affects the decoking process/reaction during the thermal stability test. The reaction rate of soft coke in the first stage is slow during the first stage. From the thermal stability study, the weight loss in this instance amounts is low. However, an increase in reaction rate attributed to raising the temperature providing a greater pace of reactions, was prevalent as the temperature rose from 400 to 600 °C (stage 2), resulting in a significant weight loss. This suggests that the predominant form of coke deposit on the spent catalyst examined is hard coke, which can be eliminated using appropriate methods for decoking. This constitutes most of the total amount of coke examined on the spent catalyst compared to soft and non-volatile coke materials (Nie et al., 2021).

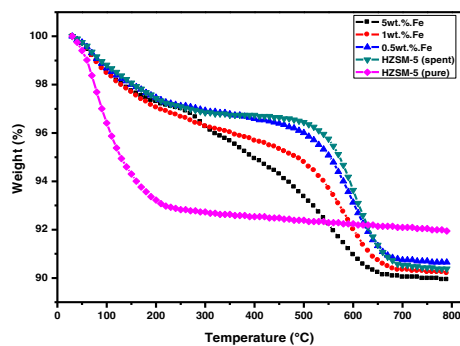
The exothermal peak temperatures in the DTA profiles (Figures 5.2b, d, f, & h) for the spent samples showed the possibility of coke deposition as the high peaks denote high chances of coking. These peaks are evident between T=450-700 °C, showing high metal concentration's propensity to carbon deposition and deactivation. They are ranked in the following order: pure HZSM-5 < spent HZSM-5 < 0.5%M < 1%M < 5%M (M=metal: Ni or Co or Fe), and a similar trend was observed for Figure 5.2h, an increase in temperature and WHSV results in an increase in peak temperatures. Such an order implied less feasibility of the carbon formation for the unmodified, low metal-doped catalyst and low temperature and WHSV operating conditions. These results correlate with the spent samples' thermal stability (Nie et al., 2021). In addition, coke deposition is closely related to the acidity of the catalyst, as shown by the observation that higher metal doping, leading to increased strong acid sites, is associated with greater coke deposition. This trend is particularly evident for catalysts modified with 10 wt% (Co, Fe, and Ni), which recorded a significant coke formation. In contrast, catalysts with lower metal doping (0.5 and 1 wt%) have a lower level of strong acid sites, resulting in reduced coke deposition. This is consistent with previous studies (Persson et al., 2019b, Masiero et al., 2009, Zhou et al., 2017). Figure 5.3 shows the evidence of carbon deposition on spent catalyst samples after

ethanol conversion at WHSV=12 h⁻¹, T=400 °C using 5 wt% metal-doped catalysts. The summary and comparative evaluation of the weight loss observed for the spent catalysts is presented in Table 5.2.

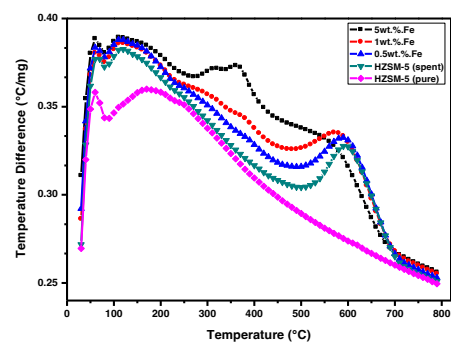
Ethylene can polymerise on the highly active Brønsted acid sites of H-ZSM-5, which initiates coke formation (Guisnet and Magnoux, 1994, Karge and Weitkamp, 1989). The rapid formation of coke can cover the more active sites, leading to a significant reduction in reaction rate within the first few minutes. The stronger acid sites are more susceptible to coking. This early catalyst deactivation is mainly due to coke deposition on these sites, as reported by Tabak and Yurchak (1990). Among the metal-doped catalysts, Ni/HZSM-5 is more selective towards long-chain (C₁₀⁺) hydrocarbons, which can result in increased coke deposition, as shown in Figures 5.1a & b. In ethanol to hydrocarbon (ETH) conversion over H-ZSM-5 catalysts, the formation of long-chain hydrocarbons, such as C₁₀⁺ hydrocarbons, can increase coke deposition on the catalyst surface. This is because the formation of C₁₀⁺ hydrocarbons requires multiple reaction steps and intermediate species, which may adsorb on the catalyst surface and undergo further reactions to form coke deposits (Zheng et al., 2017, Pinjari et al., 2018). As the coke deposits accumulate on the catalyst surface, they can block the active sites, reduce the effective surface area of the catalyst, and eventually lead to catalyst deactivation (Pinjari et al., 2018). The formation of coke deposits is also influenced by other factors such as reaction WHSV and temperature, composition, and catalyst structure. Therefore, to maintain the stability and activity of the H-ZSM-5 catalyst, it is essential to optimise the operating conditions to minimise the formation of coke deposits while maximising the selectivity towards the desired hydrocarbon products.



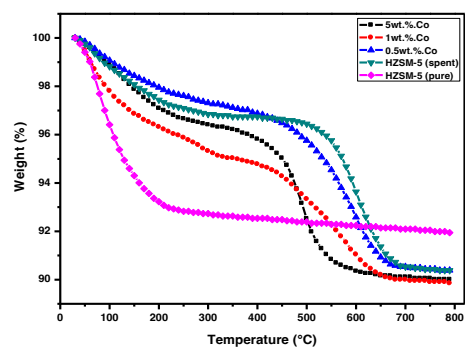
5.2c



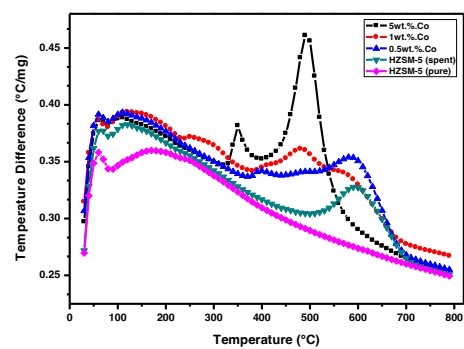
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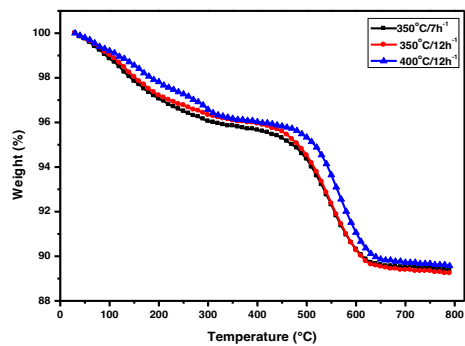
5.2e



5.2f



5.2g



5.2h

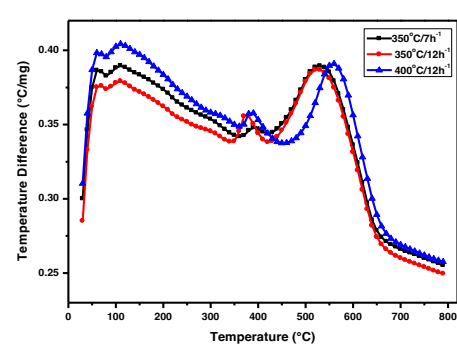


Figure 5-2. TGA & DTA curve of spent catalysts at 12 h⁻¹, 400 °C: (a & b). Ni/HZSM-5 (c & d). Fe/HZSM-5 (e & f). Co/HZSM-5 (g & h). Effect of temperature and WHSV on coke deposition for 5 % Ni/HZSM-5

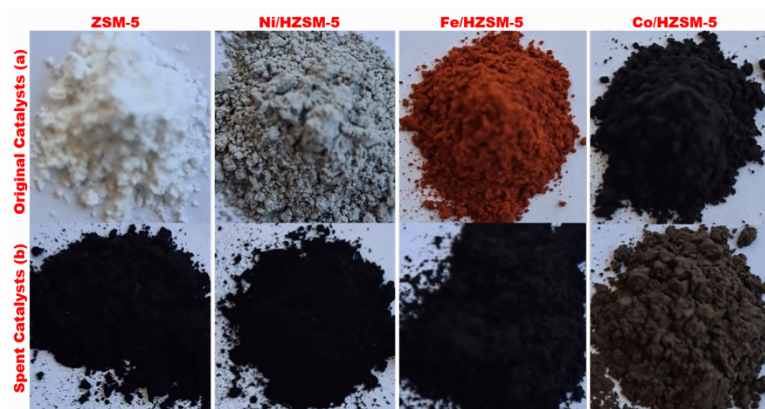


Figure 5-3. Samples of original and spent metal-doped (5 wt%) catalyst (Operating conditions: WHSV=12 h⁻¹, T=400 °C)

Table 5-2. Weight loss of spent catalyst from 200–600 °C – Comparative summary

Catalysts	Weight loss		Operating Conditions	
	mg	%	WHSV (h ⁻¹)	T (°C)
HZSM-5	0.26	1.28	12	400
(pure)				
HZSM-5	1.43	7.05		
(spent)				
0.5%Ni	1.56	7.56		
0.5%Fe	1.40	6.82		
0.5%Co	1.55	7.56		
1%Ni	1.55	7.73		
1%Fe	1.4	6.86		
1%Co	1.3	6.47		
5%Ni	1.66	8.24		
5%Fe	1.5	7.36		
5%Co	1.44	7.09		
5%Ni	1.66	8.24	12	400
5%Ni	1.63	6.94	12	350
5%Ni	1.35	6.74	7	350

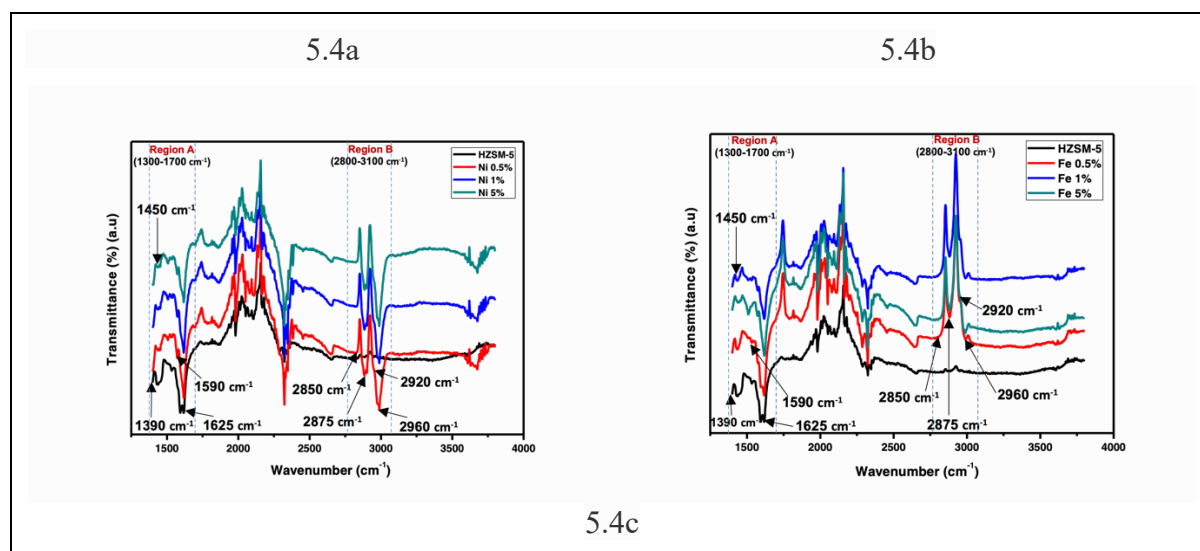
5.3.2.2 *Characterisation of Coke Composition*

Coke composition was classified using FTIR spectroscopy to identify adsorbed hydrocarbons (Karge et al., 1996). The presence of coke can be detected by the characteristic bands of the hydrocarbon molecules (Karge et al., 1996, Castaño et al., 2011). The key regions considered in the FTIR spectrum for coke characterization are region A = 1300-1700 cm^{-1} and region B = 2800-3100 cm^{-1} . Figures 8a-c depict the spectra (1300-3800 cm^{-1}) of spent catalysts in these two regions. The vibrations in the range A are associated with polycondensed aromatics, conjugated olefins, and some aliphatic bending modes, while the vibrations in the second range, region B correspond to aliphatics (asymmetric and symmetric stretching) and single-ring aromatics. To analyse each vibration, the specific spectra of the spent catalysts were identified (Karge et al., 1996, Palumbo et al., 2008, Robertson, 2002, Valecillos et al., 2022) as follows: 1390 cm^{-1} , terminal $-\text{CH}_3$ groups; 1450 cm^{-1} , combination of aliphatics (bending and scissoring) and alkyl aromatics; 1590 cm^{-1} , coke band or polycondensed aromatics; 1625 cm^{-1} , double bonds or olefins; 2850 cm^{-1} , $-\text{CH}_2$ groups; 2875 cm^{-1} , $-\text{CH}_3$ groups; 2900-2920 cm^{-1} , $-\text{CH}_2$ and $-\text{CH}$ groups; 2960 cm^{-1} , $-\text{CH}_3$ groups; 2875-3000 cm^{-1} , $-\text{CH}$ and $-\text{CH}_2$ olefinic groups (symmetric). It should be noted that these numbers are estimates and may vary due to limitations in instrumentation and sample composition and preparation techniques. Figure 1a-c shows the 1300-3800 cm^{-1} range for the spent metal-doped catalysts. The most intense band in region B corresponds to the $-\text{CH}_3$ groups (2875 and 2960 cm^{-1}) for the Ni- and Co-doped catalysts (Figures 5.4a & b). In contrast, the band at 2960 cm^{-1} was less frequent for Fe-doped catalysts, while the band at 2875 cm^{-1} was very intense. Compared to unmodified HZSM-5, these CH_3 bands are more pronounced in metal-doped samples and increase with increasing metal doping (0.5-5 wt%), indicating the presence of long or naphthenic aliphatic chains in the coke produced, especially for the Ni and Co-doped catalysts.

For region A, it was observed that the band at 1590 cm^{-1} corresponding to polycondensed aromatics was more pronounced for the metal-doped catalysts (increasing with metal doping) than for the unmodified catalysts, correlating with the TGA result. The 1590 cm^{-1} band has been associated with coke content (Karge et al., 1996, Park and Seo, 2009), and our results support this notion, as the coke content is lower for HZSM-5 than for metal-doped catalysts. However, among the metal-doped catalysts, the Ni-doped catalysts showed a more intense coke peak than the Fe- and Co-doped catalysts (Figures 5.4a-c), consistent with the TGA result. The assignment of the 1390 cm^{-1} band is difficult, but some researchers have associated it with

terminal -CH₃ groups, suggesting a higher presence of -CH₃ groups in metal-doped and HZSM-5 zeolite coke. In the case of the spent HZSM-5 catalyst, the strongest band (1450 cm⁻¹) is associated with branched aliphatics. The 1450 cm⁻¹ band has been associated with alkyl aromatics adsorbed on the zeolite (Arsenova-Härtel et al., 2000), which explains the greater abundance of this species in the HZSM-5 catalyst compared to metal-doped catalysts.

It should be noted that this band (1450 cm⁻¹) may also be attributed to aliphatics (bending and scissoring), which complicates its assignment. Compared to the unmodified catalyst, the metal-doped catalysts exhibited higher intensities of the bands at 2875-3000 cm⁻¹ at the expense of the -CH groups (2900-2920 cm⁻¹) corresponding to highly branched paraffins or naphthenes. The finding of this study agrees with other studies (Valecillos et al., 2022, Karge et al., 1996, Palumbo et al., 2008). This suggests that the ETH conversion over metal-doped catalysts is directed toward the production of long or naphthenic aliphatic chains. Understanding the nature and composition of the coke produced in catalytic processes is critical for optimizing catalyst performance and tailoring product selectivity. By analyzing the intensity and characteristics of absorption bands in specific regions, such as the region A and B, insights into the coke composition and its impact on the overall catalytic process will be gained.



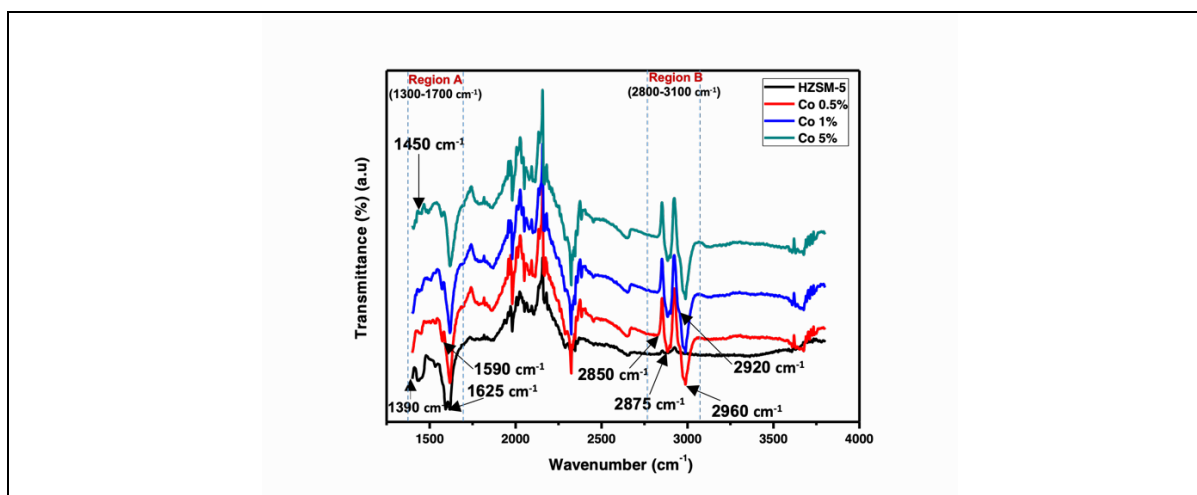


Figure 5-4. FTIR ($1300\text{--}3800\text{ cm}^{-1}$) spectrum of spent (a) Ni-doped, (b) Fe-doped and (c) Co-doped HZSM-5 catalysts

The potential reaction pathway of ETH conversion is shown in Figure 5.5. The reaction pathway involves intramolecular dehydration of ethanol to form C_2H_4 or intermolecular dehydration of ethanol to form diethyl ether (DEE), which is then converted to C_2H_4 . Ethanol can be converted to C_3H_6 through the oligomerisation of between C_2H_4 and carbene species, a transient intermediate formed by the interaction of ethylene with the -OH groups of zeolite (Takahashi et al., 2013), or to C_4H_8 through dimerisation. These olefins undergo cyclisation, dehydrogenation and aromatisation reactions to form aromatic compounds and long-chain paraffins. This explains the presence of aromatics, especially benzene and long-chain paraffins, in the product distribution, and the presence of carbonaceous components further supports this speculation. In addition, this is consistent with the coke composition reported in Figure 5.4, which shows a significantly higher abundance of hydrogen-rich long-chain alkanes than aromatic compounds. This finding aligns with the existing literature reports (Xia et al., 2010b, Li et al., 2000, Takahashi et al., 2013, Niu et al., 2020a, Iadrat and Wattanakit, 2021).

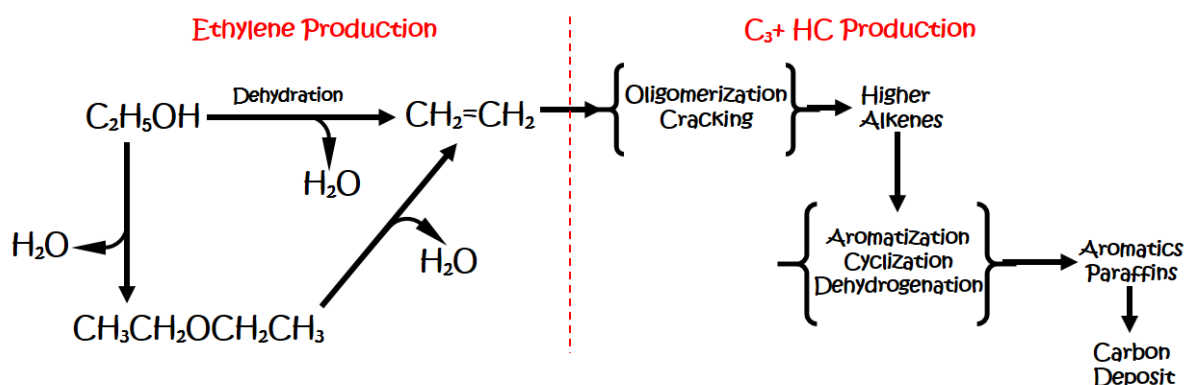


Figure 5-5. Proposed scheme of ETH conversion over HZSM-5 zeolite catalysts

5.3.2.3 *Textural Properties of Spent Catalysts*

The textural properties of spent catalysts were studied to investigate the changes in these properties after the ETH conversion. The unmodified and metal-doped spent HZSM-5 catalysts exhibit a type 1V isotherm indicating the retention of the mesoporous structures after the reaction (Figure 5.6). This is supported by a small hysteresis loop due to capillary condensation, attributed to the reduction of mesoporous volume in all catalysts. Adsorbate uptake in the P/P_0 range of 0.9-1.0 is significantly improved compared to lower pressure ranges. This demonstrates that the catalysts have a higher affinity for adsorbate molecules at higher pressures, possibly due to accessible mesopores in this range despite the coke deposits. The adsorbed volume decreases with decreasing surface area, corresponding to increased metal doping (Co, Fe and Ni) and coke deposition. At metal doping levels of 0.5, 1 and 5 wt%, the surface area decreases by 9-53 %, 34-60 % and 72-84 %, respectively, relative to the unmodified catalyst (Table 5.3). This observation suggests that incorporating metal species, especially at higher doping levels, reduces the total surface area available for adsorption due to enhanced coke deposition. Among the metal-doped catalysts, the lowest adsorption was observed at 5 wt% doping, especially for Ni. This is consistent with the trend that the 5 wt% Ni doped catalyst has the lowest surface area. Higher metal dopants can lead to more pronounced changes in the catalyst structure, resulting in a greater reduction in surface area and a decrease in adsorption capacity (Kim et al., 2020b, Lee et al., 2012). The decrease in surface area can be correlated with the results of thermogravimetric analysis (TGA), according to which catalysts with higher coke deposits have a lower surface area than those with lower coke deposits.

The increase in pore diameter of the spent catalyst (Table 5.3) compared to the pure catalyst (Table 3.2) can be attributed to several factors. First, catalytic reactions over time lead to the accumulation of carbonaceous deposits (coke) in the pores of the catalyst, which physically block smaller pores and cause an increase in pore diameter. Catalyst deactivation processes, including sintering and particle agglomeration, cause pores to merge, creating larger, interconnected pores (Ibáñez et al., 2016). In addition, cyclic exposure to high temperatures and subsequent cooling during catalytic processes can lead to thermal stresses in the catalyst, which can cause pore enlargement and the formation of larger pores. Furthermore, the mechanical forces that occur during handling and operation of the catalyst contribute to the

enlargement of the pores, often through fracture and restructuring of the particles. These collective factors highlight the differences in pore diameter between the spent and virgin catalysts, with the spent catalyst exhibiting higher mesoporosity and macroporosity due to the cumulative effects of coke deposition, deactivation, thermal stress, and mechanical stress over time (Ibáñez et al., 2016).

The observed decrease in mesopores leading to a decrease in the total pore volume of the spent catalysts can be attributed to ETH conversion and the formation of coke deposits and subsequent pore blockage. The ETH conversion, which produces long-chain and aromatics, involves complex reactions in the catalyst pores. The formation of long-chain hydrocarbons through oligomerisation and dehydrogenation, as shown in Figure 5.6 during ethanol conversion, can contribute to pore blockage and reduce surface area. Long-chain molecules tend to adsorb and accumulate on the catalyst surface, filling the available surface area and hindering access to the active sites. As a result, the surface area of the catalyst decreases. The formation of aromatic compounds often desired in ETH conversion may also contribute to the decrease in surface area and mesopore volume. Aromatisation reactions involve the formation of cyclic structures through ring closure reactions. These reactions preferentially occur in mesopores because they have a larger pore size and provide suitable conditions for ring closure reactions. When aromatics form, they can occupy the mesopores and reduce the available mesoporous volume and surface area. However, during ETH conversion, the formation of coke deposits due to secondary reactions can clog and constrict the mesopores, decreasing both mesopore volume and surface area and further limiting reactant access to the active sites (Meng et al., 2012, Ciambelli et al., 2010).

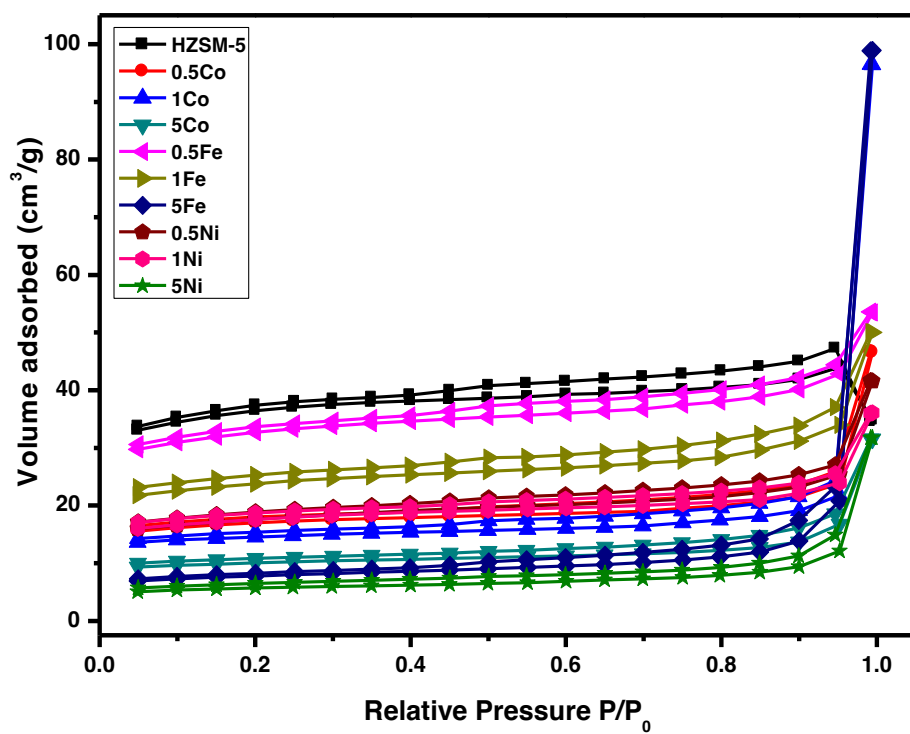


Figure 5-6. N₂ adsorption-desorption isotherms of spent catalysts

Table 5-3. Textural Properties of Spent Catalysts

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	V_{macro} (BJH) ($\text{cm}^3 \text{g}^{-1}$)	Avg pore dia. (nm)	Volume@STP ($\text{cm}^3 \text{g}^{-1}$)	Metal loading (wt.%)
HZSM-5	113.23	0.669	0.039	0.630	40.03	37.50	0.00
0.5Co	52.89	0.183	0.143	0.040	5.46	17.53	0.5
1Co	44.93	0.265	0.125	0.140	10.33	14.98	1
5Co	31.31	0.142	0.118	0.025	6.25	10.40	5
0.5Fe	102.24	0.258	0.239	0.018	3.24	33.80	0.5
1Fe	74.47	0.245	0.220	0.025	4.17	24.65	1
5Fe	24.79	0.325	0.173	0.152	24.73	8.21	5
0.5Ni	55.43	0.202	0.176	0.026	4.65	18.41	0.5
1Ni	55.07	0.174	0.154	0.020	4.06	18.31	1
5Ni	18.02	0.145	0.113	0.031	10.92	5.97	5

5.3.2.4 *Crystallinity and Morphology Study of Spent Catalyst*

Figure 5.7a shows that coke deposition can affect the crystallinity of spent metal-doped ZSM-5 catalysts after ethanol conversion to hydrocarbons. TGA-DTA results show that carbonaceous species are formed and deposited on the catalyst surface during the reaction, resulting in coke deposition. This phenomenon is common in catalytic processes and can alter the XRD patterns. The decrease in peak intensity indicates changes in the crystal structure and composition of the catalyst due to coke deposition. The greater decrease in intensity of peaks 7-9° compared to peaks 22-24° indicates that coke deposition preferentially affects certain crystallographic planes or phases of the catalyst. The reasons for this selective decrease are complex and depend on factors such as the type and concentration of metal dopants, the distribution of coke deposition, and the accessibility of certain crystal planes to coke formation. Increasing the metal doping concentration from 0.5 to 5 wt% of the Ni, Fe, and Co species further decreases the intensity of these characteristic peaks. This indicates that transition metal dopants enhance coke deposition on the catalyst. Similar trend has been reported by previous studies (Denardin and Perez-Lopez, 2020, Sridhar et al., 2020). Transition metals can facilitate the dehydrogenation reaction during the ETH conversion and the selective production of long-chain hydrocarbons, as shown by the product distribution of the metal-doped catalysts, and they can also promote the formation of carbonaceous species necessary as precursors for coke synthesis. The enhanced coke deposition leads to more significant changes in the XRD pattern. Despite the coke deposition and decreased peak intensities, the MFI framework of the zeolite catalyst was preserved. The preservation of the MFI framework suggests that coke deposition does not cause substantial damage or collapse of the zeolite structure. When examining characteristic peaks, it is likely that peaks associated with the zeolite framework remain relatively unchanged. This indicates that coke deposition primarily occurs on the catalyst's external surface or in larger pores (Wan et al., 2018). The selective reduction in the intensity of specific peaks may be attributed to the accessibility of these external sites or larger pores to coke precursors.

Figure 5.7b shows the scanning electron microscopy (SEM) images of the spent unmodified and Fe-doped ZSM-5 catalysts, which provide valuable insights into the surface properties and their relationship with coke deposition during the conversion of ethanol to hydrocarbons at the operating conditions of 400 °C and 12 h⁻¹. From the results of TGA-DTA, the amount of coke

deposition increases with higher metal doping. This indicates that the presence of Fe dopants promotes the formation and deposition of coke on the catalyst. Therefore, the images from SEM help to better understand the surface properties and their relationship with coke deposition. The surface appearance observed in the images from SEM can vary depending on the amount of coke deposited on the catalyst. The surface of the unmodified ZSM-5 catalysts appears relatively clean and has minimal coke deposition, which revealed less coke deposition as observed in the TGA study. However, slight changes related to coke deposition were observed with increasing Fe doping concentration (from 0.5 to 1 to 5 wt% Fe). At lower Fe dopants (0.5 to 1 wt%), the SEM images show small coke deposits on the external surface of the catalyst, consistent with the TGA result (Wan et al., 2018). The size and distribution of these coke deposits can vary depending on the specific reaction conditions. As the Fe doping concentration approaches 5 wt%, images from SEM show more coke deposition on the catalyst surface. These coke deposits may partially cover the catalyst particles and acid sites resulting in a more uneven and textured surface appearance and deactivation. It should be noted that the distribution and morphology of coke deposits can be influenced by factors such as catalyst site accessibility, temperature gradients, and flow patterns within the reactor. These factors can affect the size, shape, and distribution of coke deposits. Therefore, the images from SEM are supplemented with other analytical techniques to provide a comprehensive understanding of coke deposition.

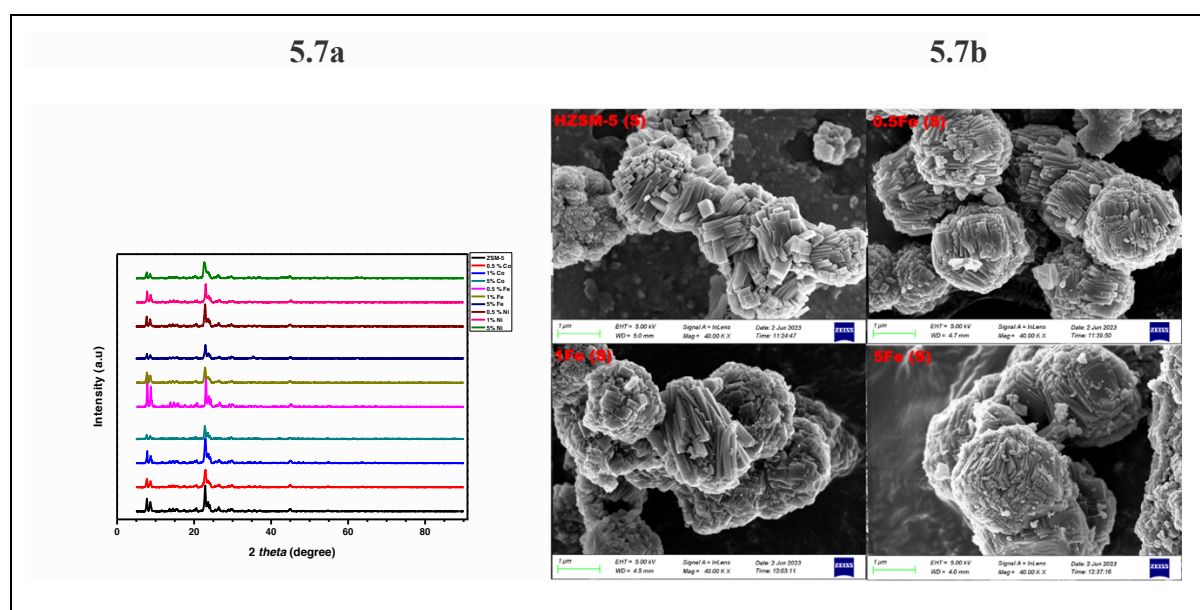


Figure 5-7. XRD and SEM Images of spent Catalysts

5.4 Conclusion

This study investigated the effects of operating conditions on the ETH conversion over ZSM-5 catalysts doped with various transition metals (Ni, Fe, and Co). The influence of metal loading, temperature, and WHSV on product selectivity, phase selectivity, conversion, and coking was studied. ZSM-5 zeolite catalyst doped with various concentrations (0.5-5 wt%) of transition metals (Co, Fe, and Ni) was synthesised and evaluated in the ETH conversion. Catalyst characterisation revealed the presence of metal species in the doped catalysts and showed that the incorporation of metals affected the catalyst's surface area, porosity, particle size and morphology. Based on the catalytic study, it can be deduced that the catalytic activity of ZSM-5 zeolite can be significantly altered by doping with transition metals such as Ni, Fe and Co. Transition metal-doped HZSM-5 catalysts were found to be active for the conversion of ethanol to hydrocarbons. Increasing the WHSV favoured the production of liquid hydrocarbons, while a change in reaction temperature showed no significant changes in the selectivity of gaseous hydrocarbons. Selectivity for target products can be improved by incorporating a small amount of transition metal into the parent catalyst, as low amounts of metals in the catalysts favour the liquid hydrocarbon selectivity, while a higher concentration leads to a shift from liquid to gaseous hydrocarbons. At 350 and 400 °C, ethanol conversion was >97% for all catalysts. However, the selectivity for the different products varies with the change in reaction conditions, such as temperature and WHSV. The unmodified catalyst exhibited the highest selectivity for gaseous hydrocarbons and the lowest for liquid hydrocarbons, while metal-doped catalysts exhibited higher selectivity for liquid hydrocarbons. Among the catalysts tested, the Ni-doped catalysts exhibited considerable selectivity for C₉-C₁₂ and liquid hydrocarbon production, the Co-doped preferred C₅-C₈ and benzene, while the Fe-doped catalysts enhanced benzene production. The thermal stability study of the spent catalyst showed that catalyst coking increased with increasing metal doping, which led to catalyst deactivation. Moreover, with increasing temperature and WHSV, coke deposition increased as most consisted of hard coke (400-600 °C). Co-doped catalyst recorded the lowest weight loss (1.3 and 1.4 mg for 1 and 5 wt% Co-doping) compared to Fe- (1.4 and 1.5 mg) and Ni-doped catalysts (1.6 and 1.7 mg). Analysis of the spent catalysts showed that the catalyst framework was preserved despite coke deposition, with reduced crystallinity,

surface area, and mesoporous volume due to coke deposition. Consistent with the TGA results, the decrease in crystallinity and textural properties correspond to increased coke deposition and metal doping. Consistent with the TGA results, the decrease in crystallinity and textural properties including a decrease in surface area from 306 - 440 m²g⁻¹ to 18 - 113 m²g⁻¹, and reduction in mesopore volume correspond to increased coke deposition and metal doping. Overall, the results conclude that the catalytic performance of ZSM-5 can be enhanced by doping with transition metals and optimising the reaction conditions can lead to desired product selectivity while reducing catalyst deactivation.

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CHAPTER 6

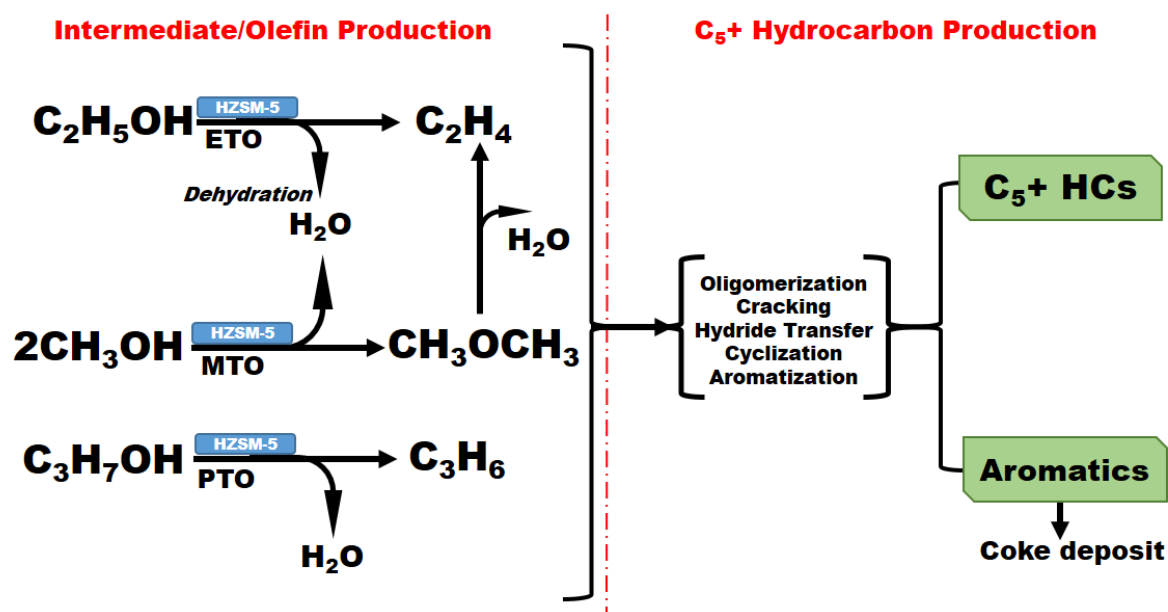
Performance Evaluation of Transition Metal-doped HZSM-5 on Single-step Conversion of C₁-C₃ Alcohol to Fuel-range Hydrocarbons

Abstract

This chapter investigated the performance of metal-doped HZSM-5 catalysts in the conversion of low alcohols to hydrocarbons (LATH). Catalysts, including unmodified HZSM-5 and metal-modified (Ni, Fe, and Co) HZSM-5, were evaluated at 350 and 400 °C with space velocities of 7 and 12 h⁻¹ for LATH conversion. The catalyst evaluation results revealed consistent selectivity of the catalysts towards C₅-C₈ and C₉-C₁₂ hydrocarbons in MTH conversion (>99 % conversion). ETH and PTH conversions exhibited similar product distribution trends with >98 % conversion for all catalysts. In LATH conversion, Ni/HZSM-5 demonstrated the highest selectivity for C₁₂⁺, C₉-C₁₂, and BTX, while Co/HZSM-5 favoured BTX and C₅-C₈. Fe/HZSM-5 showed higher selectivity for C₅-C₈, BTX, and C₉-C₁₂ in MTH, ETH, and PTH conversions, respectively. The modified catalysts displayed enhanced selectivity towards liquid fuel-range hydrocarbons, surpassing the performance of unmodified catalysts in LATH conversion. Unmodified catalysts exhibited significant selectivity towards C₁₂⁺ only in ETH conversion. The study on coke deposition indicated that Ni/HZSM-5 exhibited stability with minimal coke formation, while Co/HZSM-5 experienced higher coke deposition and deactivation tendency in MTH and ETH conversions, respectively. Co/HZSM-5 exhibited the lowest weight loss, whereas Fe/HZSM-5 showed lower stability in PTH conversion. Notably, Ni/HZSM-5 demonstrated remarkable stability and performance in LATH conversion. These findings contribute to the advancement of catalysis and the transition towards a sustainable energy future.

Keywords: Catalyst, Coke deposition, Ethanol, Methanol, Propanol, Zeolite, ZSM-5

Graphical Abstract



6.1 Introduction

In the twenty-first century, the world faces two critical challenges: the depletion of oil resources due to rising energy demands and the issue of global warming. It is widely recognised that the increased presence of carbon dioxide (CO₂) in the atmosphere is the primary driver of global warming. Recently, the urgency of addressing global warming has surged to the forefront of societal concerns, leading to heightened international awareness and a shared understanding of the need to reshape our society to tackle the root causes of CO₂ emissions and related pollution issues, including fine dust pollution (Stambouli et al., 2012). Moreover, these challenges stem from our heavy reliance on fossil fuels as the primary energy source. While petroleum remains the most readily available fossil fuel for transportation, the current consumption rates project the depletion of oil reserves within the next 50 years, with natural gas reserves estimated to last approximately 70 years (Stambouli et al., 2012). The discovery of new oil and gas reserves could delay the complete depletion of fossil fuels. However, it is crucial to recognise that significant fuel scarcity issues are anticipated in the future. Consequently, seeking an alternative sustainable energy source that can effectively address the challenges of projected energy scarcity and greenhouse gas emissions becomes imperative.

The C₁-C₃ alcohols, which are low alcohols (methanol, ethanol and propanol), have emerged as highly promising oxygenated fuels for decarbonising the road transport sector (Han et al., 2020, Zhu et al., 2021). These alcohols offer several advantages, including a wide range of

feedstocks and simplified production processes. In terms of fuel properties, low-carbon alcohols exhibit notable advantages over diesel and gasoline. These advantages encompass a high latent heat of vaporisation, lower adiabatic flame temperature, oxygenated molecular structure, absence of C-C bonds, higher oxygen content, lower viscosity, high H/C ratio, low sulfur content, and efficient evaporative cooling (Kim et al., 2020a, Zhu et al., 2021). Despite its advantages, the lower calorific value of low alcohols compared to gasoline and their corrosiveness pose limitations on using 100% low alcohol in modern automobiles. As a result, the catalytic conversion of low alcohols using acid catalysts provides a viable approach for upgrading them into fuel-range hydrocarbons (HCs). The conversion of low alcohols under optimal temperature conditions and in the presence of an acid catalyst such as ZSM-5 zeolite catalyst transforms low alcohol into intermediates and subsequently higher hydrocarbons (oligomers) (Van der Borgh et al., 2015b). Olefins, paraffins and aromatics with a C₅+ have appreciable fuel properties.

Since the introduction of Mobil's methanol-to-gasoline (MTG) process (Chang and Silvestri, 1977), significant research has been dedicated to exploring the reaction and catalyst deactivation mechanisms involved in the transformation of alcohols for the production of liquid hydrocarbon fuels and light olefins using ZSM-5 zeolite as the catalyst (Ramasamy et al., 2014). ZSM-5 zeolites, which possess a uniform pore structure, high surface area, and adjustable acidity, have been extensively utilised in low alcohol to hydrocarbon (LATH) reactions, particularly methanol and ethanol. The LATH process typically involves a three-step approach before fractionation to meet fuel requirements, including alcohol dehydration, oligomerization, and hydrogenation. Alternatively, a one-step approach known as the consolidated alcohol dehydration and oligomerization (CADO) process has been proposed by Narula et al. (2015). It aims to achieve dehydration and oligomerization of alcohols in a single reactor. It has been observed that the dehydration of low alcohol typically occurs at temperatures below 300 °C (Le Van Mao et al., 1987, Le Van Mao et al., 1989, Phillips and Datta, 1997, Sun and Wang, 2014, Zaki, 2005, Nguyen and Le Van Mao, 1990a, Qi et al., 2015a), and in some cases, even lower than 200 °C (Zhi et al., 2015, Le Van Mao et al., 1987). Higher temperatures (>350 °C) promote secondary reactions of ethylene, such as oligomerisation and cracking, leading to the formation of longer-chain hydrocarbons, including gasoline-range HCs derived from light olefins (Aguayo et al., 2010, Liu et al., 2023, Van der Borgh et al., 2015b, Van der Borgh et al., 2016). Researchers have been exploring the

potential of zeolites for the conversion of alcohols, with a particular focus on methanol and ethanol (Derouane et al., 1978). The LATH conversion on ZSM-5 zeolites allows for producing a wide range of products, following the established understanding that methanol can be converted into olefins similar to ethanol (Johansson et al., 2009). Early research primarily concentrated on converting ethanol to ethylene, and later investigations delved into the production of higher HCs over ZSM-5 zeolite catalyst (Nguyen and Le Van Mao, 1990b, Aguayo et al., 2002b). To enhance catalyst performance, post-synthesis modifications are often employed. These modifications involve impregnation and ion exchange of zeolites with metal salts, phosphorus modification, alkali treatment, and steaming. These modifications of zeolites are commonly reported in research studies. They are claimed to improve hydrothermal stability, reduce deactivation, increase activity, or enhance selectivity towards specific product classes in the LATH process (Rahimi and Karimzadeh, 2011a). Furthermore, the choice of catalyst substitution method significantly impacts the catalyst's yield and lifespan (Juybar et al., 2019).

In the conversion of ethanol to hydrocarbons (ETH), the addition of various metals to HZSM-5 catalysts, including Ni, Ga, Fe, Mo and rare earth metals, has been examined (Gayubo et al., 2010b, Inaba et al., 2007, Machado et al., 2005, Goto et al., 2010b, Barthos et al., 2006). It has been observed that the addition of Ni improves the hydrothermal stability of the catalyst by affecting the balance of acid sites, which in turn impacts product distribution. Conversely, the addition of Ga to HZSM-5 has been reported to increase the synthesis of aromatics, while the addition of Fe is claimed to limit the formation of aromatics and paraffins. These effects can be attributed to a reduction in the number of hydrogen transfer processes or an increase in their rate (Van der Borght et al., 2015b). The presence of water in low-alcohol can also influence the catalytic process. Zhi et al. (2015) observed that the water content in 1-propanol impacted the unimolecular dehydration process by affecting the surface coverage of reactive intermediates during propanol dehydration. In the study by Bi et al. (2014), methanol-to-hydrocarbon (MTH) conversion was enhanced over Zn-modified HZSM-5, promoting aromatisation. However, the type of Zn species in the catalyst significantly altered the acidity of the catalyst surface, as coke deposition weakened olefin cyclisation in the early phase of the reaction. In the conversion of industrial ethanol to aromatics (ETA), Ga- and Zn-doped HZSM-5 catalysts were found to enhance catalyst lifespan and increase HC yield at the temperature of 360 °C (Saha and Sivasanker, 1992). Tynjälä et al. (1998) investigated the conversion of

alcohols (C_1 – C_4) at 370 °C using HZSM-5 and trimethyl-phosphite-modified ZSM-5 zeolites, both exhibiting weak acidity. The conversion of low alcohols, such as methanol and ethanol, on trimethyl phosphite-treated ZSM-5 primarily produced ethers. However, due to the insufficient acidity of the weak acid sites, the further conversion of ethers into longer-chain HCs was not observed (Tynjälä et al., 1998). Over time, HC products, notably aromatics, present within zeolite pores undergo a series of reactions facilitated by the hydrocarbon pool mechanism. These processes involve the methylation of aromatics formation of char and polyaromatic precursors such as coke. The accumulation of coke deposits within the zeolite pores leads to pore blockage, hindering the entry of reactants and products. Consequently, the acidic sites within the pores become inaccessible, resulting in decreased HC synthesis and catalyst stability during the reaction (Kim et al., 2010).

Despite previous studies on the LATH conversion focusing on methanol and ethanol using non-commercial ZSM-5 zeolite catalysts, there is notable limited research on propanol conversion to fuel-range HCs using similar catalysts. Specifically, the performance evaluation of newly synthesised transition metal-doped ZSM-5 zeolite catalysts for C_1 – C_3 alcohol conversion to fuel-range HCs remains unexplored. This study aims to fill this knowledge gap by investigating the relative performance of transition metal (Ni, Fe and Co) incorporation in a novel HZSM-5 catalyst (Si/Al=40) for a single-step conversion of C_1 – C_3 alcohols into C_5 + HCs. Understanding the mechanisms behind coke deposition, its correlation with catalyst properties, and the significant role of certain metals in inhibiting coke formation is essential for maintaining catalyst performance and longevity. As a result, these findings offer prospects for exploring new catalyst formulations, optimising operating conditions, and developing coke-resistant catalysts, thereby enhancing the efficiency of the LATH process.

6.2 Materials and Methods

This study made use of the following chemicals: sodium silicate solution ($(Na_2O)SiO_2 \cdot H_2O$), aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$), tetrapropyl ammonia bromide ($C_{12}H_{28}BrN$), sodium hydroxide (NaOH, 97%), sulfuric acid (H_2SO_4 , 98% conc.), ammonium nitrate (NH_4NO_3). Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), iron nitrate ($Fe_2(NO_3)_2 \cdot 18H_2O$), and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) are the precursors that are used for transition metals. Methanol, propanol, and ethanol are the feedstocks. Sigma-Aldrich supplied all chemicals. A hydrothermal reactor made of stainless steel and Teflon with a capacity of 200 mL was used to synthesise the catalyst. The support and modified catalysts were prepared, characterised and evaluated

according to *Section 3.2.2* while the TGA was conducted according to the method described in *Section 4.2*.

6.3 Results and Discussion

6.3.1 C₁-C₃ conversion over transition metal-doped catalysts

The result of the low alcohol (C₁-C₃) conversion over transition metal-doped catalysts is presented below. MTH, ETH and PTH conversion was conducted at 350 and 400 °C and WHSV of 7 and 12 h⁻¹.

6.3.2 Methanol-to-Hydrocarbon (MTH) Conversion over Transition Metal-doped HZSM-5

The MTH conversion was conducted under different operating conditions to investigate the influence of these parameters and transition metal doping on product selectivity and methanol conversion. At an operating condition of 350 °C and a WHSV of 7 h⁻¹, both unmodified (HZSM-5) and metal-modified catalysts exhibited a preference for gaseous and C₅-C₈ hydrocarbons, with over 55 % selectivity at this condition. However, the unmodified catalyst showed a significant selectivity towards C₁-C₄ hydrocarbons, reaching 40.6 %. Transition metal doping improved methanol conversion and BTX (Benzene, Toluene, and Xylene) selectivity, with the doped catalysts achieving 100 % conversion compared to 88 % for the unmodified catalyst (Figure 6.1a). BTX selectivity increased from 1.7 % for HZSM-5 to 3.9 %, 4.7 %, and 8.7 % with Co, Ni, and Fe-doped HZSM-5, respectively. Among the doped catalysts, Fe/HZSM-5 demonstrated a wide product distribution than others at this operating condition, with an appreciable preference for BTX and C₉-C₁₂ HCs. When the temperature was increased to 400 °C while maintaining a WHSV of 7 h⁻¹, the unmodified HZSM-5 catalyst exhibited increased BTX selectivity by 6.0 % and C₅-C₈ selectivity by 1.8%, resulting in a 7.8% decrease in the gaseous product compared to T=350 °C, with a conversion of 100 %. The modified catalysts showed similar selectivity towards C₅-C₈ hydrocarbons but declined gaseous HC selectivity. Co/HZSM-5 exhibited a wider product distribution, with appreciable selectivity towards C₉-C₁₂ (7.89 %) and BTX (11.9 %) compared to other doped catalysts. Ni-doped catalysts favoured C₁₂⁺ hydrocarbon production with 23 % selectivity. Increasing the WHSV to 12 h⁻¹ altered the product distribution, promoting the production of C₅-C₈ HCs (>81%) at 350 °C and (>67%) at 400 °C, with a significant decrease in gaseous products and >99 % conversion for all catalysts tested (Figure 6.1b). The reduction in C₅-C₈ HCs at 400 °C

can be attributed to a shift in the reaction pathway with an increase in temperature promoting HC cracking and other secondary reactions that alter product selectivity. While Ni-doped and HZSM-5 catalysts showed selectivity towards a wide range of liquid HCs, Co and Fe-doped catalysts did not favour C₉-C₁₂ and C₁₂+ HCs at both investigated temperatures (350 and 400 °C) at WHSV 12 h⁻¹. Among the tested catalysts, Co-doped catalysts demonstrated the most significant selectivity towards BTX (19.4%) at a WHSV of 12 h⁻¹ and 350 °C. Overall, the MTH process exhibited a preference for C₅-C₈ and BTX liquid hydrocarbon products over the tested catalysts.

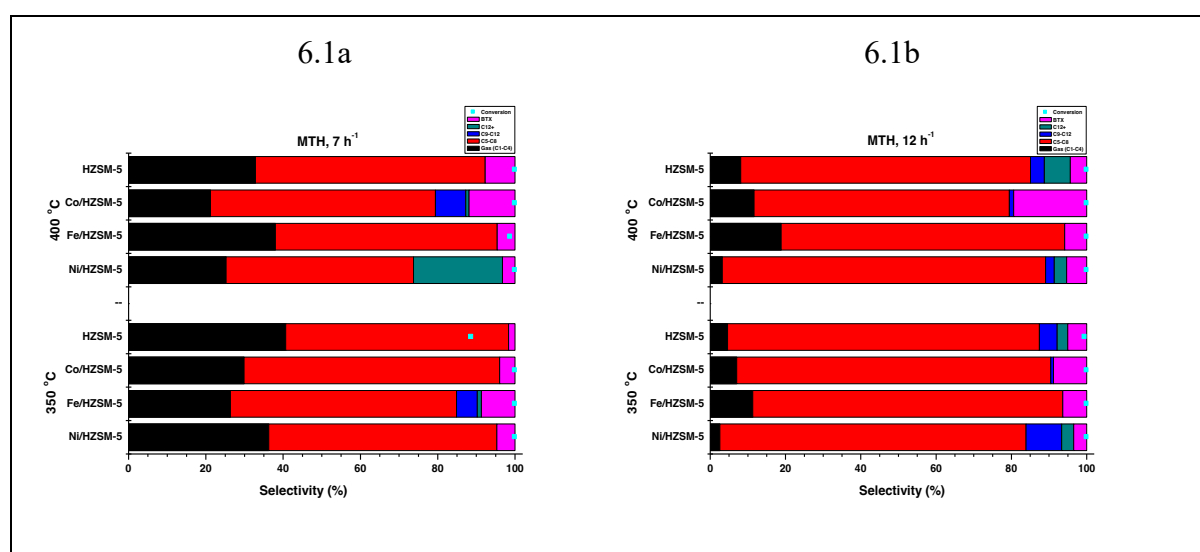


Figure 6-1a & b. Product distribution and methanol conversion in the MTH process

6.3.3 Ethanol-to-Hydrocarbon (ETH) Conversion over Transition Metal-doped HZSM-5

The ETH conversion was investigated at similar operating conditions (WHSV = 7 and 12 h⁻¹ and T= 350 and 400 °C). At a WHSV of 7 h⁻¹, the doped catalysts exhibited preference towards C₅-C₈, C₉-C₁₂, and BTX HC, while the unmodified catalysts favoured C₁₂+ hydrocarbons at both temperatures. Among the metal-doped catalysts, Ni/HZSM-5 showed selectivity towards C₉-C₁₂ (49.9%) and BTX (10.6%), whereas Co/HZSM-5 favoured C₅-C₈ HCs at 7 h⁻¹ and 350 °C. The unmodified HZSM-5 catalyst exhibited the highest C₁₂+ (65.8%) hydrocarbon selectivity, followed by Co/HZSM-5 (29.1%). Increasing the temperature to 400 °C at the same WHSV of 7 h⁻¹ resulted in increased C₅-C₈ HC selectivity for all catalysts, accompanied by a decrease in gaseous products (C₁-C₄) and >99 % ethanol conversion (Figure 6.2a). Co/HZSM-5 and Fe/HZSM-5 catalysts showed increased C₅-C₈ selectivity by 15.6% and 25.8% and BTX selectivity by 0.87 % and 10.5 %, respectively. Ni/HZSM-5 exhibited a 2.9% increase in C₉-

C₁₂ selectivity and a corresponding 2.1% decrease in C₁₂⁺ selectivity, while HZSM-5 showed a 36.1 % decrease in C₁₂⁺ selectivity. Higher temperatures promoted rearrangement and cyclisation reactions, favouring the formation of higher-molecular-weight hydrocarbons. This can be attributed to the secondary reactions of reactive intermediates formed during ethanol conversion, leading to C₅⁺ HCs through alkylation, cyclisation, and rearrangement reactions (Gamliel et al., 2017). Increasing the WHSV to 12 h⁻¹ resulted in reduced gaseous HCs (C₁-C₄), increased C₁₂⁺ selectivity, and >98 % ethanol conversion, indicating a shift towards liquid HC production at all temperatures investigated (Figure 6.2b). This can be attributed to less contact time created by the increased WHSV promoting the production of liquid HCs while hindering the HC cracking process. Metal-modified catalysts showed selectivity towards C₅-C₈, C₉-C₁₂, and BTX HCs, while the unmodified catalysts improved C₁₂⁺ HCs at 7 h⁻¹ and 350 °C. Among the catalysts, Ni/HZSM-5 exhibited the highest C₅-C₈ (48.4 %) and BTX (5.0 %) selectivity, and Fe/HZSM-5 enhanced C₉-C₁₂ (37.0 %). Similarly, HZSM-5 showed the highest C₁₂⁺ selectivity (52.1 %), followed by Co/HZSM-5 (40.1 %) at 7 h⁻¹ and 350 °C. Increasing the temperature to 400 °C at a WHSV of 12 h⁻¹ resulted in a shift in product distribution, with increased C₅-C₈ (51-75 %) and BTX (>2 %) selectivity compared to the operating temperature of 350 °C. However, C₉-C₁₂ HCs were not favoured by all catalysts at this operating temperature, indicating the influence of reaction kinetics and catalyst properties on selectivity.

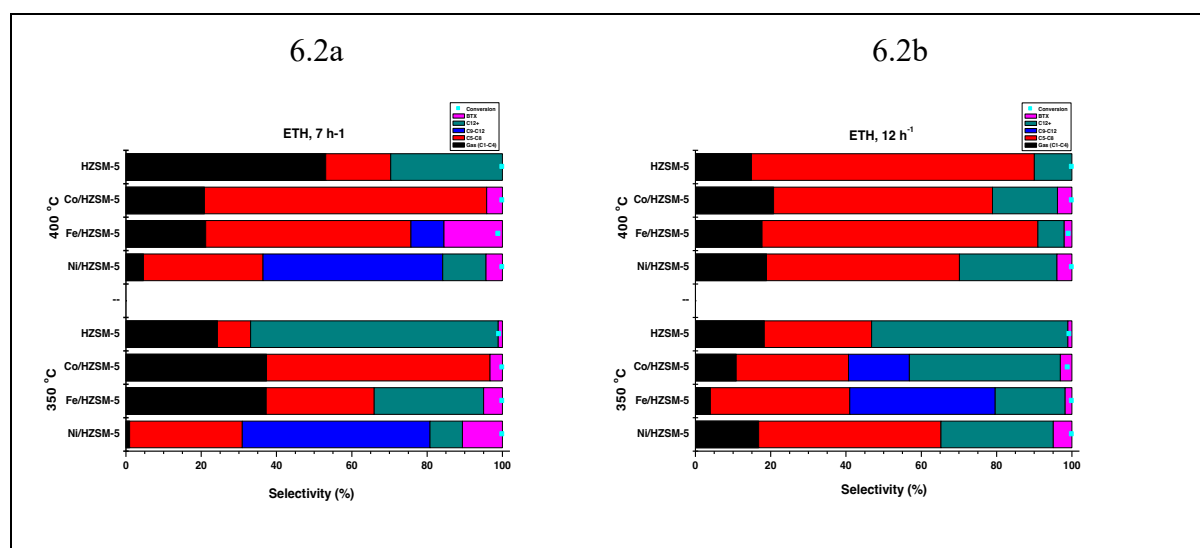


Figure 6-2a & b. Product distribution and ethanol conversion in the ETH process

6.3.4 Propanol-to-Hydrocarbon (PTH) Conversion over Transition Metal-doped HZSM-5

The PTH conversion was investigated at WHSV of 7 and 12 h⁻¹ and temperatures of 350 and 400°C (Figure 6.3a & b). At a WHSV of 7 h⁻¹, propanol conversion rates exceeding 96 % were achieved, and all catalysts exhibited broad product distributions with significant selectivity towards gaseous products (C₁-C₄), C₅-C₈, and C₁₂⁺, at both temperatures. Among the catalysts tested at a WHSV of 7 h⁻¹ and a temperature of 350 °C, Ni/HZSM-5 exhibited the highest selectivity towards BTX (12.4 %) and C₁₂⁺ HCs (22.1 %), while Fe/HZSM-5 favoured C₅-C₈ (53.1 %) and C₉-C₁₂ (6.3 %). Co/HZSM-5 showed a preference for C₅-C₈ (43.9 %) and C₁₂⁺ (21.7 %) HCs. Increasing the temperature to 400°C at a WHSV of 7 h⁻¹ slightly altered the product distribution. The metal-doped catalysts exhibited high selectivity towards specific HC fractions, particularly C₅-C₈ (34.1 - 57.4%) and BTX (2.6 - 19.4 %). Co and Ni-doped catalysts displayed the highest selectivity towards these HC fractions. For Ni/HZSM-5, a decrease in the selectivity of C₁-C₄ and C₁₂⁺ HCs led to a corresponding increase in C₅-C₈, C₉-C₁₂, and BTX by 12.5 %, 3.7 %, and 7.1%, respectively. Fe/HZSM-5 exhibited an increase of 9.0% in C₁-C₄, 9.6% in C₁₂⁺, and 2.3% in BTX, with a decline of >1.5 % in the selectivity of other HC fractions. Co/HZSM-5 recorded a 13.5 % increase in C₅-C₈ selectivity, decreasing the selectivity of other HC fractions. The unmodified catalyst showed a 1-6 % increase in all HC fractions, except for C₅-C₈ HC, which experienced a 16.8 % decrease in selectivity at 7 h⁻¹ WHSV and temperature of 400°C.

At a WHSV of 12, the PTH conversion revealed a significant decline in gaseous HCs, leading to an increase in the selectivity of liquid HCs fraction (C₅⁺) at all temperatures tested. Different catalysts exhibited the highest selectivity for various HC fractions: Ni/HZSM-5 achieved 89.8% selectivity for C₁₂⁺, Co/HZSM-5 reached 88.6% selectivity for C₅-C₈, and Fe/HZSM-5 recorded selectivities of 22.0%, 11.6%, and 1.9% for C₉-C₁₂, C₁-C₄, and BTX HC fractions, respectively, at 12 h⁻¹ and 350°C. However, the unmodified catalyst exhibited a product distribution comparable to the metal-doped catalysts at this operating condition. At 400°C and 12 h⁻¹, with a propanol conversion rate of >98%, a moderate change in the product distribution was observed, including a decline in gaseous products and an increase in BTX. Although a similar trend was observed at a WHSV of 7 h⁻¹, the changes varied across different HC fractions. Compared to the selectivity at 350°C, the unmodified HZSM-5 catalysts showed a significant selectivity towards C₁₂⁺ HCs (80.0 %), decreasing the selectivity of other fractions.

Ni/HZSM-5 promoted the selectivity of C₅-C₈, C₉-C₁₂, and BTX by 51.7 %, 6.6 %, and 10.8 %, respectively, attributed to a significant decrease in C₁₂⁺ selectivity. On the other hand, Fe and Co-doped HZSM-5 catalysts drastically increased the selectivity of C₅-C₈ and C₁₂⁺ HCs by 16.6% and 8.3%, respectively. These findings demonstrate the influence of temperature, WHSV, and catalyst type on the product distribution and selectivity of HC fractions in the PTH process.

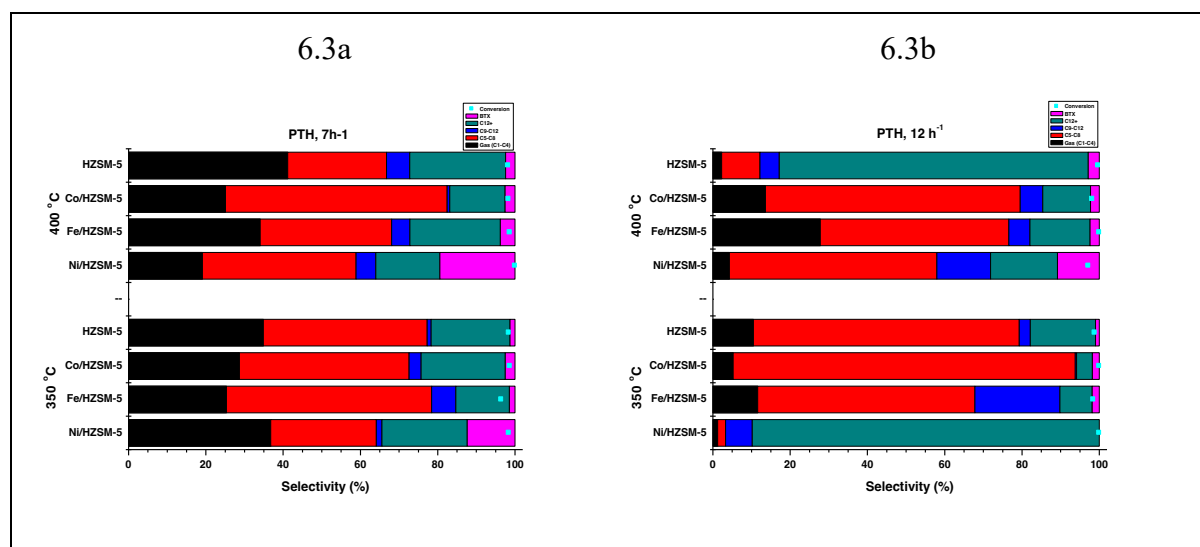


Figure 6-3a & b. Product distribution and propanol conversion in the PTH process

6.3.5 Comparative Evaluation of Catalyst Performance in LATH Conversion

Table 6.1 presents the average performance of various catalysts in the LATH conversion, while Figure 6.4 illustrates their average conversion and phase selectivity of different low alcohols. All values reported in this comparative study are average values. In the MTH process, there is no significant change in selectivity towards C₅-C₈ and C₉-C₁₂ HCs, with all catalysts recording an average selectivity of 68-69 % and 1-3%, respectively. Ni-doped HZSM-5 exhibited the highest selectivity for C₁₂⁺, while Co/HZSM-5 favours BTX among all the tested catalysts. The unmodified catalyst lags behind the modified catalysts by approximately 3 % in methanol conversion. Additionally, compared to other catalysts, Ni and Co-doped HZSM-5 demonstrated slightly higher selectivity towards liquid HCs, with 83 % and 82 %, respectively. In the PTH process, the highest selectivity of 63.9 % for C₅-C₈ is observed over Co/HZSM-5, Fe/HZSM-5 recorded a selectivity of 9.6 % for C₉-C₁₂, Ni/HZSM-5 showed selectivity of 36.4 % for C₁₂⁺ and 10.7 % for BTX. All catalysts exhibited similar propanol conversion rates, averaging 98.7%. Similar to MTH, PTH also favours liquid HCs in terms of phase selectivity, with Ni and Co-doped HZSM-5 catalysts showing slightly higher selectivity compared to

Fe/HZSM-5 and HZSM-5, which exhibited slightly higher selectivity towards gaseous HCs (C_1 - C_4). Furthermore, in the ETH process, all tested catalysts achieved approximately 100% conversion, with similar phase selectivity except for Ni/HZSM-5, which recorded the highest selectivity of 89.7% towards liquid HCs. Ni/HZSM-5 and Co/HZSM-5 demonstrate the highest average selectivity for C_9 - C_{12} and C_5 - C_8 at 24.4 and 55.6 %, while Fe/HZSM-5 and HZSM-5 promote the production of BTX (6.1 %) and C_{12+} (39.4%) HCs respectively. Compared to methanol feedstock, the performance of ethanol in LATH conversion displays a strong correlation with propanol, as evidenced by their similar percentage selectivity to HC fractions, as shown in Table 6.1. While methanol feedstock exhibits greater selectivity towards C_5 - C_8 and BTX, ethanol and propanol show a broader product distribution, favouring longer-chain HCs. This suggests that the feedstock type is another determining factor in altering the product distribution, in addition to the influence of different catalysts and operating parameters. The observed trend exhibited by different feedstocks may be attributed to several factors, including the molecular size of low alcohols, carbon chain length, and diffusion rates.

Methanol has the smallest molecular size; hence higher adsorption uptake among the three low-alcohol feedstocks investigated, followed by ethanol and propanol (kinetic diameter, $3.6 \text{ \AA} < 4.3 \text{ \AA} < 4.9 \text{ \AA}$) (Tang et al., 2019, Song et al., 2015). This size difference influences their behaviour within the 1D pores). The size of the alcohol molecule affects the reactivity and diffusion properties during catalytic conversion. Smaller molecules like methanol are generally more reactive than larger molecules like ethanol and propanol (Hamins and Seshadri, 1986, Tang et al., 2019). In addition, higher diffusion rates tend to favour the production of smaller chain hydrocarbons in low-alcohol conversion processes. Diffusion plays a crucial role in the reaction kinetics and mass transfer during the conversion of alcohols to hydrocarbons. When the diffusion rate is high, reactant molecules can more readily access the catalyst's active sites, leading to a higher frequency of collisions and a higher reaction rate. However, in the case of low alcohol conversion, higher diffusion rates also promote the rapid transport of intermediates and products away from the active sites, limiting their further reactions. With higher diffusion rates, the intermediates and products are more likely to diffuse away before undergoing further reactions, resulting in a greater proportion of smaller chain hydrocarbons in the case of methanol feedstock. On the other hand, slower diffusion rates can promote longer chain growth by allowing more time for the intermediates to interact with the catalyst and undergo subsequent reactions, such as oligomerisation and polymerisation, leading to the formation of

larger hydrocarbon molecules as exhibited in ETH and PTH process. Furthermore, the carbon chain length and the functional group bound impact the low alcohol reactivity, product type and distribution. Methanol is one-carbon alcohol, ethanol is two-carbon alcohol, and propanol is three-carbon alcohol, all possessing different alkyl groups. The functional group attached to a methyl group experiences less steric hindrance than one attached to an ethyl or larger hydrocarbyl group (Lamy et al., 2001, Zhou et al., 2004, Hamins and Seshadri, 1986). Longer carbon chains tend to favour the production of higher molecular weight HCs in the case of ethanol and propanol. However, it's important to note that aside from low alcohol feedstock, specific conditions, such as catalyst type, temperature, and WHSV, also influence product distribution in low alcohol conversion processes. The impact of diffusion rates should be considered in conjunction with these factors to understand the overall outcome of the process. Table 6.2 present the average catalyst preference for HC fractions in LATH conversion.

Table 6-1. Summary of (average) product selectivity and conversion (%) in LATH (C₁-C₃) conversion over metal-doped HZSM-5 catalysts

MTH Conversion							
Catalysts	Gas (C₁-C₄)	C₅-C₈	C₉-C₁₂	C₁₂+	BTX	Conversion	Liquid
ZSM-5	21.54	69.24	2.09	2.44	4.69	97.03	78.46
Ni/HZSM-5	16.80	68.70	2.94	7.36	4.19	100.00	83.20
Fe/HZSM-5	23.60	68.42	1.34	0.26	6.38	99.69	76.40
Co/HZSM-5	17.44	68.90	2.43	0.21	11.02	100.00	82.56
Average	19.85	68.81	2.20	2.57	6.57	99.18	80.15

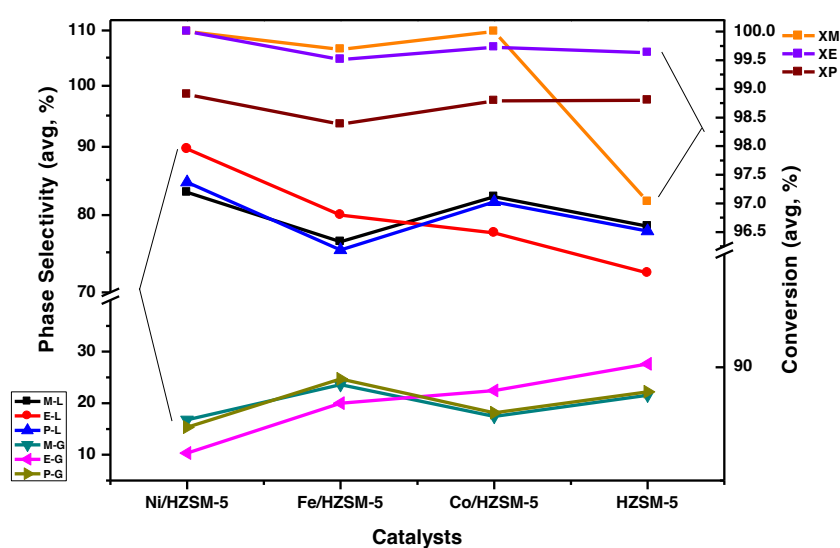
ETH Conversion							
Catalysts	Gas (C₁-C₄)	C₅-C₈	C₉-C₁₂	C₁₂+	BTX	Conversion	Liquid
ZSM-5	27.63	32.44	0.00	39.38	0.54	99.63	72.37
Ni/HZSM-5	10.32	40.35	24.41	18.94	5.99	100.00	89.68
Fe/HZSM-5	20.02	48.38	11.85	13.68	6.08	99.51	79.98
Co/HZSM-5	22.45	55.58	4.04	14.33	3.60	99.72	77.55
Average	20.11	44.19	10.08	21.58	4.05	99.72	79.89

PTH Conversion							
Catalysts	Gas (C₁-C₄)	C₅-C₈	C₉-C₁₂	C₁₂+	BTX	Conversion	Liquid

ZSM-5	22.20	36.67	3.72	35.51	1.90	98.80	77.80
Ni/HZSM-5	15.35	30.70	6.84	36.45	10.66	98.90	84.65
Fe/HZSM-5	24.69	48.04	9.61	15.29	2.38	98.38	75.31
Co/HZSM-5	18.15	63.93	2.48	13.16	2.28	98.79	81.85
Average	20.10	44.84	5.66	25.10	4.30	98.72	79.90

Table 6-2. Catalyst preference for HC fractions in LATH (C_1 - C_3) conversion: *An average evaluation*

Catalysts	Gas (C_1 - C_4)	C_5 - C_8	C_9 - C_{12}	C_{12}^+	BTX	Conversion	Liquid
ZSM-5	23.79	46.12	1.94	25.78	2.38	98.49	76.21
Ni/HZSM-5	14.16	46.58	11.40	20.92	6.95	99.63	85.84
Fe/HZSM-5	22.77	54.95	7.60	9.74	4.95	99.19	77.23
Co/HZSM-5	19.35	62.80	2.98	9.23	5.63	99.50	80.65



(XM, XE, XP – M, E, & P conversion; M-L, E-L, P-L and M-G, E-G, P-G – Liquid and gaseous HC products from MTH, ETH, PTH)

Figure 6-4. Average phase selectivity and conversion in the LATH process over metal-doped catalysts

The conversion of low alcohols to hydrocarbons (LATH) has been extensively investigated using various catalysts, predominantly zeolites/modified zeolites (Gayubo et al., 2001, Aguayo et al., 2002a, Gayubo et al., 2010b, Gayubo et al., 2011, Sun and Wang, 2014). Depending on the catalyst employed, different reaction mechanisms have been proposed. In the case of ZSM-

5 zeolite catalysts, the mechanism of LATH is suggested to involve an intermediate species, with hydrocarbon production occurring through secondary reactions (Chang, 1991, Sun and Wang, 2014). Specifically, for this study, we hypothesised that low alcohols initially undergo dehydration to form olefins, followed by the conversion of olefins into hydrocarbons (including C_3+ olefins, BTX, and C_5+) via acid-catalysed oligomerisation-cracking and oligomerisation-aromatisation mechanisms. Similar pathways have also been reported in other studies (Dongliang et al., 2021, Sun and Wang, 2014). Generally, the mechanism of MTH consists of methanol dehydration and hydrocarbon production via the hydrocarbon pool mechanism. The MTH pathway is an autocatalytic process which proceeds through several steps. Initially, methanol molecules are adsorbed onto the acid sites of the ZSM-5 catalyst through hydrogen bonding and van der Waals interactions. Dehydration of the adsorbed methanol occurs, forming dimethyl ether (DME - CH_3OCH_3) as intermediate. This intermediate, CH_3OCH_3 , can undergo further reactions, including carbocation formation through proton transfer from the acid site to the methoxy group. Subsequently, alkyl migration within the zeolite channels or pores leads to structural rearrangements and the formation of different HC isomers, while oligomerisation and polymerisation reactions promote the growth of HC chains (C_5+). Furthermore, other reactions, such as cracking and fragmentation, can break down larger HC molecules into smaller fragments, generating various HC products. Ultimately, the hydrocarbon products desorb from the catalyst surface, providing the desired products of the MTH conversion process (Chang, 1991, Sun and Wang, 2014, Dongliang et al., 2021).

It was believed that ethanol primarily undergoes intermolecular dehydration to form ethylene and diethyl ether (DEE) through a concerted mechanism (Tanabe, 2012). DEE can undergo cracking to produce additional ethylene, providing an alternative reaction pathway (Fig. 6.5). The cracking of DEE occurs via acid-catalysed or radical mechanisms. Ethylene generated from dehydration and DEE cracking can undergo dehydrogenation to form ethyl radicals. These ethyl radicals from dehydrogenation react with adsorbed HC species on ZSM-5 catalyst, forming carbocations, which participate in secondary reactions such as aromatisation leading to aromatics (BTX) and long chain (C_5+) HCs through oligomerisation (Sun and Wang, 2014, Tanabe, 2012, Ramasamy and Wang, 2014, Iadrat and Wattanakit, 2021). Similar mechanisms apply to secondary and tertiary alcohols like isopropanol, where propene is an intermediate produced via dehydration. Propene can undergo further reactions to yield various hydrocarbon

products (Kwak et al., 2011, Roy et al., 2012, Janik et al., 2009). The presence of metal species in the doped HZSM-5 catalysts promotes the initial dehydration of low alcohol to form intermediate including olefins, followed by the oligomerisation and cracking of this intermediate to form a range of hydrocarbons and coke deposition. For this study, we believe that intermediate formation is favoured by the presence of Ni^{2+} or Co^{2+} or Fe^{3+} species, which act as active Lewis acid sites, promoting the dehydration of low alcohols (Sun and Wang, 2014, Chang, 1991). However, the presence of Co^{2+} species on the catalyst surface can also promote the formation of methane, which is undesirable in the ETH reaction. In addition, the presence of Fe^{3+} species can also promote coke formation via a mechanism involving the dehydrogenation of ethylene to form ethyl radicals, followed by the addition of ethyl radicals to form higher hydrocarbons and coke. The formation of coke can lead to the deactivation of the catalyst and the loss of activity and selectivity towards the desired hydrocarbon products (Sun and Wang, 2014).

Furthermore, the appreciable performance of the novel catalyst used in this study can also be attributed to the low Si/Al (40). Costa et al. (1985) established that the production of liquid HCs is more favourable on HZSM-5 zeolites with low Si/Al ratios. In a separate investigation, Talukdar et al. (1997) studied the conversion of a 50 % ethanol aqueous solution using two ZSM-5 catalysts with Si/Al of 20 and 103. The zeolite with a Si/Al of 20 exhibited superior yields in liquid HCs, whereas the catalyst with a higher ratio (103) predominantly favoured light molecular weight ($\text{C}_2\text{-C}_4$) HCs. This demonstrates the suitability of zeolite catalysts with lower Si/Al ratios and increased acidity for converting ethanol into C_5+ HCs. In recent research (Madeira et al., 2012), ZSM-5 catalysts with different Si/Al (16 to 500) were evaluated for their potential for ETH conversion. The catalyst with low Si/Al (<50) demonstrated significant stability and product selectivity towards heavier molecular (C_5+) HCs, indicating an equilibrium between the Brønsted acid sites and radicals on the active catalysts.

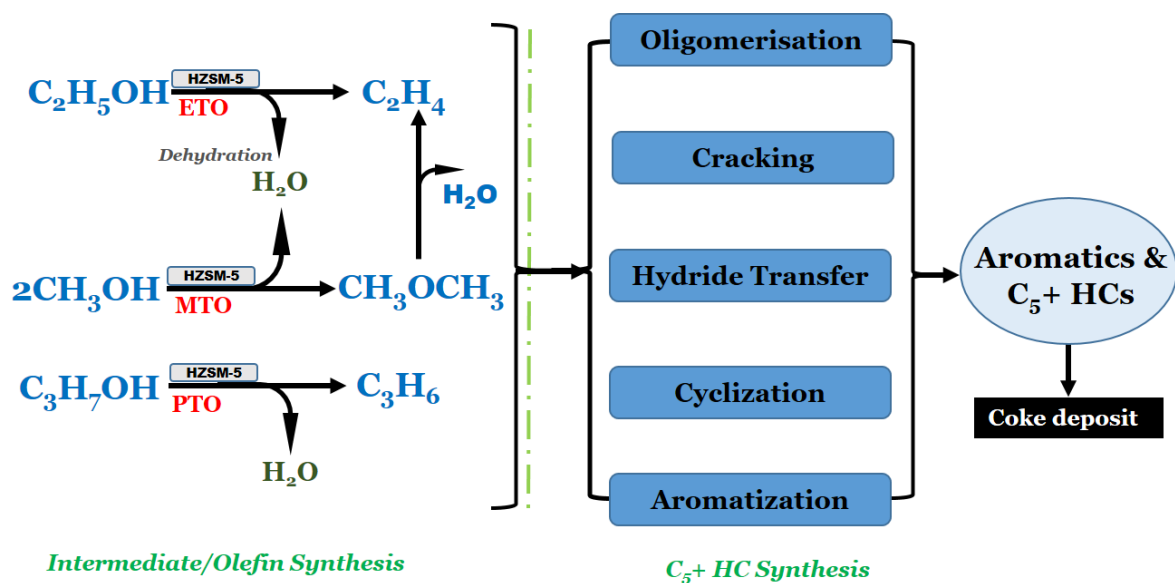


Figure 6-5. Reaction pathway for the conversion of low alcohols (methanol, ethanol and propanol) to hydrocarbons

6.3.6 Analysis of Spent Catalysts

6.3.6.1 Catalyst Coking and Deactivation – TGA-DTA Study

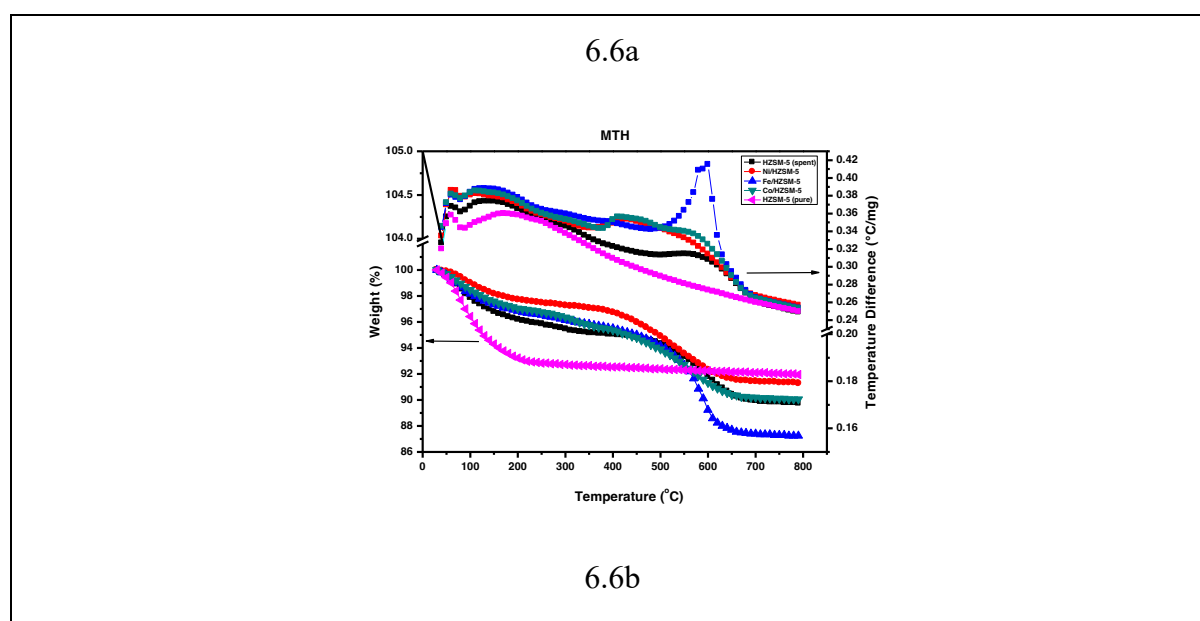
The deposition of coke on spent catalysts after LATH ($T=350^{\circ}\text{C}$ and $\text{WHSV}=7\text{ h}^{-1}$) was investigated using TGA-DTA. The calculation of coke deposition excluded the weight loss in the temperature range of $0\text{--}200^{\circ}\text{C}$, which mainly corresponds to the removal of absorbed water and volatile compounds. Weight loss between $200\text{--}400^{\circ}\text{C}$ and $400\text{--}600^{\circ}\text{C}$ was attributed to the combustion of soft and hard coke, respectively, while weight loss between $600\text{--}800^{\circ}\text{C}$ indicated the removal of non-volatile and heavy compounds attached to the catalyst after the reaction (Ahmed et al., 2011). The pure sample, denoted as HZSM-5 (pure), served as a reference and showed the lowest weight loss (at $200\text{--}800^{\circ}\text{C}$) among all the processes, as it did not undergo HC reaction and had no coke deposition. In the MTH process, Fe/HZSM-5 exhibited the lowest deposition of soft coke, with a weight loss of 0.99 wt% among the spent catalysts, followed by the Ni and Co-doped catalysts, while the unmodified catalysts showed the highest soft coke deposit (1.7 wt%) (Figure 6.6a). This showed the ability of metal species to impede the formation of coke. Ni/HZSM-5 demonstrated exceptional stability with the least coke deposition (3.3 wt%) between $400\text{--}600^{\circ}\text{C}$, whereas Co/HZSM-5 exhibited the highest weight loss (6.3 wt%) due to increased deposition of hard coke, making it prone to deactivation. The accumulation of non-volatile compounds was more evident in the Ni-doped catalyst, resulting

in the highest weight loss (2.1 wt%) compared to other spent catalysts. The trend of weight loss due to the burning of coke deposits (200-600°C) followed the order: Ni/HZSM-5 < Fe/HZSM-5 < HZSM-5 < Co/HZSM-5.

Similar to MTH, Ni/HZSM-5 exhibited significant stability with the least weight reduction at 200-400°C (0.6 wt%) and 400-600°C (2.8%) among the spent catalysts in ETH conversion (Figure 6.6b). The unmodified catalyst also demonstrated comparable stability, accounting for 0.7 and 3.1 wt% weight loss from the combustion of soft and hard coke, while the Co-doped catalyst exhibited the least stability and a higher tendency for deactivation, with weight losses of 2.2% and 4.5% respectively. However, compared to other catalysts, the unmodified catalyst (HZSM-5) showed the highest accumulation of non-volatile and heavy compounds, resulting in a significant decrease in catalyst weight (3.3 wt%) at 600-800°C, while other catalysts recorded weight losses ranging from 1.2 to 1.8 wt%. The trend of coke deposition and weight loss in the ETH process followed the pattern: Ni/HZSM-5 < HZSM-5 < Fe/HZSM-5 < Co/HZSM-5, with weight losses of 3.4, 3.7, 5.0, and 6.7 wt% respectively. Interestingly, Co/HZSM-5 exhibited the lowest weight loss in the PTH conversion as opposed to MTH and ETH, with 0.8% and 2.8% attributed to the burning of soft and hard coke and 1.4% due to the removal of non-volatile compounds (Figure 6.6c). Fe/HZSM-5 displayed the least stability in the PTH process, with coke deposition accounting for 3.3% and 3.7%, respectively. The trend of coke deposition in the PTH process followed the order: Co/HZSM-5 < HZSM-5 < Ni/HZSM-5 < Fe/HZSM-5, i.e., 3.6, 4.5, 4.2, 7.0 wt% weight loss respectively. Due to the presence of an additional carbon atom in propanol compared to ethanol, it exhibits higher susceptibility to carbon-carbon bond cleavage reactions. As a result, more reactive intermediates are formed, which can further polymerize into coke precursors. This explains the increased deposition of coke in the PTH process.

The discrepancies in stability and coke deposition of different catalysts examined can be attributed to different factors. It is important to note that coke deposition in zeolite catalysts is a complex phenomenon influenced by multiple factors which can interact. Experimental conditions, such as temperature, space velocity, metal type, catalyst properties, feedstock type, and reaction pathway and kinetics, including the rate of dehydrogenation and subsequent reactions, can play a role in determining coke deposition. Contrary to MTH and ETH, the lowest coke deposition exhibited by Co/HZSM-5 in PTH was suggested to be due to different molecular structures and properties of the low alcohol feedstock. Among the catalysts

investigated for coke deposition from the LATH conversion, Ni/HZMS-5 exhibited the highest stability with the lowest cumulative coke deposition (12.0 wt%) followed by HZSM-5 (14.1 wt%), Fe/HZSM-5 (17.4 wt%) and finally Co/HZSM-5 which recorded the highest cumulative weight loss at 17.9 wt%. The significant stability exhibited by the incorporation of Ni into the zeolite framework can be due to strong metal-support interactions, which enhance the stability of the catalyst. This suggests that the presence of active metals, in some cases, can suppress coke formation and promote the cracking of coke precursors to enhance the formation of desired products. Other studies have reported a similar trend (Persson et al., 2019a, Su et al., 2016). The weight loss observed in the Thermogravimetric Analysis (TGA) pattern corresponds to the Differential Thermal Analysis (DTA) profile in Figures 6.6a-c. Notably, the DTA peaks associated with coke combustion align with the weight loss observed in the TGA patterns. This correlation indicates the tendency of coke deposition and subsequent catalyst deactivation in the examined spent catalysts. Table 6.3 presents the average weight loss of spent catalysts after LATH conversion.



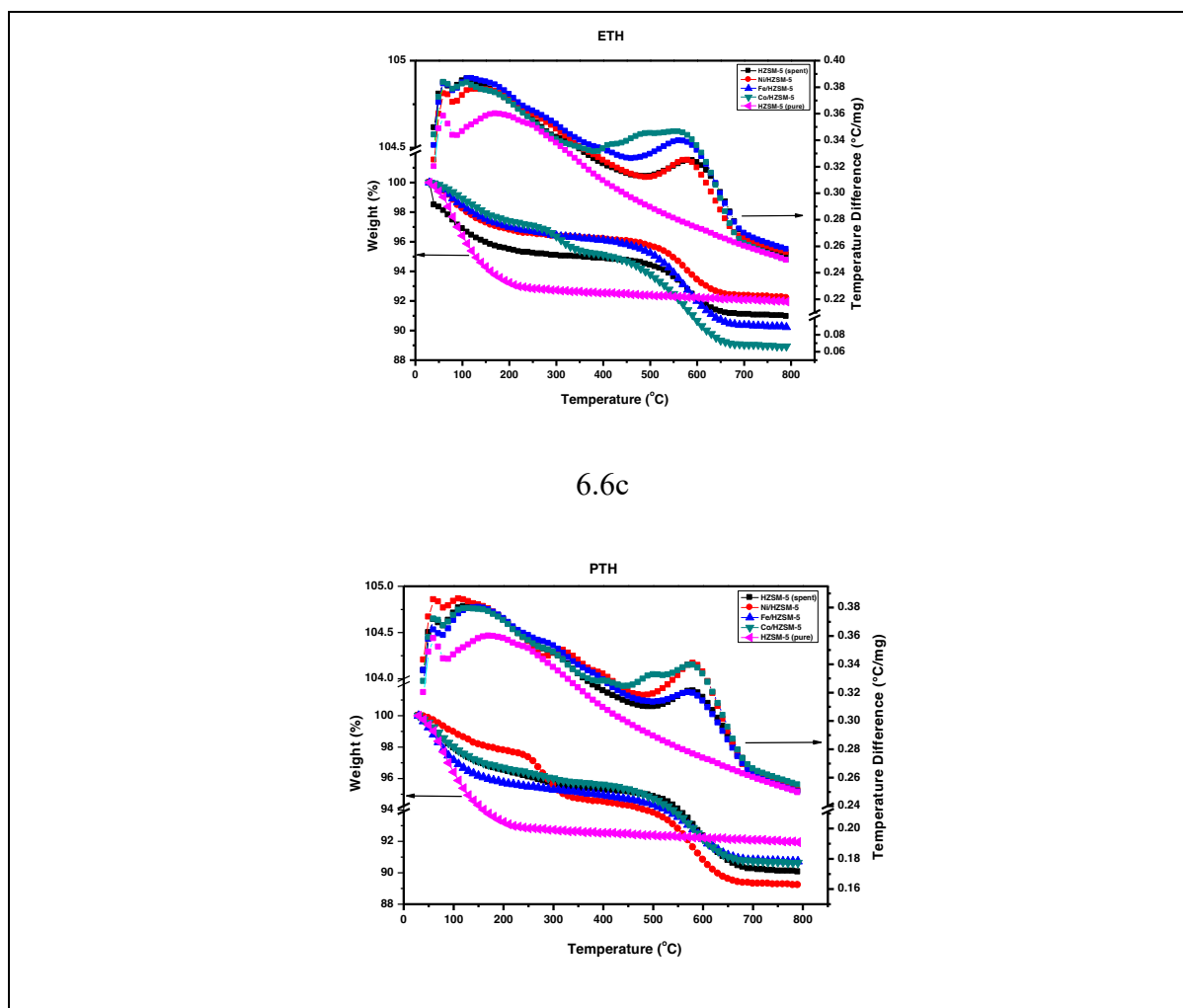


Figure 6-6a, b & c. TGA-DTA profile of (a) MTH, (b) ETH and (c) PTH conversion at $T=350^{\circ}\text{C}$ and $\text{WHSV}=7\text{ h}^{-1}$

Table 6-3. Comparative evaluation of average weight loss (wt%) of spent catalysts at $T=350^{\circ}\text{C}$ and $\text{WHSV}=7\text{ h}^{-1}$

Temperature	Ni/HZSM-5	Fe/HZSM-5	Co/HZSM-5	HZSM-5 (spent)	HZSM-5 (pure)
MTH					
0-200 (W+V)	3.8	2.28	3.16	2.96	6.78
200-600 (S+H)	4.39	5.39	7.61	5.71	0.98
200-800 (WV+SH+NV)	6.46	6.43	9.58	7.00	1.28
ETH					
0-200 (W+V)	3.21	2.99	2.61	2.57	6.78

200-600 (S+H)	3.35	5.01	6.74	3.80	0.98
200-800 (WV+C+NV)	4.59	6.77	8.46	7.05	1.28
PTH					
0-200 (W+V)	9.95	10.79	9.28	9.37	8.06
200-600 (S+H)	4.21	6.96	3.57	4.54	0.98
200-800 (WV+C+NV)	6.48	8.58	5.01	6.07	1.28

Weight loss due to W+V – absorbed H₂O & volatiles; S+H – soft and hard coke; NV – non-volatiles

According to reports by Chen et al. (2007a). and Guisnet (2002), the retention of organic species within the ZSM-5 zeolite plays a crucial role in the LATH process. Initially, these organic species act as active sites, but as the process progresses, they inhibit catalytic activity. During the induction phase, the proposed mechanism is based on the hydrocarbon pool model, which suggests that the active sites in the zeolite are hybrid organic-inorganic structures consisting of cyclic organic species within the zeolite framework. Interestingly, the yields of olefins and aromatics do not remain high during the initial reaction. Olsbye et al. (2005) investigated the retained material in catalysts such as Hbeta, SAPO-34, and H-ZSM-5 after conversion. They found that the development of the hydrocarbon pool involves the breakdown of reactants, and once the pool is formed, the olefins and aromatics desorb from the catalysts. However, the active organic species can transform into larger aromatic molecules, depositing in the catalyst's pores and surface, which leads to pore blockage and decreased catalytic performance. At low temperatures, carbonaceous deposits known as soft coke mainly consist of oligomers and polymers derived from the reactant through condensation and rearrangement processes. In contrast, high-temperature coke or coke formed over a prolonged time-on-stream is primarily composed of polyaromatics (hard coke), requiring not only condensation and rearrangement steps but also various hydrogen-transfer and dehydrogenation steps on acidic catalysts (Zhang et al., 2014).

The presence of active metals can affect the production and distribution of coke deposits on the catalyst's surface and the coke deposits' nature and content. Metal-loading of the catalyst greatly increases the amount of coke production, which can be attributed to an increased concentration of total acid sites compared to HZSM-5. However, Ni-doped displayed appreciably greater stability than HZSM-5 catalysts. It is possible to ascribe the amount of coke created on the catalyst to depend on the strength of the acid sites and the metal impregnated on

the catalyst. Co/HZSM-5 and Fe/HZSM-5 are two examples of catalysts that display the most severe coking, which suggests a short lifetime in continuous operations. The addition of metals, on the other hand, speeds up the combustion of coke. According to the findings of the TGA, the temperature at which the catalyst is regenerated falls within the range of 500–600 °C. Further, the regeneration temperature may be lower for metal-loaded catalysts. This can be attributed to the catalytic effect that impregnated metals have on burning carbonaceous materials (Weisz and Goodwin, 1966). A lower catalyst regeneration temperature reduces strain on the catalyst, potentially leading to an extended lifetime in industrial applications (Gayubo et al., 2004, Persson et al., 2019b).(Gayubo et al., 2004, Persson et al., 2019b). Nevertheless, further research is required to validate this hypothesis.

6.3.6.2 *Structural and Morphological Properties of spent catalysts from ETH*

The XRD analysis of spent HZSM-5, Ni/HZSM-5, Fe/HZSM-5, and Co/HZSM-5 catalysts after ETH conversion provided valuable information about the structural changes in the catalyst after the catalytic reaction. The XRD patterns of spent catalysts show a decrease in the intensity of diffraction peaks which is more prominent in Co/HZSM-5 catalyst due to the catalytic reaction and the accumulation of coke deposits (Figure 6.7a). The intensity reduction is more pronounced in the (101) and (200) planes, which are the most sensitive to structural changes. In addition, the XRD pattern also revealed that the MFI zeolite framework was retained after the catalytic process, irrespective of the carbon deposition. The extent of framework collapse is less pronounced in the Ni-doped catalysts than in other catalysts. This suggests that active Ni metal can stabilise the zeolite structure and somewhat mitigate framework collapse. Nevertheless, the substantial decrease in the characteristic peak (7-9°) of the Co/HZSM-5 catalyst corresponds to an increased coke deposit on the catalyst. This observation aligns with the TGA-DTA results, which indicate that Ni/HZSM-5 and Co/HZSM-5 exhibited the lowest and highest coke deposition after the ETH conversion. The SEM images of spent catalysts typically show surface features such as aggregates of small crystals to form microspheres (Figure 6.7b) similar to the original catalyst. The SEM images can also partly observe coke deposits on the catalyst surface as dark regions. The presence of active metals can influence the formation and distribution of coke deposits on the catalyst surface, which may affect the modified catalyst's surface features.

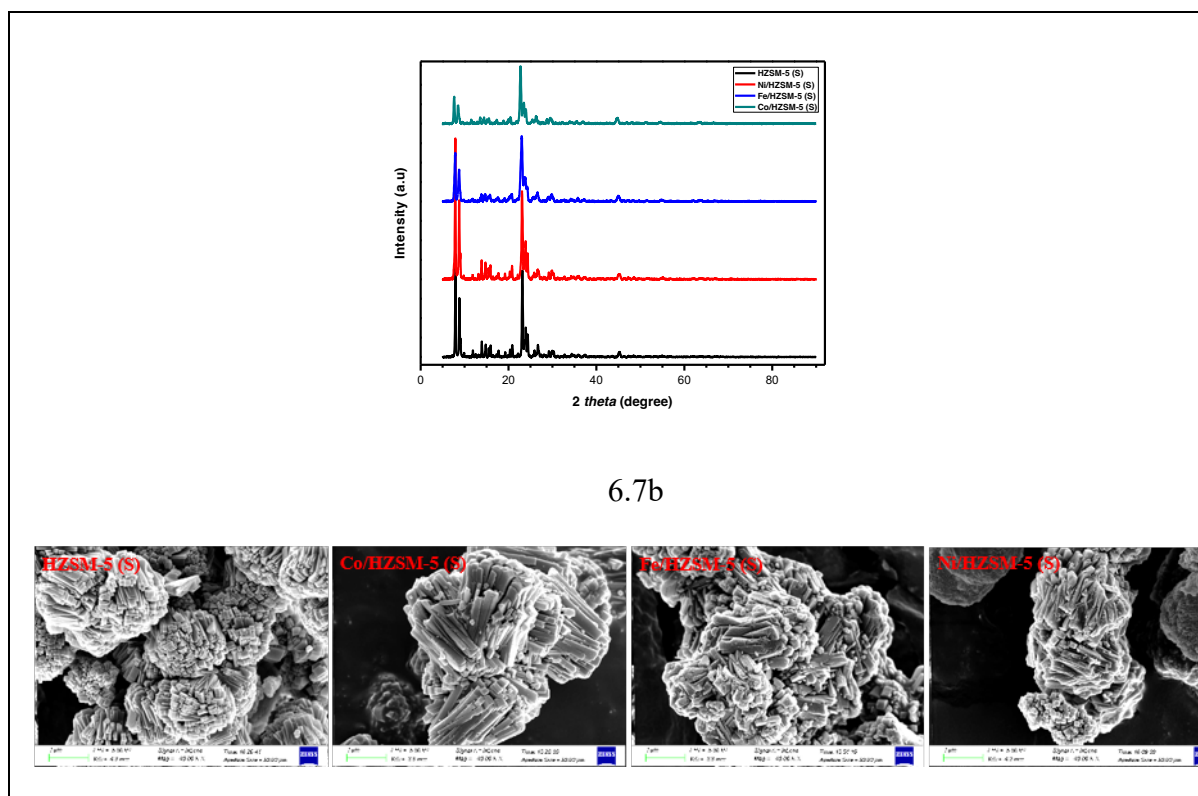


Figure 6-7 (a) XRD pattern and (b) SEM images of spent catalysts

(Operating conditions: 350 °C and 7 h⁻¹)

The FTIR spectra of spent catalysts typically show the presence of various functional groups and species, including adsorbed water, silanol groups, and coke deposits (Figures 6.8a & b). The decrease in the absorption band is more pronounced at 1064 cm⁻¹, with the Co-doped HZSM-5 showing the most significant reduction compared to other catalysts (Figure 6.8a). The observation corresponds to the XRD pattern and TGA-DTA of the spent catalysts. The FTIR result showed that the functional groups of the spent catalyst were preserved despite the coke deposition after the LATH conversion. FTIR spectroscopy was used to identify the bond vibrations of the catalyst and adsorbed HCs on spent catalysts after the LATH conversion. The characteristic bands of HC molecules can detect the presence of coke. The key regions in the FTIR spectrum for coke characterization are 1300-1700 cm⁻¹ and 2800-3100 cm⁻¹. Figure 6.8b depicts the spectra of spent catalysts within these regions (1300-3800 cm⁻¹). The vibrations in the first range (1300-1700 cm⁻¹) are associated with polycondensed aromatics, conjugated olefins, and some aliphatic bending modes, while the vibrations in the second range (2800-3100 cm⁻¹) correspond to aliphatics (asymmetric and symmetric stretching) and single-ring aromatics. To analyse each vibration, the spectra of the spent catalysts were identified by

individual peaks (Karge et al., 1996, Palumbo et al., 2008, Robertson, 2002, Valecillos et al., 2022): 1390 cm^{-1} , terminal $-\text{CH}_3$ groups; 1450 cm^{-1} , combination of aliphatics and alkyl aromatics; 1595 cm^{-1} , coke band or polycondensed aromatics; 1620 cm^{-1} , double bonds or olefins; 2850 cm^{-1} , $-\text{CH}_2$ groups; 2960 cm^{-1} , $-\text{CH}_3$ groups. It is important to note that these numbers are estimates and may have some discrepancies due to factors. Compared to the unmodified catalyst, the most abundant band seen more clearly in the Fe- and Co-doped HZSM-5 in the 2800-3100 cm^{-1} range corresponds to the CH_2 (2850 cm^{-1}) and $-\text{CH}_3$ (2960 cm^{-1}) groups, indicating the presence of long or naphthenic aliphatic chains in the coke produced on the catalyst. In this region, a higher concentration of CH_3 groups than CH_2 groups was observed in the coke, following the order Fe/HZSM-5 > Co/HZSM-5 > Ni/HZSM-5 > HZSM-5.

However, the band in this range (2800-3100 cm^{-1}) exhibits lower intensity indicating that the coke is predominately unsaturated. In addition, the most abundant band in the 1300-1700 range at 1625 cm^{-1} is more pronounced in the metal-doped samples than in the unmodified catalysts. This indicates that more double-bonded or olefinic HCs are formed with the metal-doped catalyst than unmodified ones. The findings of this study are consistent with those of previous studies (Valecillos et al., 2022, Karge et al., 1996, Palumbo et al., 2008). It can be suggested that the presence of metal species shifted and facilitated coke composition towards olefin HCs and long aliphatic chains, attributed to further secondary reactions, including aromatization and oligomerization favoured by these metal species. The reaction products and adsorbed HC trends discussed and shown in Figures 2c and 2d are consistent with typical expectations for the LATH conversion reaction (Valecillos et al., 2020, Ilias and Bhan, 2013, Valecillos et al., 2022). These trends showed the production of olefins which correlates directly with the extent of conversion, indicating their role as reaction intermediates, while the formation of heavy aliphatics and aromatics represent the final products (Ilias and Bhan, 2013). These results are consistent with the overall mechanism of the LATH reaction.

6.8a	6.8b
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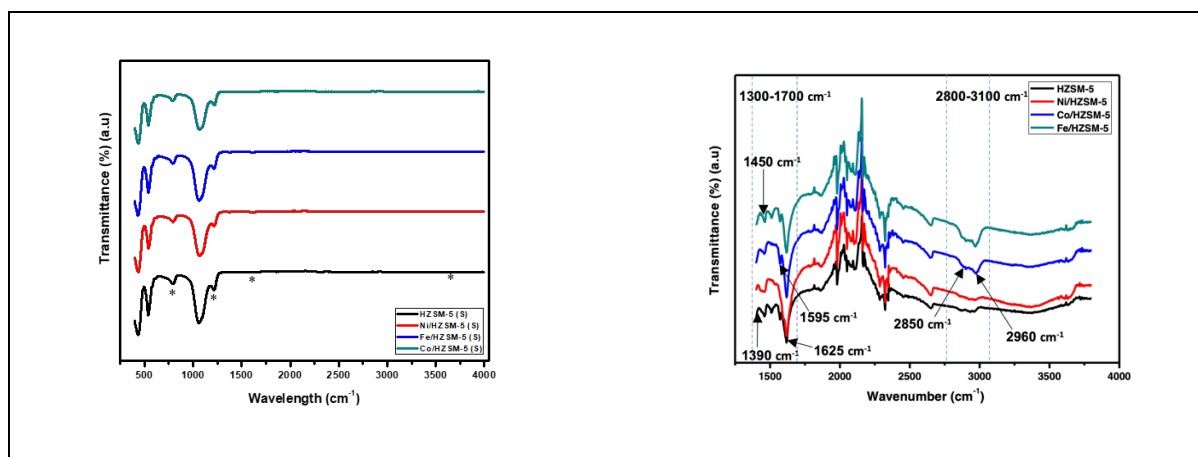


Figure 6-8. FTIR spectra (a) 400-4000 cm^{-1} (b) 1300-3800 cm^{-1}

6.4 Conclusion

The catalytic performance of transition metal-doped catalysts in low alcohol to hydrocarbon (LATH) conversion was investigated under different conditions, with temperatures of 350 and 400 $^{\circ}\text{C}$ and WHSV of 7 and 12 h^{-1} . Catalyst characterisation using different techniques successfully incorporated transition metals (Ni, Fe and Co) into ZSM-5 zeolite catalyst. The evaluation of these catalysts in LATH conversion revealed their activity across different low-alcohol feedstocks. The evaluation study demonstrated a consistent selectivity towards $\text{C}_5\text{-C}_8$ and $\text{C}_9\text{-C}_{12}^+$ HCs, with all catalysts achieving $>99\%$ conversion in the MTH process. Notably, Ni-doped HZSM-5 exhibited the highest selectivity for C_{12}^+ , while Co/HZSM-5 and Fe/HZSM-5 favoured the production of BTX and $\text{C}_5\text{-C}_8$ HCs, respectively. Product selectivity was strongly correlated in the ETH and PTH, as all catalysts achieved $>98\%$ conversion. Specifically, Ni/HZSM-5 displayed the highest selectivity towards $\text{C}_9\text{-C}_{12}$, Co/HZSM-5 favoured $\text{C}_5\text{-C}_8$, and Fe/HZSM-5 and HZSM-5 promoted the synthesis of BTX and C_{12}^+ HCs, respectively in the ETH process. For the PTH conversion, Co/HZSM-5 demonstrated the highest selectivity for $\text{C}_5\text{-C}_8$, Fe/HZSM-5 for $\text{C}_9\text{-C}_{12}$, and Ni/HZSM-5 for C_{12}^+ and BTX. Increasing the WHSV and temperature favoured the production of liquid hydrocarbons (C_5^+), with a specific increase in $\text{C}_5\text{-C}_8$ HCs observed in the LATH process. The evaluation of the catalysts revealed that the modified catalysts enhanced selectivity towards liquid hydrocarbons and outperformed the unmodified catalysts in LATH conversion, which exhibited appreciable selectivity towards C_{12}^+ products only in the ETH process.

The coke deposition study revealed important insights into coke deposition on spent catalysts in the LATH conversion. The TGA-DTA study showed that Ni/HZSM-5 exhibited excellent

stability with the least coke deposition, while Co/HZSM-5 had a higher tendency for coke deposition and deactivation attributed to significant weight loss (9.6 and 8.5 wt%) in MTH and ETH conversion. In the PTH process, Co/HZSM-5 displayed the lowest weight loss (5.0 wt%), and Fe/HZSM-5 exhibited the least stability. Among the catalyst tested, Ni/HZSM catalyst exhibited appreciable stability and catalytic performance in LATH conversion. The structural evaluation of the spent catalysts revealed that, despite the coke deposition, they retained their characteristic framework throughout the LATH conversion process. These findings are instrumental in comprehending the selectivity and behaviour of different catalysts during LATH conversion and offer valuable insights for optimising catalyst selection and operating conditions to minimise coke deposition and maximise catalyst stability. These findings enhance our understanding of LATH conversion processes and have significant implications for exploring strategies to mitigate coke formation and improve the overall efficiency of these processes. This study contributes to the advancement and development of more efficient catalysts in the conversion of low alcohol to fuel-range hydrocarbons.

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CHAPTER 7

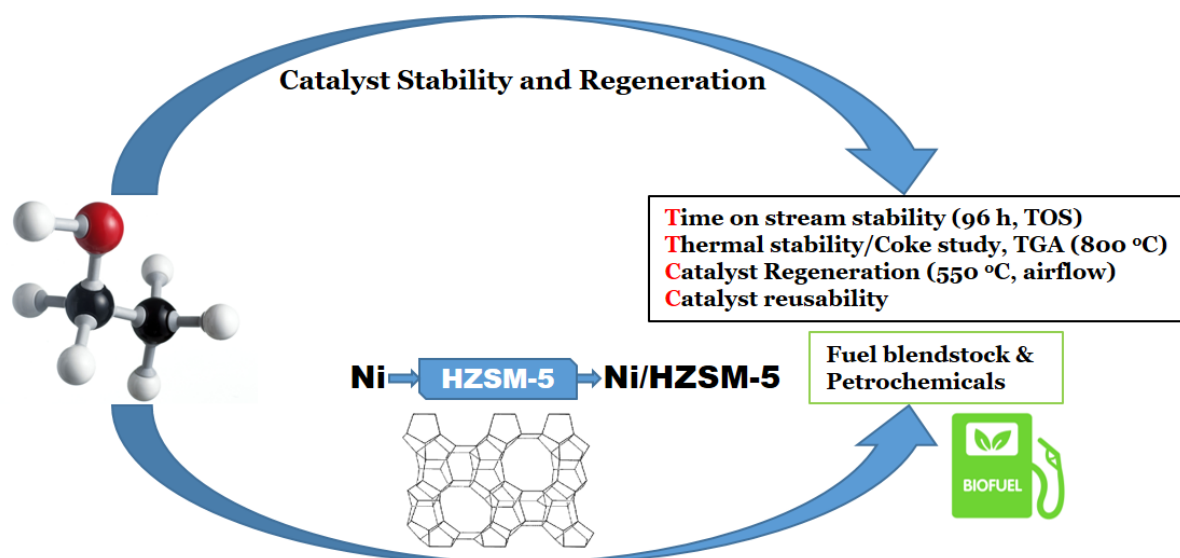
Stability, Deactivation and Regeneration Study of HZSM-5 and Ni-doped HZSM-5 Zeolite Catalysts for Ethanol-to-Hydrocarbon Conversion

Abstract

This chapter evaluates the stability, deactivation, and product distribution of hydrothermally synthesised ZSM-5 doped with 0.5 wt% Ni and the performance of regenerated catalysts in ethanol-to-hydrocarbon production. Ethanol conversion and stability were studied at 350 °C and 7 h⁻¹ for three cycles, each running for 96 hours on stream. The regeneration study was conducted after 96 hours on stream under airflow for two cycles. The catalytic evaluation indicated that the as-synthesised catalysts were efficient in ethanol conversion, with the unmodified catalyst, Z5, exhibiting high stability with 100% ethanol conversion, while the Ni-doped catalyst, NiZ, maintained 100% stability for up to 48 hours on stream before a decline. The regenerated catalysts exhibited similar product distribution, stability, and catalytic performance to the as-synthesised catalysts. The unmodified catalysts were selective to BTX, while the Ni-doped catalysts were more preferential to C₅-C₈, C₉-C₁₂, and C₁₂+ HCs. Overall, the results suggest that the unmodified catalyst exhibited considerable stability compared to Ni-doped catalysts attributed to high coke deposition on NiZ, leading to deactivation. However, Ni-doped catalysts exhibited a broader product distribution than unmodified ones. The regeneration process improved the catalytic activity of the spent (and deactivated) catalysts, particularly for the Ni-doped catalyst. The catalysts retained their activity after the regeneration process, indicating the potential of the regeneration process to extend the lifespan of the catalysts and reduce the cost of catalyst replacement.

Keywords: Catalyst, Ethanol, Regeneration, Stability, ZSM-5

Graphical Abstract



7.1 Introduction

The development of substitutes for petroleum has become a pressing issue worldwide due to the impending petroleum crisis and the need to reduce CO₂ emissions. One promising option is biomass, a renewable resource that is both abundant and carbon emissions-free. Biomass can be utilised directly to generate heat and electricity. It can also be converted thermochemically or biochemically into combustible liquids such as bio-oils, methanol, and ethanol, as well as gases like methane and hydrogen (Zhang et al., 2010a). The fermentation of biomass feedstocks, such as sugarcane, sugar beets, and starch crops, is a widely utilised biochemical conversion process, with bioethanol being one of the most easily produced end products. The global bioethanol production in 2020 was 29.66 billion litres (Anekwe et al., 2021a). While bioethanol is commonly used as fuel or fuel additive for motor vehicles, recent attention has been given to its use as a feedstock for the chemical industry, particularly in producing ethylene through catalytic dehydration of ethanol.

Zeolites, a family of catalysts widely used in petroleum refining and fluid catalytic cracking (FCC), are useful in converting methanol and ethanol to hydrocarbons. Zeolite HZSM-5, developed by Mobil Oil Corporation in 1972, has been a widely used catalytically active material for converting methanol and ethanol to hydrocarbons due to its effectiveness as an additive in FCC catalysts or hydrocracking (Argauer and Landolt, 1979). Due to its frequent use in these processes, a vast array of distinct post-synthetic modification possibilities are available for zeolite HZSM-5. Post-synthesis procedures contribute to tuning its activity and

selectivity, respectively, as well as its stability and regenerability. Additionally, the synthesis process results in several variations in the Si/Al ratio, further contributing to the catalyst's versatility (Lago et al., 1986, Göhlich et al., 2011, Sousa et al., 2014, Brunner et al., 1989).

The process of ethanol-to-hydrocarbon (ETH) conversion is a complex one that involves several types of chemical interactions. The latest research has delved into the reactions that Lewis and Brønsted acid sites catalyse. After ethanol is rapidly and almost entirely dehydrated, producing ethene and diethyl ether, a process referred to as "hydrocarbon pool" emerges. This process involves a series of carbocation-based events, including oligomerisation, cracking, cyclisation, isomerisation, and hydride transfer reactions. These reactions occur on various hydrocarbon species located on different acid sites in the active surface of the porous catalyst material, resulting in the formation of a hydrocarbon pool of homologating compounds (Seifert et al., 2020, Chowdhury et al., 2019, Cumming and Wojciechowski, 1996, Van der Borghet et al., 2016). To achieve higher levels of selectivity in the ETH process, researchers have explored the possibility of modifying ZSM-5 zeolites by adding metals such as Fe or W and La (Murata et al., 2008). Studies have been carried out to enhance the catalyst's stability since zeolites undergo irreversible deactivation throughout the reaction. One promising approach has been to incorporate phosphorus into the ZSM-5 zeolites, which can improve their hydrothermal stability. Recent studies have shown that phosphorus-modified ZSM-5 (P-ZSM-5) catalysts have improved selectivity for propylene synthesis and strong catalytic stability (Xue et al., 2007, Xue et al., 2010b, Zhuang et al., 2004). Despite these promising results, it is still not entirely clear how the addition of phosphorus influences the ZSM-5 catalysts during the conversion of ethanol to hydrocarbons. Further research is needed to fully understand this process's complex interactions and chemical pathways.

The ZSM-5 catalyst has proven to be a viable option for hydrocarbon reactions. However, due to catalyst coking, zeolites tend to experience rapid deactivation, necessitating their routine regeneration throughout the fluid catalytic cracking (FCC) process to restore their catalytic performance. Although coking with feedstocks can deactivate zeolites, oxidative treatments can bring them back to life (Jong et al., 1998). This process has been the subject of extensive research, and a dilute air stream is a standard effective method for coke removal from zeolites. This air stream is used to control the rate of oxidation, which in turn limits the exothermic processes and steam generation that might result in irreversible dealumination of the catalyst. It is worth noting that although general techniques for coke removal from zeolites can be

utilised for various kinds of reactions, the type of coke is determined by the feedstock from which it originates. The extent of regeneration is influenced by the catalyst and reaction conditions employed to produce the coke (Guisnet and Magnoux, 1997). Therefore, protocols for regeneration must be designed for each application, considering factors such as feedstock, catalyst, process conditions, etc (Yung et al., 2019).

Benito et al. (1996) studied the regeneration of ZSM-5, utilised in converting methanol to gasoline. They found the catalyst susceptible to thermal destruction. Still, it could be reactivated at 550 °C in air, provided it had been exposed to the same temperature before its initial activity was determined. Other studies have also been conducted on the regeneration of ZSM-5, which has been utilised for in-situ and ex-situ biomass conversion to hydrocarbons. The temperatures ranged from 450 °C to 700 °C, and the number of reaction cycles ranged from 1 to 10 (Carlson et al., 2011, Paasikallio et al., 2013). Williams and Horne (1995) discovered that the efficiency of an HZSM-5 zeolite in converting oils produced by biomass pyrolysis into aromatic compounds decreased after the zeolite had been regenerated up to five times. To regenerate the spent catalyst, it was extracted from the reactor and subjected to air heating at 550 °C for eight hours in an oven. Carlson et al. (2011) studied a ZSM-5 catalyst for ten reaction/regeneration cycles, with regeneration performed for three hours in air. They discovered a modest reduction in low-temperature acid sites, characterised by ammonia temperature-programmed desorption. They also found that metals from the biomass were deposited on the catalysts, despite no investigation or optimisation of the regeneration process being reported. In their research, Paasikallio et al. (2013) carried out catalyst regeneration at temperatures ranging from 923 to 943 K. Over 100 hours, they observed a slight shift in the product's composition. They reported that catalyst deactivation was limited but noticeable, with negligible loss of total surface area and a decrease of approximately 30% in micropore surface area and the micropore volume (Paasikallio et al., 2013).

The previous studies that have been conducted on catalyst regeneration have primarily focused on commercial ZSM-5 for low alcohol conversion to olefins or synthesised ZSM-5 for biomass or bio-oil conversion into hydrocarbons. In addition to the aforementioned studies, research has also explored the incorporation of phosphorus to improve catalyst stability. However, it is essential to note that while this approach may enhance catalyst stability, it may not necessarily improve the selectivity towards target products. As a result, there has not been a sufficient study on the stability and regeneration of newly fabricated ZSM-5 zeolite catalysts, specifically

in converting ethanol to liquid hydrocarbons. In this study, we seek to address this gap in the literature by investigating the stability and deactivation of newly synthesised ZSM-5 and Ni-doped ZSM-5 zeolite catalysts, without the incorporation of phosphorus, in the conversion of ethanol to liquid hydrocarbons. Furthermore, we aim to compare the performance of unmodified and Ni-doped ZSM-5 catalysts to explore the effect of transition metals on catalyst stability during the ethanol-to-hydrocarbon (ETH) process. In addition, we investigated catalyst deactivation due to coke deposition and regeneration to determine its impact on the stability and product distribution of both ZSM-5 and Ni/HZSM-5 catalysts. Through these investigations, we aim to provide valuable insights into the design of more stable and effective catalysts for the conversion of ethanol to liquid hydrocarbons, with the potential to advance the field of sustainable bioenergy production.

7.2 Materials and Method

The following chemicals were utilised for this study: silica source: sodium silicate solution, aluminium source: aluminium sulfate, organic template: tetrapropyl ammonia bromide, sodium hydroxide (97 %), sulfuric acid (98 % conc.), ammonium nitrate. Nickel nitrate precursor was employed for the introduction of nickel. Ethanol was employed as the feedstock for the catalytic test, and all chemicals were obtained from Sigma-Aldrich. A Teflon-lined stainless-steel hydrothermal reactor of 200 mL was used for the catalyst synthesis. Catalysts were synthesised and characterised according to the method described in *Section 3.2.2* while the TGA was conducted according to the method described in *Section 4.2*.

The catalytic stability and performance of HZSM-5 and Ni/HZSM-5 (denoted Z5 and NiZ) were studied at a temperature of 350 °C and weight hourly space velocities (WHSV) of 7 h⁻¹ for 96 hours (with 8 hours sampling) in the conversion of ethanol into hydrocarbons. Glass beads and glass wool were used as structural support for the catalyst bed, and an HPLC pump was used to introduce the feedstock into the reactor after the initial activation of the catalyst at 400 °C. Product selectivity (Si) and conversion (X) were calculated based on the work of Sun et al. (2020). HZSM-5 and Ni/HZSM-5 catalysts, initially labelled as Z5 and NiZ, were regenerated after 96 hours on-stream by exposing them to an 80 mL/min airflow at 550 °C for 5 hours. The regenerated catalysts were designated Z5/R1 and NiZ/R1 for the first regeneration (R1) and Z5/R2 and NiZ/R2 for the second (R2).

7.3 Results and Discussion

7.3.1 Catalyst Stability in Ethanol Conversion

Catalyst stability was investigated through a study involving three cycles of ethanol conversion. Each cycle comprised a continuous run of 96 h of time on stream (TOS) followed by two regeneration phases. The first cycle used as-synthesised or fresh catalysts (Z5 and NiZ for the pure and Ni-modified ZSM-5 catalyst) for ethanol conversion. After the first cycle, the catalysts were regenerated (first regeneration cycle, R1), denoted as Z5/R1 and NiZ/R1, and utilised for the second cycle of ethanol conversion. Following the second cycle, the catalysts were regenerated (second regeneration cycle, R2), denoted as Z5/R2 and NiZ/R2, and used for the third conversion cycle.

Figures 7.1a and b show the conversion of ethanol and phase selectivity for each catalyst among the gaseous and liquid products. Aromatics (BTX: benzene, toluene, xylenes), C₅-C₈, and C₉+ hydrocarbons were the main liquid products, and their selectivity changed over time on stream. Ethanol conversion remained constant at approximately 100% for Z5 catalysts, while Ni-doped catalysts, NiZ, showed a decline in ETH conversion after 48 h on stream. The decline in conversion can be attributed to the incorporation of Ni species, which increases the acid site concentration, making the catalyst more susceptible to coking and leading to catalyst deactivation and a reduction in ethanol conversion. The unmodified catalyst, Z5 demonstrated considerable stability with a high ETH conversion of approximately 100% from 8 to 96 h on stream. The selectivity of this Z5 catalyst was significant for C₅-C₈ and BTX, while C₉-C₁₂ HCs were more evident at the early stages of the reaction (8 h) and after 56 h on stream. For the Ni-doped catalyst, NiZ, the ETH conversion gradually decreased from 100% to 62.4% after 40 hours on stream. This decrease in conversion can be attributed to the further oligomerisation of ethylene formed by ethanol dehydration in the early stages of the reaction (Guisnet and Magnoux, 1994). Additionally, after 32 and 40 h on stream, the selectivities of the NiZ catalyst to C₅-C₈ and BTX decreased, respectively, shifting towards C₉-C₁₂ and C₁₂+ selectivity. However, the ETH conversion rate gradually increased to approximately 100 % at 56 h but then reduced to 39.5 % after 80 h and later increased to 78.6 % after 88 h on stream. The selectivity to C₅-C₈ showed a sharp increase after 64 h on stream, possibly due to the weakened strength of acid sites during deactivation.

For the Z5 catalyst, there appeared to be a correlation between BTX selectivity and C₅-C₈ selectivity and an inverse correlation between C₅-C₈ selectivity and C₁₂⁺ selectivity. This suggests that the Z5 catalyst is more selective to C₅-C₈, BTX, and a few C₉-C₁₂ hydrocarbons, not favouring long-chain (C₁₂⁺) HCs. Gaseous HCs (C₁-C₄) decreased with increasing TOS, with a considerable decrease recorded after 64 h on stream for both catalysts (Figure 7.1c). Compared to Z5, NiZ showed a wider product distribution, with a strong correlation between BTX and C₅-C₈ HCs due to their selectivity at all TOS and a weak correlation between C₉-C₁₂ and C₁₂⁺ attributed to their selectivity after 40 h on stream (Figure 7.1d). While both catalysts demonstrated considerable selectivity towards C₅-C₈ hydrocarbons, Z5 showed the highest selectivity towards C₅-C₈ (86.4 %), C₉-C₁₂ (11.1 %), and BTX (46.6 %) at 24, 40, and 40 h on stream, respectively. NiZ recorded the highest selectivity at 72, 96, 88, and 96 h on stream for C₅-C₈ (89.9%), C₉-C₁₂ (11.8%), BTX (10.6%), and C₁₂⁺ (10%). Comparatively, Z5 showed higher (average) selectivity for C₁-C₄ (16.5%) and BTX (10.9%), while NiZ showed considerable (average) selectivity to C₅-C₈ (79.2%), C₉-C₁₂ (4.1%), and C₁₂⁺ (4.5%) after the first cycle. This showed that incorporating Ni reduced the formation of BTX and gaseous hydrocarbons and increased the selectivity towards C₅⁺ hydrocarbons. Overall, Z5 catalyst exhibited considerable stability than NiZ. However, NiZ showed a wider product distribution after the first cycle using the fresh catalyst.

7.3.2 Catalyst Regeneration and Reusability Study

Catalysts were subjected to a regeneration process after the first cycle. The results of the first regeneration process (R1) indicated an improvement in the catalytic performance of the spent and deactivated catalysts, particularly for the Ni-doped catalyst. The Z5/R1 catalysts, which had been regenerated, maintained an appreciable ETH conversion (>96%) and showed improved catalytic performance, especially with regard to (average) selectivity towards BTX (18.1%) and C₉-C₁₂ (5.4%) (Figure 7.1e). This was a substantial improvement from the Z5 catalyst, which recorded 10.9% and 2.5% for these HC fractions, respectively. Unlike Z5, the Z5/R1 catalyst showed increased C₉-C₁₂ selectivity over time on stream, with the highest selectivity recorded at 72 h (16.7%). The selectivity towards BTX also increased with increasing time on stream and plateaued after 56 hours at 55.4%, gradually declining to 53.5% at 72 h, and then decreasing more rapidly afterwards. Like Z5, the Z5/R1 catalyst showed selectivity towards C₉-C₁₂ after 40 h on stream and considerable selectivity towards C₅-C₈, with a dip in the latter at 64 and 72 h on stream attributed to a shift to BTX selectivity. The

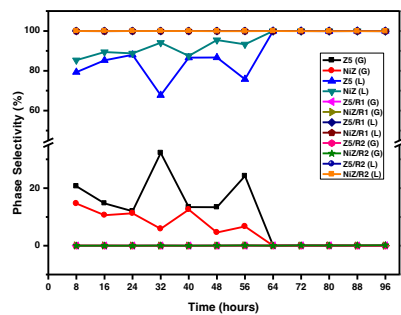
regenerated metal-doped catalyst, NiZ/R1, showed an improved catalytic activity after regeneration following the deactivation and a decrease in ETH conversion was observed in the first cycle after 96 h on stream. Yung et al. (2019) and Li et al. (2022b) reported a similar trend. Like the fresh NiZ, the NiZ/R1 catalyst exhibited a stable ETH conversion of approximately 100% up to 48 h on stream, where a decrease to 60.6% was recorded, followed by a continuous gradual decline after 56 h on stream (Figure 7.1f). In contrast to NiZ, an increase in the production of C₅-C₈ (5.9% average increase in selectivity), resulting in a decrease in C₉-C₁₂ and C₁₂⁺ selectivity, was observed with the NiZ/R1 catalyst. Both regenerated catalysts, Z5/R1 and NiZ/R1, showed a drastic reduction in selectivity towards gaseous HCs with increasing TOS. It can be deduced from the regeneration (R1) and application of regenerated catalysts that the catalysts retained their catalytic activity after the first regeneration cycle, which showed that the catalyst did not undergo irreversible dealumination during the long TOS in the ETH process (Wang et al., 2017, Li et al., 2022b). The product distribution for the second cycle of ETH conversion showed that Z5/R1 favoured C₉-C₁₂ and BTX, while NiZ/R1 was more preferential towards C₅-C₈ and slightly C₁₂⁺ HCs. This is similar to the product distribution for the first cycle, except that the NiZ catalyst was more selective towards C₉-C₁₂ than Z5

The results of the third cycle of ETH conversion using the second regeneration cycle catalysts Z5/R2 and NiZ/R2 are presented below. The operating conditions used were similar to those described in the previous cycle. The results showed that the catalysts retained their activity at the same TOS as the fresh catalysts. The Z5/R2 catalyst maintained 100% conversion up to 96 h on stream with the same selectivity to C₅-C₈, BTX, and slightly C₉-C₁₂ without favouring C₁₂⁺ HCs. At 24 h on stream, the selectivity towards BTX showed a considerable increase with 50.8% selectivity resulting in a decrease in C₅-C₈ selectivity (Figure 7.1g). However, with an increase in TOS, the selectivity towards BTX experiences a drastic dip after 24 h on stream. As mentioned earlier, the selectivity towards C₅-C₈ was more prominent (>50% selectivity) except for 24 h on stream, while C₉-C₁₂ was observed after 64 h. However, just like other catalysts, Z5/R1 and Z5, the Z5/R2 catalyst did not favour the synthesis of C₁₂⁺ HCs. However, the third cycle of ETH conversion using the regenerated NiZ/R2 exhibited an appreciable stable conversion like its other counterpart with >92% ETH conversion up to 48 h on stream, where a significant decrease to 52.9% was experienced. However, conversion increased to 70 and 100% afterwards at 56 and 64 h, respectively, before recording a continuous reduction till 96 h on stream. NiZ/R2 showed a wider product distribution similar to its other counterpart. However, compared to NiZ/R1, it recorded an average increase in selectivity for C₉-C₁₂, C₁₂⁺,

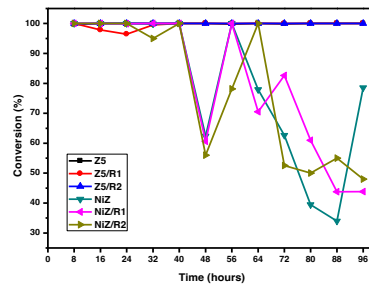
and BTX by 3.8%, 1.5%, and 5.0%, respectively, after 96 h on stream (Figure 7.1h). From the second cycle of ETH conversion, it can be deduced that both catalysts (Z5/R2 and NiZ/R2) were more selective to liquid HCs (>83%), just like other catalysts evaluated. However, while the Z5/R2 catalyst was preferential to BTX with an average of 10.1%, NiZ/R2 favoured C₅-C₈, C₉-C₁₂, and C₁₂+ with 73.2%, 4.4%, and 2.1% selectivity, respectively, after 96 h time on stream. The catalytic evaluation of R2 catalysts in the third cycle of ETH conversion showed that the catalytic properties of the catalysts were restored after the regeneration process. The comparative review of the original and regenerated catalyst is presented in Table 7.1.

Based on the results obtained from the experiment, it can be deduced that the as-synthesised novel catalyst, Z5 maintained considerable stability with ETH conversion of approximately 99.5 % for three conversion cycles, each lasting for 96 h on stream each and even after two regeneration cycles. However, the deactivation of the metal-doped catalyst, NiZ catalyst, was not caused by dealumination or structural distortion resulting from prolonged time on stream. Instead, this deactivation can be attributed to the formation of carbon deposits that block the active sites, leading to a decrease in ETH conversion. As a result, the employed regeneration technique proved to be highly effective in removing the coke deposits, thereby reviving the catalytic properties of the catalyst without damaging the structural framework. Furthermore, the application of the regenerated catalysts demonstrated that they all retained their catalytic performance after the regeneration process. However, it was observed that the unmodified catalyst exhibited more excellent stability than the Ni-doped catalyst, which can be attributed to the presence of Ni species in the NiZ catalyst. These species were found to increase coke formation and subsequent deactivation, thereby reducing the overall effectiveness of the catalyst.

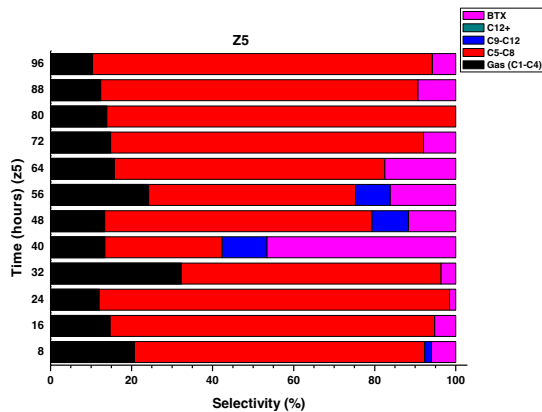
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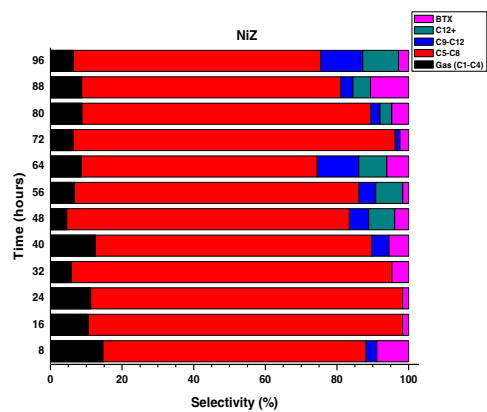
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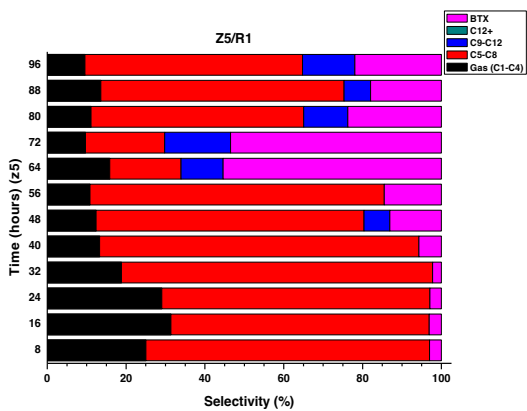
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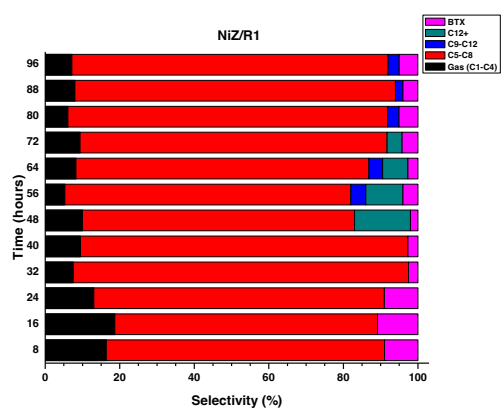
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7.1f



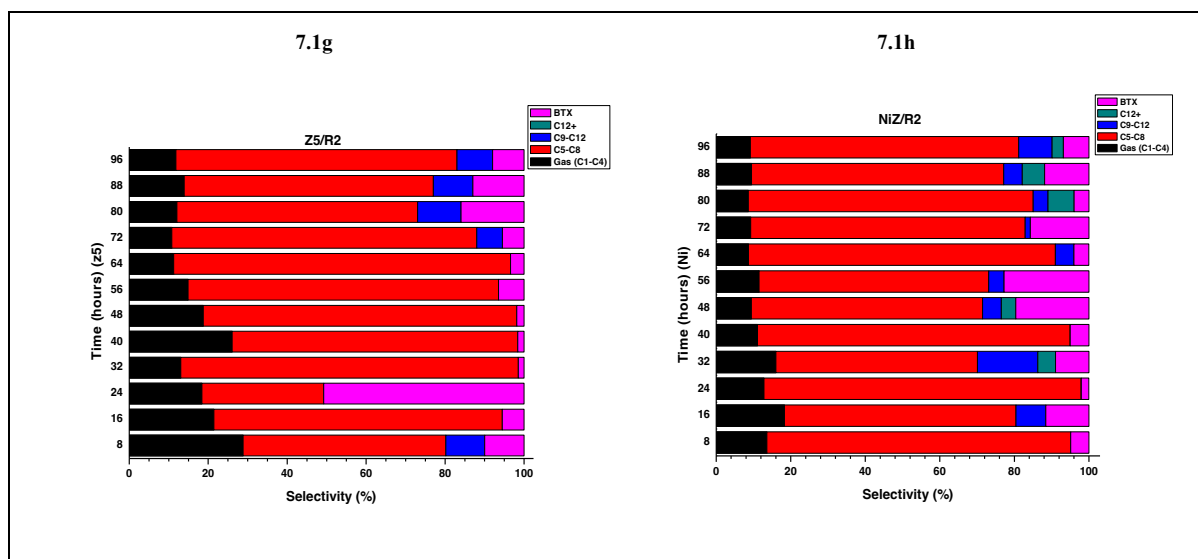


Figure 7-1a & b. Phase selectivity and Ethanol conversion, (c & d) Product distribution of Z5 and NiZ catalysts from the first cycle, (e & f) Z5/R1 and NiZ/R1 from 2nd cycle, (g & h) Z5/R2 and NiZ/R2 from 3rd cycle ETH conversion at 350 °C, 7 h⁻¹ WHSV and 96-hour TOS.

Table 7-1. Comparative evaluation of product distribution (average) of fresh and regenerated catalysts

Catalysts	C ₁ -C ₄ (%)	C ₅ -C ₈ (%)	C ₉ -C ₁₂ (%)	C ₁₂ + (%)	BTX (%)	X (%)	Liquid HC (%)
Z5	16.48	70.05	2.53	0.00	10.94	99.94	83.52
NiZ	8.76	79.23	4.07	3.40	4.53	79.57	91.24
Z5/R1	16.72	59.77	5.43	0.00	18.09	99.48	83.28
NiZ/R1	9.91	85.12	0.56	0.57	3.84	80.19	90.09
Z5/R2	16.77	69.08	3.86	0.00	10.29	100.00	83.23
NiZ/R2	11.48	73.21	4.40	2.05	8.86	73.41	88.52

ZSM-5 zeolite is a widely used catalyst in converting ethanol to fuels to valuable chemicals such as aromatics. It is believed that the initial rates of ethylene synthesis during ethanol dehydration and other secondary reactions via the direct and sequential routes are attributed to the active Brønsted acid and high Lewis acid sites in the as-synthesised catalysts (Sun and

Wang, 2014). Researchers argue that these active sites create a molecular constraint within the HZSM-5 channels, leading to a rate of diffusion that is less than that of production. Consequently, this helps with oligomerisation reactions of ethylene and other subsequent reactions (Ali et al., 2020, Guisnet and Magnoux, 1994, Aguayo et al., 1994). Studies have revealed that the incorporation of transition metals like nickel in zeolite acid catalysts can enhance their catalytic performance. These transition metals help increase the total number of acid sites and improve the catalyst's selectivity towards specific products, making it more efficient in catalysing the conversion process (Iliopoulou et al., 2012, Ding et al., 2020, Van der Borgh et al., 2015a) for improved (broader) product distribution as demonstrated by the Ni-doped catalyst. However, the deactivation of ZSM-5 is a major challenge, which can significantly affect its catalytic performance and efficiency. The deactivation of ZSM-5 in ethanol conversion is caused by coke deposition. The use of transition metals while improving catalytic performance and product distribution has also been found to increase the tendency to coke deposition, leading to the blocking of catalyst pores and the subsequent deactivation of the catalyst, which results in a decline in catalytic performance and ethanol conversion (Rostamizadeh et al., 2018b, Maia et al., 2010a).

The coke is formed due to the adsorption and polymerisation of the reaction intermediates on the catalyst surface, leading to pore blockage and reduced accessibility of the active sites. One of the main reasons for the deactivation of nickel-doped ZSM-5 compared to unmodified HZSM-5 is the poisoning of active sites by coke deposition (Li et al., 2011, Abdullah, Du et al., 2016a). During the reaction, the hydrocarbon molecules can undergo dehydrogenation, cracking, and polymerisation, forming carbonaceous species that adsorb on the catalyst surface and block the active sites. The deposition of coke is more pronounced in nickel-doped ZSM-5 due to the high activity of nickel towards the dehydrogenation reaction, which promotes the formation of carbonaceous species (Pinjari et al., 2018, Maia et al., 2011). The stronger acid sites are more susceptible to coking, and this early deactivation of the catalyst is primarily caused by coke deposition on these sites (Tabak and Yurchak, 1990). The coke deposition can lead to a decrease in the surface area of the catalyst, reducing the accessibility of the reactants to the active sites and, therefore, decreasing the catalytic activity. Low-temperature coke (473 K) is usually olefinic or paraffinic, with species having >10 carbon atoms that cover these catalytic sites (Karge and Weitkamp, 1989). Coke produced at higher temperatures (>573 K), such as in the current investigation (350 °C), is often more hydrogen deficient (Phillips and

Datta, 1997). However, owing to the ability to regenerate the catalyst while maintaining its catalytic performance, it is believed that the deactivation of Ni-doped catalysts was not due to dealumination. Various factors, such as exposure to acids, bases, or high-temperature steam, can cause dealumination. Dealumination can result in a decrease in the catalyst's activity and selectivity and can be irreversible. Regeneration of dealuminated ZSM-5 catalysts can be challenging and may require complex treatments to reintroduce the lost acidic sites (Roy et al., 2008, Zhang et al., 2003, Ibáñez et al., 2016). The catalysts used in this study were not exposed to high reaction temperatures ($>550\text{ }^{\circ}\text{C}$) or acidic media, making it possible to regenerate the spent catalysts.

Another factor that contributes to the deactivation of nickel-doped ZSM-5 is the pore blockage by the nickel particles. The addition of nickel to ZSM-5 can lead to the formation of larger particles (as revealed by the PSD analysis) that can block the pores and channels of the zeolite, hindering the diffusion of the reactants and products. The blockage of the pores can also lead to a decrease in the surface area and acidity of the catalyst, reducing the catalytic activity (Mlimi, 2021, Wan et al., 2018). The pore blockage is more pronounced in nickel-doped ZSM-5 due to the higher propensity of nickel to form larger particles than other metals, such as platinum or palladium (Masalska, 2005). The ni-doped catalyst was more selective to long-chain HCs. Consequently, coke deposition on nickel-doped ZSM-5 can lead to a decrease in the selectivity towards long-chain hydrocarbons and an increase in coke generation, leading to catalyst deactivation. Furthermore, the sintering of the nickel particles can also contribute to the deactivation of the catalyst. During the reaction, the nickel particles can undergo agglomeration and sintering, decreasing the active surface area and the number of active sites. The sintering of the nickel particles is more pronounced at high temperatures or under oxidative conditions, which can lead to the migration and coalescence of the particles (Sarkar et al., 2016, Liu et al., 2022c). The sintering can be mitigated by controlling the reaction conditions or using a support material stabilising the nickel particles. However, in some cases, sintering may be irreversible and lead to a loss of catalyst activity and selectivity, ultimately requiring catalyst replacement.

On the contrary, some studies have reported that the incorporation of transition metals in the HZSM-5 catalyst has been shown to enhance its performance and stability in the conversion of ethanol into hydrocarbons. Doping these transition metals creates strong and stable acid sites in the catalyst, promoting catalytic activity and preventing the leaching of aluminium ions that

can lead to catalyst deactivation. According to Kostyniuk et al. (2020), introducing some transition metals into the HZSM-5 zeolite improved the catalyst's hydrothermal stability and a higher aromatics yield. This behaviour was ascribed to the dehydrogenating activity of nickel and the moderate acidity strength brought about by the presence of the metal. The appreciable stability exhibited by the catalyst in the isomerisation of 1-hexene can be attributed to the bimetallic metal loading on the catalyst (denoted as Mo-Ni/HZSM-5) (Kostyniuk et al., 2020). To overcome the deactivation challenge, monitoring and controlling the amount of coke produced during the catalytic reaction is crucial to maintain the catalyst's performance and prolong its lifespan. Therefore, the addition of transition metals to zeolite acid catalysts holds promise as a potential strategy to enhance their effectiveness in ethanol conversion, provided proper coke control and regeneration measures are implemented.

7.3.3 Assessing Coke Deposition on Spent Catalysts through TGA-DTA

Catalytic reactions involving hydrocarbons often result in the deposition of carbonaceous species, commonly referred to as coke, on the catalyst surface. Coke deposition is a major problem in the catalytic process, as it leads to catalyst deactivation and reduces its activity and selectivity. The coke deposition of HZSM-5 and nickel-doped HZSM-5 (Ni/HZSM-5) catalysts during ethanol conversion was studied.

The initial weight loss at 0-200°C can be attributed to removing absorbed water and volatile compounds. HZSM-5 and Ni/HZSM-5 have a large surface area and can adsorb water and volatile compounds during ethanol conversion. Weight loss in this temperature range is to be expected and is not related to coke deposition. The HZSM-5 zeolite catalyst is known for its high acidity, which promotes coke deposition during ethanol conversion. The Z5 catalyst recorded a weight loss of 3.1 and 2.1 wt% at 200-400 °C and 400-600 °C (Figure 7.2a) due to the combustion of soft and hard coke. This catalyst had more soft coke, which is relatively easy to burn at lower temperatures than hard coke. The coke deposition observed in Z5 catalysts is due to its high acidity, which promotes the cracking of ethanol into smaller molecules and favours coke formation. This also was reported by Xia et al. (2023). The NiZ catalyst, on the other hand, exhibited a more significant deposition of hard coke, up to 2.8 wt% and 2.5 wt% soft coke. The increased deposition of hard coke observed for the NiZ catalyst is attributed to nickel, which promotes coke formation and enhances the combustion of soft coke. This results in less soft coke accumulation on the catalyst surface and higher selectivity for long-chain hydrocarbons, as evidenced by a wider product distribution of the NiZ catalyst. The enhanced

combustion of soft coke on the NiZ catalyst is due to the catalytic effect of nickel in the oxidation of coke. This catalytic effect is due to the large surface area of the NiZ catalyst and the redox properties of nickel (Kawi et al., 2015). In this case, soft coke formation is due to the accumulation of intermediates such as acetaldehyde on the catalyst surface, which form long-chain hydrocarbons and coke by further polymerisation, leading to the deactivation of the NiZ catalyst. To further support the findings of this study, it is worth noting that several other studies (Li et al., 2017, Mohamed et al., 2022, Singh et al., 2020a) have reported similar trends regarding high coke deposition on Ni-doped catalysts and their activity, further validating the results of our study. These findings suggest consistency in the behaviour of spent catalysts and reinforce the significance of coke deposition studies.

The pure (unused) HZSM-5 catalyst exhibited the least weight loss during the reaction because it was not exposed to the reactants, and no coke deposits occurred. However, the weight loss at 0-200°C was high due to the removal of absorbed water and volatile compounds. The weight loss observed for spent catalysts (Z5 and NiZ) at 600-800°C was due to the removal of non-volatile compounds from the ethanol conversion. The removal of non-volatile compounds is facilitated by high temperatures and an oxidative environment that promotes cracking and oxidation of these non-volatile heavier molecules absorbed at the catalyst surface during the reaction. The differential thermal analysis (DTA) curve showed a slightly higher peak for the NiZ catalyst, indicating a tendency toward coking (Figure 7.2b). This is consistent with the heavy coke deposition observed for NiZ catalysts. Figure 7.2c presents the images of spent and regenerated Z5 and NiZ catalysts.

From the coke deposition study, it can be inferred that the rapid deactivation of the NiZ catalyst, which exhibits lower ethanol conversion after 48 hours compared to the more stable Z5 catalyst, is partly due to the increased deposition of hard coke. This deactivation can also be attributed to nickel doping and increased selectivity for long-chain hydrocarbons. The increased selectivity for long-chain hydrocarbons in this catalyst is due to the decreased acidity and increased pore size due to the nickel doping. The reduced acidity leads to less cracking and condensation, forming long-chain hydrocarbons. The larger pore size allows the diffusion of larger molecules and reduces the accessibility of active sites, resulting in lower catalytic activity, faster deactivation, and lower ethanol conversion rate. Increased coke deposition on the NiZ catalyst also contributes to its faster deactivation, as it reduces the availability of active sites and increases the diffusion resistance of reactants and products.

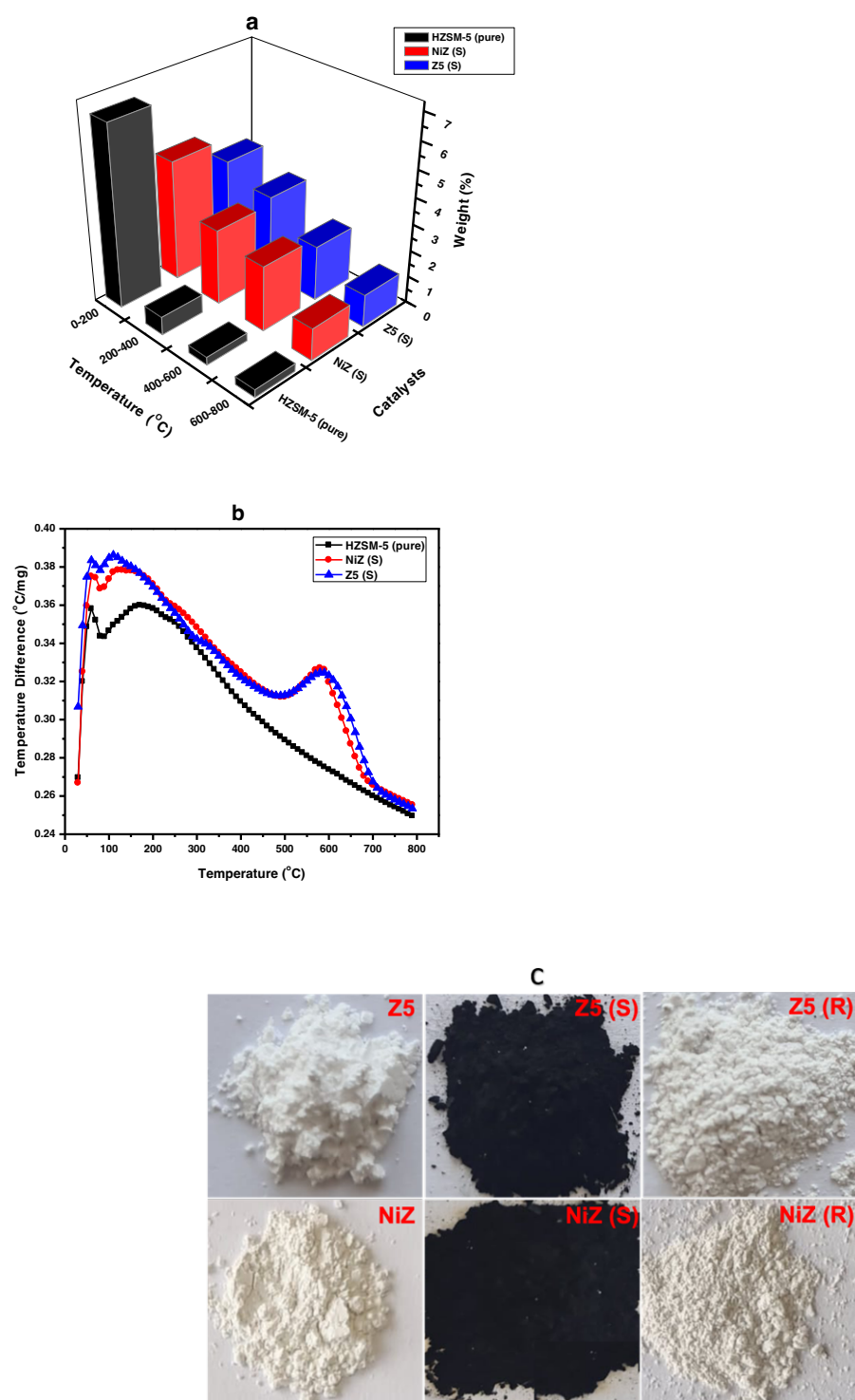


Figure 7-2 (a & b). TGA-DTA of spent catalysts; (2c). Images of as-synthesised (Z5 and NiZ), spent (Z5 (S) and NiZ (S)) and regenerated (Z5 (R) and NiZ (R)) catalysts

7.3.4 Characterisation of Regenerated Catalysts

7.3.4.1 *Functional Groups, Structural, and Crystallinity Study of Regenerated Catalysts*

The XRD patterns of regenerated ZSM-5 and Ni/HZSM-5 catalysts were studied after the ETH process at 96 hours TOS. The results showed that the XRD patterns of the regenerated catalysts were similar to those of the original catalysts, indicating that the catalysts maintained their MFI zeolite characteristic peaks at $2\theta = 7-9^\circ$, 14.81° and $23-25^\circ$ and structural stability during the reaction (Figure 7.3a). The maintenance of the crystal structure and phase composition of the catalysts indicates that they can withstand the harsh conditions of the reaction without undergoing significant structural changes. This ensures the stability and longevity of the catalysts and maintains their catalytic activity and selectivity over time. Previous studies have also reported similar observations regarding the structural stability of ZSM-5 and Ni/HZSM-5 catalysts during the ETH process. For instance, a study by Zhou et al. (2018) reported that the XRD patterns of regenerated Ni/HZSM-5 catalysts were similar to those of the fresh catalysts, indicating that they maintained their structural stability during the reaction. Similarly, a study by Gardner et al. (2015) reported that the crystal structure of ZSM-5 catalysts remained intact after the reaction.

The FTIR spectra of regenerated catalysts after the ETH process showed no significant changes in the absorption bands compared to the original catalysts (Figure 7.3b). The bands at around 2925 and 2855 cm^{-1} corresponding to the stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively, were observed in both catalysts, indicating the preservation of the hydrocarbon products on the catalyst surfaces (Pino et al., 2018). This observation agrees with previous studies on the preservation of hydrocarbons on ZSM-5 and Ni/HZSM-5 catalysts during the ETH process. The preservation of hydrocarbons on the catalyst surface is essential for maintaining the activity and selectivity of the catalysts. In addition, the bands at around 1064 cm^{-1} , corresponding to the Si-O-Si stretching vibrations, were observed in the FTIR spectra of both regenerated ZSM-5 and Ni/HZSM-5 catalysts (Anjaneyulu et al., 2016, Liang et al., 2021). The preservation of the Si-O-Si vibrations indicates the preservation of the zeolite framework of the catalysts. The zeolite framework is an essential structural feature of ZSM-5 and Ni/HZSM-5 catalysts, which provides the necessary acidic sites for catalysing the conversion of ethanol to hydrocarbons.

SEM analysis was used to investigate the effect of the regeneration technique employed in the present study on the morphology and microstructure of regenerated ZSM-5 and Ni/HZSM-5 catalysts after the ethanol to hydrocarbon (ETH) conversion process at 96 hours TOS. The SEM images of the regenerated catalysts showed no significant changes in morphology compared to the original catalysts (Hernández-Giménez et al., 2022). The images revealed the presence of well-defined zeolite crystals with aggregated particles, indicating that the ETH process did not cause significant changes in the morphology and microstructure of the catalysts (Figure 7.3c). These findings are important because they suggest that the regeneration process used in this study effectively restored the catalysts' original morphology and microstructure. This is crucial because the morphology and microstructure of the catalysts play a vital role in determining their catalytic activity and selectivity (Shi et al., 2018, Sun et al., 2016). Therefore, the fact that the regenerated catalysts showed similar morphology and microstructure to the original catalysts suggests that they are likely to exhibit similar catalytic performance in ethanol conversion and product distribution. Figure 3 shows the images of as-synthesised, spent and regenerated catalysts after the ETH process.

Overall, the fact that the morphology, microstructure, and functional groups of the catalysts remained unchanged after the ETH process suggests that the catalysts are likely to exhibit similar catalytic performance to the original catalysts. This finding is essential for the potential application of these synthesised catalysts in the ETH process as it ensures their reusability, longevity, stability, and catalytic performance over time. The preservation of the as-synthesised catalysts' surface chemistry and structure after the reaction provides insights into their long-term stability and durability, which are essential for their practical application in industry.



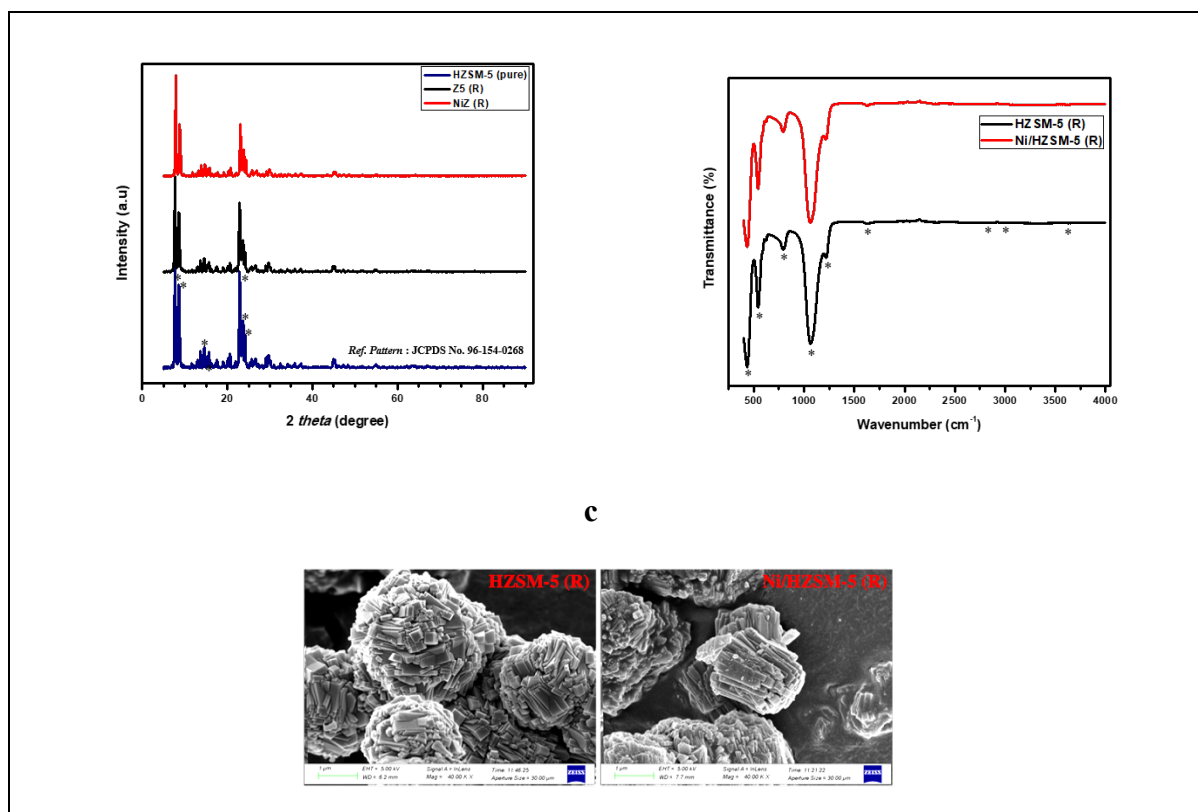


Figure 7-3. XRD (a), (b) FTIR and SEM image (c) of the regenerated catalyst (HZSM-5 (R) and Ni/HZSM-5 (R)) after three cycles of ETH conversion at 96-hour TOS each

7.3.4.2 Textural Properties of Regenerated Catalysts

The textural properties of the regenerated catalysts were studied after the regeneration process. The unmodified and Ni-doped regenerated catalysts show a type-1V isotherm with a hysteresis loop, indicating that mesoporous structures are preserved after regeneration. Adsorbate uptake was greatly enhanced in the P/P_0 range of 0.9-1.0 compared to lower pressure ranges. This showed that the catalysts have a higher affinity for adsorbate molecules at higher pressures, probably due to the accessible mesopores in this range (Figure 7.4). The adsorbed volume decreases with the addition of Ni species, which is consistent with the original catalysts. The regenerated ZSM-5 and Ni/HZSM-5 catalysts have a considerable surface area (308.2 and 295.4 m²/g, respectively) (Table 7.2), indicating that the regeneration process successfully preserved the overall porous structure of the catalysts. However, it should be noted that the surface area of the unmodified catalysts is larger than the Ni-doped catalysts due to the presence of Ni species that can affect the accessibility of the active sites and limit the available surface area for adsorption and reaction. A reduction in surface area and average pore diameter was observed when comparing the regenerated catalysts to the unused catalysts. Notably, the regeneration process may result in the loss of active sites and structural changes in the catalyst,

reducing surface area. In addition, the presence of coke deposits and other carbonaceous species, often formed during the catalytic reaction and accumulating on the catalyst surface, can contribute to the reduction in surface area. However, despite the reduction in surface area and average pore diameter, the total pore volume of the regenerated catalysts increases. This increase can be attributed to the formation of mesopores during the regeneration process. The regeneration process, which often involves high-temperature treatments, can lead to the restructuring of the catalyst and the formation of mesopores. These mesopores can contribute to the total pore volume of the catalyst, compensating for the decrease in surface area and average pore diameter. The increase in mesopores in the regenerated catalysts can have important implications for the improved catalytic performance of the regenerated catalysts. Mesopores can provide improved diffusion pathways for reaction molecules and enhance mass transport within the catalyst, leading to better accessibility of active sites and potentially improving catalytic activity and selectivity. This result agrees with previous studies (López et al., 2011, Li et al., 2022b)

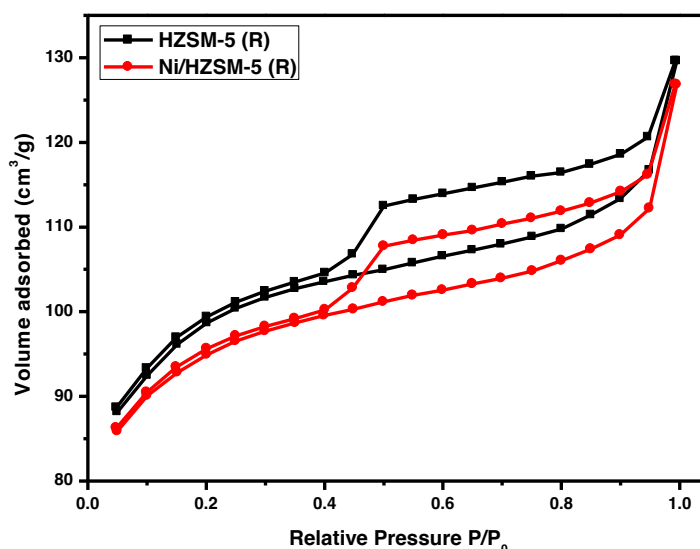


Figure 7-4. N₂ adsorption-desorption isotherms of regenerated catalysts

Table 7-2. Textural Properties of Regenerated Catalysts

Catalysts	S _{BET} (m ² g ⁻¹)	V _{total} (BJH) (cm ³ g ⁻¹)	V _{micro/meso} (BJH) (cm ³ g ⁻¹)	V _{macro} (BJH) (cm ³ g ⁻¹)	Avg pore dia. (nm)	Volume@STP (cm ³ g ⁻¹)
HZSM-5	308.16	0.681	0.664	0.017	2.61	101.69
0.5Ni	295.39	0.697	0.663	0.034	2.66	97.70

7.4 Concluding remark

This study investigates the stability and regeneration of as-synthesised ZSM-5 zeolite catalyst in ethanol conversion into hydrocarbons at 350 °C and 7 h⁻¹ WHSV for 96 h on stream. Catalyst regeneration was conducted after 96 h on stream for two cycles. Product distribution revealed that aromatics, C₅-C₈, and C₉+ hydrocarbons were the main liquid products, and their selectivity changed over time on stream. The Z5 catalyst maintained high-level stability in ethanol conversion, while the Ni-doped catalyst, NiZ, decreased conversion over time. Both catalysts showed selectivity towards C₅-C₈ hydrocarbons, but Z5 had higher selectivity for C₅-C₈ and BTX, while NiZ had higher selectivity for C₅-C₈, C₉-C₁₂ and C₁₂+ hydrocarbons. Incorporating Ni reduced the formation of BTX and gaseous hydrocarbons and increased selectivity towards C₅+ HCs.

The regeneration process for both catalysts improved their catalytic performance, particularly for the Ni-doped catalyst. The Z5/R1 catalyst maintained a high ethanol conversion (>96%) and showed an increase in selectivity towards BTX (20.17%) and C₉-C₁₂ (5.42%) compared to the as-synthesised Z5 catalyst. On the other hand, the NiZ/R1 catalyst exhibited stable ethanol conversion (~100%) up to 48 h on stream, with a decrease to 60.6% at 72 h and a considerable increase in selectivity towards C₅-C₈ hydrocarbons. Both regenerated catalysts showed a significant reduction in selectivity towards gaseous hydrocarbons, and their product distribution remained similar to the first cycle. The third cycle of ETH conversion using Z5/R2 and NiZ/R2 catalysts from the second regeneration cycle demonstrated that these catalysts retained their activity and product distribution up to the same time on stream as the as-synthesised catalysts. This suggests that the regeneration process successfully restored the catalytic properties of the catalysts. Z5/R2 catalyst maintained 100% conversion up to 96 h on stream, with selectivity to C₅-C₈, BTX, and slightly C₉-C₁₂. NiZ/R2 also exhibited stable conversion, with > 92% ETH conversion up to 48 h on stream, before experiencing a significant decrease. Both catalysts were more selective to liquid HCs (> 99%). Z5/R2 catalyst was preferential to BTX, while NiZ/R2 favoured C₅-C₈, C₉-C₁₂, and C₁₂+. Overall, Z5 demonstrated greater stability than NiZ, while the regeneration process improved the catalytic activity of the spent and deactivated catalysts, indicating the potential for catalyst reuse and sustainability. The study on regenerated catalysts revealed that the structural and functional groups of the catalysts remained unchanged, retaining the MFI framework of zeolite catalyst after the ETH

process. This confirms the ability of the regenerated catalysts to exhibit comparable catalytic performance to that of the original catalysts. The NiZ catalyst showed higher coke deposition (with 2.8 wt% weight loss attributed to hard coke) than the unmodified HZSM-5 catalyst (2.1 wt%). The Ni on the NiZ catalyst promotes coke formation and enhances combustion, resulting in increased selectivity for long-chain hydrocarbons and faster deactivation.

The results of this study provided valuable insights into the stability and effectiveness of the as-synthesised catalysts, Z5 and NiZ, in ETH conversion. Specifically, it was observed that this catalyst (Z5) maintained a high level of stability, achieving an ETH conversion rate of approximately 100% for three conversion cycles, each lasting 96 hours on stream. However, NiZ maintained stability up to 48 h on stream before gradually declining. This level of stability was maintained even after the catalyst underwent two regeneration cycles. The study of the regenerated catalysts showed that the applied regeneration method successfully preserved the textural and morphological properties of the catalyst while improving the catalytic performance. Understanding the coke deposition behaviour of HZSM-5 and Ni/HZSM-5 catalysts is critical for optimising the catalytic process and developing effective strategies to mitigate coke formation and deactivation. Such findings suggest that these catalysts may be attractive for industrial applications, where catalyst stability and longevity are crucial considerations. Overall, these results indicate that the catalysts could be a promising solution to address the challenges associated with ETH conversion, providing a stable and effective catalyst option for future use.

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CHAPTER 8

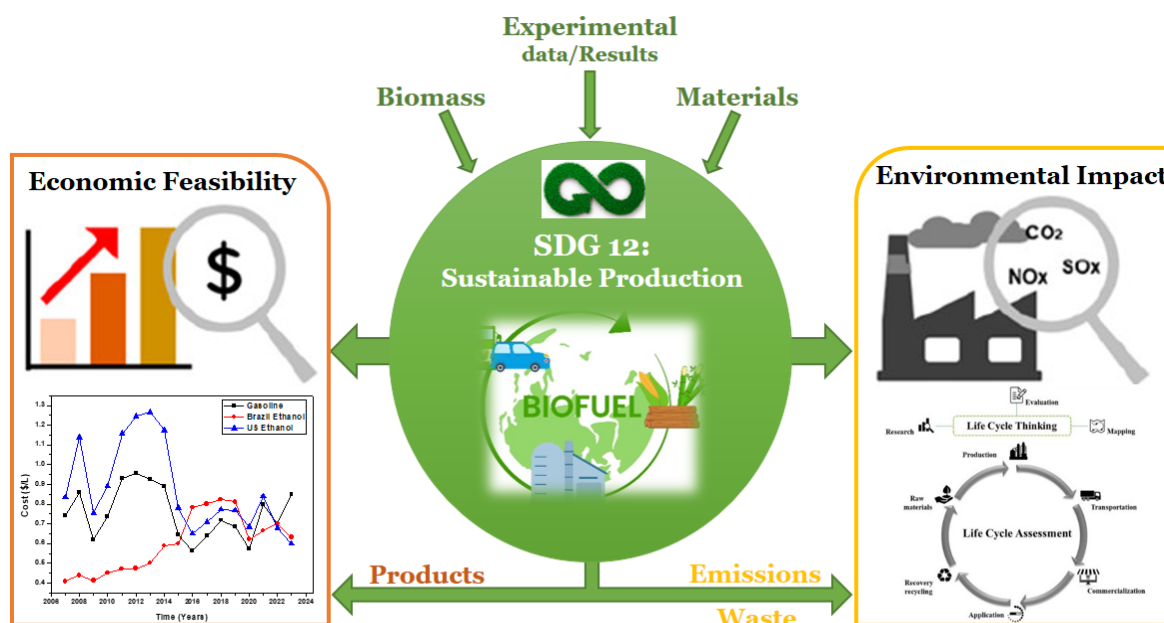
Techno-economic and Life-cycle Analysis of Single-step Catalytic Conversion of Bioethanol to Fuel Blendstocks over Ni-doped HZSM-5 Zeolite Catalyst

Abstract

This chapter presents techno-economic and life-cycle studies focusing on the catalytic transformation of ethanol into hydrocarbon fuel blendstocks. These analyses benefit from recent advancements in catalyst and process development. The consolidated alcohol dehydration and oligomerization for ethanol-to-hydrocarbon (CADO-ETH) conversion approach, described here, achieves a single-step transformation of wet ethanol vapour into hydrocarbons and H₂O using a Ni-doped HZSM-5 catalyst. Catalyst cost estimation using CatCost model showed that commercial synthesis of Ni/HZSM-5 incurred significant processing costs, which varied greatly depending on the manufacturing scale. Hence, catalyst production using 100 % baseline scale production (BSP) and 50 % BSP requirement showed a net catalyst cost of \$31.4 and \$69.9/kg, respectively. Although current CADO products closely resemble petrol blendstocks, they can also be blended with gasoline fuel at low levels. There is potential for higher-level blending in the future. The operating and annualized capital costs for converting wet ethanol into fuel blendstocks are predicted to be \$0.05/L at present and projected to decrease to \$0.03/L in the future. This cost is comparable to the unit energy cost of synthesising anhydrous ethanol from wet ethanol, which is \$0.02/L. When oil is priced at \$100/bbl, the predicted minimum selling prices for fuel blendstocks produced through CADO are similar to those of traditional gasoline fuel. However, at an oil price of \$60/bbl, the estimated minimum selling prices for CADO-derived blendstocks are not competitive with conventional gasoline fuel. Nevertheless, considering existing production incentives, the estimated minimum selling price of fuel blendstocks remains comparable to the \$60 per barrel oil price scenario. The reductions in life-cycle greenhouse gas emissions achieved by CADO-derived fuel blendstocks are similar to those obtained from ethanol feedstock. Developing and adopting biofuels also present economic opportunities, as they can contribute to job creation, promote domestic energy production, and reduce dependence on imported fossil fuels. Moreover, biofuels have the potential to revitalize rural economies by providing a market for agricultural and forestry residues, as well as dedicated energy crops.

Keywords: Ethanol, Greenhouse gases, Life Cycle Analysis, Techno-economic Analysis, ZSM-5

Graphical Abstract



8.1 Introduction

Recently, there has been a surge in the interest in renewable fuels due to the depletion of fossil fuels and growing concerns about climate change and air pollution. Liquid fuels such as petrol and diesel contribute approximately 40 % of global energy consumption (Ramasamy et al., 2014). The global transport industry witnessed a substantial increase in greenhouse gas (GHG) emissions, surpassing emissions from any other sector. The transport sector has now become the primary source of carbon emissions in most countries, overtaking electricity generation. Most industry analysts agree that combining electric vehicles with low-carbon electricity production is the most promising strategy for minimizing fossil fuel emissions in the commercial transportation sector. However, incorporating energy storage systems utilizing batteries or hydrogen onboard poses significant challenges in non-light-duty transportation sectors (aviation, ocean shipping, etc.) (Hannon et al., 2020). Hence, energy-dense liquid hydrocarbon (HC) fuels are expected to continue being utilized in these areas. Despite aggressive efforts to minimize travel growth, promote mass transport means, enhance efficiency, and promote the commercialisation of electric and H₂-powered automobiles, it is projected that liquid fuels will still be necessary to meet around 50 % of the required

transportation fuel by 2075 (Fulton et al., 2015). Biofuels, fuels produced from biomass, are considered the most advantageous option for generating low-carbon liquid fuels.

To reduce fossil emissions in the transport sector, active efforts are underway to explore various strategies involving biofuels. These strategies include the production of fuel-range HCs other than biomass from biomass, engine modification to utilize E100, and converting ethanol into hydrocarbon fuels. Among these approaches, the latter shows promise due to the low cost of ethanol and its extensive production capacity. Similar to the methanol-to-gasoline (MTG) technology, which Mobil pioneered, the ethanol-to-hydrocarbon/gasoline process offers a viable approach for ETH conversion. Several other alcohol-to-hydrocarbon processes are currently under development, including the ethanol-to-olefin/ethylene (ETO and ETE) and methanol-to-olefin/propylene (MTO and MTP). While extensive research has been conducted on methanol, there has been limited exploration of the transformation of higher alcohols, such as ethanol, propanol, and butanol, into HCs. There has been significant interest in the catalytic conversion of ethanol into hydrocarbons (ETH) to produce renewable fuel. The typical approach involves a three-step process that includes ethanol dehydration, ethylene oligomerisation, and hydrogenation to produce a final renewable fuel suitable for blending with conventional fuels. Researchers have extensively investigated the chemistry and methods involved in this ethanol-to-hydrocarbon conversion process. Various companies have been exploring the feasibility of these three-step processes (Hannon et al., 2020).

Another approach involves a one-step ethanol-to-hydrocarbon (ETH) blendstock transformation utilizing a metal-doped zeolite catalyst. This consolidated alcohol dehydration and oligomerisation (CADO) process, proposed by Narula et al. (2015), aims to achieve dehydration and oligomerisation of alcohols in a single reactor without needing external H₂ addition. Narula et al. (2015) showed complete ETH over ZSM-5 and a single reactor setup in laboratory experiments. The researchers found that the percentage of ethanol in H₂O had no significant effect on the ETH conversion rate or product selectivity. The study also suggested a mechanism for HC formation that bypasses the intermediate production of ethylene, directly transforming ethanol into long-chain HCs and H₂O. Extensive studies have been conducted on the catalytic transformation of low alcohols, particularly producing liquid HCs fuels and light olefins using ZSM-5 catalyst (Gil-Horán et al., 2020, Wang et al., 2019b, Xia et al., 2021, Li et al., 2019a). The deoxygenation of methanol, catalysed by HZSM-5 zeolite, has been extensively studied under mild reaction conditions, leading to chain growth and the production

of HCs < C₁₀ (gasoline range). HZSM-5 zeolite demonstrates an appropriate balance of activity, shape selectivity, slow deactivation, and hydrothermal stability, making it the preferred catalyst among the tested zeolite catalysts. Moreover, the HZSM-5 catalyst can easily be regenerated by burning off accumulated coke deposits without altering its catalytic characteristics. These properties contribute to the viability of HZSM-5 catalyst for low alcohols and oxygenate conversion into HCs. Compared to traditional three-step methods, adopting a simplified one-step process for ETH blendstocks brings various potential benefits. These advantages encompass cost reduction and environmental impact mitigation. The CADO for ethanol-to-hydrocarbon (CADO-ETH) technology has shown compelling findings of greenhouse gas emission reductions by 40 to 96 %. This innovative approach holds great promise in enabling the development of environmentally friendly and sustainable gasoline production for transportation purposes. The CADO-ETH process offers several advantages over traditional catalytic upgrading methods. It can be conducted in a single step at temperatures ranging from 275 to 350 °C, close to atmospheric pressure, and does not require the addition of external hydrogen. These characteristics make CADO-ETH potentially more cost-effective (Hannon et al., 2020).

The field of catalysis study intends to optimize the performance and accessibility of valuable commodities, such as energy, chemicals, pharmaceuticals, and consumer products, while reducing ecological environmental impacts. The International Energy Agency estimates that advancement in catalytic processes can reduce carbon-intensive chemical products' energy consumption by 20-40%. These products account for 80% of the energy consumed in the chemical industry and 75% of greenhouse gas emissions (Van Allsburg et al., 2022). To contribute effectively to this goal, new catalysts must be evaluated based on their traditional aspects, such as activity, selectivity, and productivity/lifetime and by considering the costs and ecological effects related to their use. Before investing in commercial catalysts, suppliers and consumers thoroughly assess their costs. According to Van Allsburg et al. (2022), out of a total of 250,643 entries in the dataset from a comprehensive literature review and frequency survey conducted to investigate the cost of catalysts (2010-2020), 5.80 % of the articles were identified as containing the words 'cost' or 'costs' in either the title or abstract. Among these articles, only 0.25 % featured terms in their titles or abstracts that indicated a specific discussion on the cost of catalysts. These terms included "catalyst(s) cost," "manufacturing cost," "synthesis cost," "material(s) cost," "production cost," or "economic cost (Van Allsburg et al., 2022). This

literature review and frequency survey serve as a valuable resource for understanding insufficient information related to the cost aspects of catalysts. However, many researchers in this field lack the necessary information to conduct such assessments.

The combustion of pure biofuels generally produces fewer harmful emissions such as particulate matter, sulfur dioxide and air pollutants than the combustion of fossil fuels. This is particularly evident with diesel fuel. Blends of biofuel and petroleum also generally result in lower emissions than fuels without biofuels. However, the combustion of biodiesel can produce roughly higher levels of nitrogen oxides than petroleum-based diesel fuel. Ethanol and ethanol-gasoline blends have cleaner combustion than non-ethanol gasoline and offer higher octane levels (Damyanov and Hofmann, 2019). However, they have more evaporative emissions from fuel tanks and dispensers. Gasoline without ethanol, on the other hand, has a lower octane rating. These emissions evaporate and aid the formation of ground-level ozone and smog, both of which are harmful. To solve this problem, additional gasoline processing before blending it with ethanol is required to reduce evaporative emissions (Wu et al., 2020, Mohammed et al., 2021). The combustion of biofuels releases CO₂, which contributes to greenhouse gas emissions. However, international agreements do not include CO₂ emissions from biofuel utilization in national greenhouse gas inventories. This exemption assumes that the cultivation of biomass used for biofuel production has the potential to offset CO₂ emissions from combustion. The ecological effect of biofuel use in terms of CO₂ emissions is based on biofuel production and whether emissions from cultivation are accounted for (Machado et al., 2017). There is an ongoing debate about using land, fertilizers, and energy to grow biofuel crops versus food crops. In some regions, large amounts of natural vegetation and forests have been cleared or burned to make way for soybeans and palm oil trees used to produce biodiesel. In addition, many companies that produce ethanol, renewable diesel, renewable heating oil, and renewable aviation fuel rely on fossil fuels as the primary heat source for the production process. While some ethanol producers in the United States use corn stalks as a heat source, Brazilian ethanol producers use sugarcane stalks, known as bagasse, for heat and energy generation.

However, the liquid fuel yields obtained so far have been relatively low, and further development of the catalyst process is needed. Currently, research efforts are focused on catalyst and process development for the CADO-ETH technology and, there have been limited techno-economic analyses (TEA) or life-cycle assessments (LCA) for CADO-ETH. The

objective of this study was to conduct an economic analysis to evaluate the feasibility and cost of the commercial synthesis of the novel Ni-doped HZSM-5 zeolite catalyst, and the production of hydrocarbon fuel blendstock via the CADO-ETH process. Additionally, we assessed the life-cycle greenhouse gas emissions associated with the combustion and utilization of the gasoline fuel blendstock derived from the CADO-ETH process.

8.2 Materials and Methods

The study employed several chemicals, including sodium silicate solution ($\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), tetrapropyl ammonia bromide ($\text{C}_{12}\text{H}_{28}\text{BrN}$), sodium hydroxide (NaOH, 97%), sulfuric acid (H_2SO_4 , 98% conc.), and ammonium nitrate (NH_4NO_3). Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as a precursor for transition metals. Sigma-Aldrich provided the ethanol feedstock. A hydrothermal reactor with 200 mL stainless steel and Teflon capacity was utilized for catalyst synthesis. Catalysts were synthesised and characterised and tested according to *Section 3.2.2*. The catalytic performance of HZSM-5 and Ni/HZSM-5 were studied at a temperature of 350 °C and weight hourly space velocities (WHSV) of 7 h⁻¹ for 96 hours TOS (with 8 hours sampling) in the conversion of ethanol into hydrocarbons. HZSM-5 and Ni/HZSM-5 catalysts were regenerated according to *Section 7.2*.

8.2.1 Ni/HZSM-5 Catalyst Cost Estimation

Laboratory-scale synthesis methods serve as the basis for designing industrial processes. Building upon these laboratory techniques, conceptual catalyst production techniques were established and optimized in the Catcost Excel version. These procedures were designed to be sustainable, aiming to minimize raw material utilization by recycling unreacted reactants and reducing waste generation in wastewater and air pollutants. Process heat integration was also employed to maximize energy efficiency by reclaiming high-value heat and minimizing heat rejection. Material and energy flows derived from the process model were employed for equipment sizing. These process designs were crucial for cost analysis and have been implemented as process templates in CatCost for easier analysis. The catalyst manufacturing scale in a biorefinery was established as the baseline. The consumption rate of catalysts in the biorefinery, measured in grams of catalyst per global gram equivalent (GGE) of product, was determined based on various sources of information according to (Van Allsburg et al., 2022). For example, the consumption rate for the ZSM-5 catalyst was 18.12 grams per GGE, as reported by the National Renewable Energy Laboratory (NREL). On the other hand, the annual

catalyst demand in the biorefinery, which processes 2,000 dry tonnes of biomass per day and produces 47.0 million GGE per year, was estimated to be 911 tonnes (baseline scale production [BSP] requirement) for ZSM-5 only during catalyst replacement years.

To estimate the cost of the Ni/HZSM-5 catalysts, the CatCost v1.1.0 spreadsheet tool was utilized, and the cost estimates were compiled in Microsoft Excel and the Catcost web version. The Appendix section comprehensively describes the assumptions, input costs, cost factors, and other variables used in the calculations. All values were converted to US dollars in 2016, using either the Chemical Producer Price Index or the Chemical Engineering Plant Cost Index, depending on the nature of the expenditure. The prices of raw materials were determined using various sources, including vendor quotations, publicly available and proprietary price databases, and insights from industry experts. Multiple sources were considered to calculate an average price and validate the estimates. Two methodologies, the Step technique and the CapEx and OpEx Factors method, were used to estimate the processing costs. For the present study, we employed the CapEx and OpEx Factors methods for cost estimation. For the CapEx and OpEx Factors method, a BSP for a dedicated catalyst synthesis plant was assumed to be the annual biorefinery catalyst demand for ZSM-5. Detailed breakdowns of the calculation steps and equipment lists for the estimation method are provided in the Appendix (Appx.) Figures 1a-k. The capital costs, including installation, piping, instrumentation, and buildings, as well as indirect costs and working capital, were estimated using fixed factors (multipliers) based on the total cost of purchased equipment (Figure 8.1). Similar calculations and factors were used to determine operating costs, such as supervisory labour and maintenance supplies, as well as fixed/indirect costs and general expenses. Continuous operation (8,760 hours per year) with full staffing levels, including maintenance downtime, was assumed. A worker rate of \$48 per hour was used for production, according to (Van Allsburg et al., 2022), which accounted for additional perks.

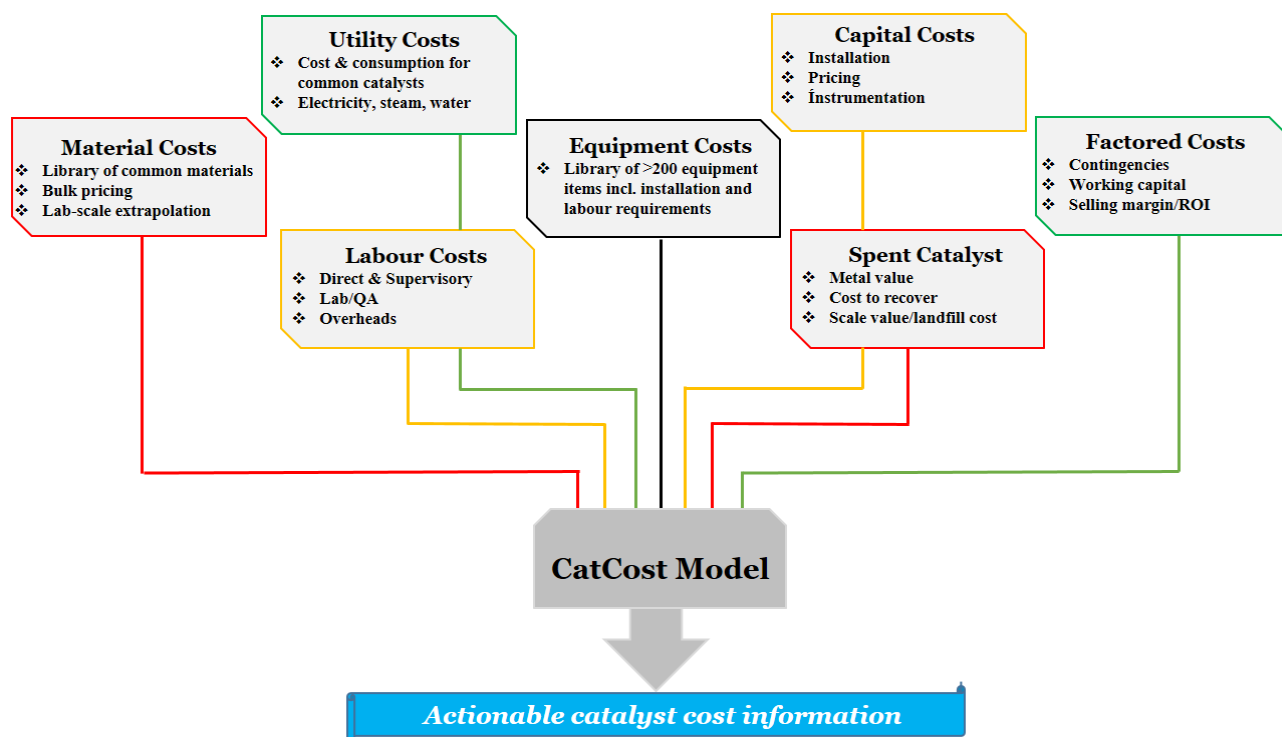


Figure 8-1. Catcost Model components for catalyst cost estimation

8.2.2 CADO-ETH Techno-economic Analysis (TEA) Methodology

The operational costs of CADO-ETH technology were estimated according to Hannon et al. (2020). This was done by conducting mass and energy balances and considering various factors such as wastewater treatment, catalyst expenses, electricity, waste disposal, insurance and taxes, and labour. It was assumed that the water produced during the process would be treated in a standard wastewater facility, costing \$1.85 per 1000 litres or \$7 per 1000 gallons. For the existing CADO-ETH technology, it was estimated that the reactor catalyst would need replacement every 6 months at \$70/kg. As for the future CADO technology, the catalyst replacement was projected to occur every 9 months at \$31.42/kg, corresponding to the net catalyst cost from 100% BLSP estimated from the CatCost model. The electricity unit cost used for calculations, at \$0.05/kWh, represented the average in the Midwest, the primary US ethanol synthesis region (Hannon et al., 2020). The electricity demand in this region mainly powered compressors and pumps. Insurance and municipal taxes were estimated to account for 2.0% of the total installed capital (TIC), while maintenance and labour were projected to make up 3.0% and 1.0% of the TIC, respectively. The NREL's mass and energy balances and unit costs were utilized to convert from wet alcohol to anhydrous ethanol. To estimate the capital costs, equipment sizes were determined based on energy balances and combined with costs

from comparable equipment, as stated in NREL TP 47764 (Humbird, 2011) and (Hannon et al., 2020, Tao et al., 2017). The scaling factor of 0.60 was employed to evaluate the change in equipment costs when scaling up from the reference sizes provided by NREL (Humbird, 2011). Installation factors similar to NREL TP 47764 were applied. Equipment costs were adjusted for inflation by increasing them by 1.5% (the average annual inflation rate for equipment over the past ten years) to 2023. The installation variables from NREL Technical Paper 47764 were used to calculate the installed capital costs according to (Hannon et al., 2020, Humbird, 2011).

8.2.3 Life Cycle Analysis (LCA) Methodology

The LCA Methodology involved calculating the life-cycle greenhouse gas (GHG) emissions for producing 1 MJ of hydrocarbons from corn starch and corn stover using current and advanced conversion technologies. The Argonne National Laboratory developed the GREET model with funding from the Office of Energy Efficiency and Renewable Energy in the US Department of Energy, which was applied for this purpose. The GREET model also provided results for producing conventional gasoline fuel from fossil sources. In addition, the life-cycle GHG emissions of ethanol synthesis from cane juice and cane cellulose in Brazil were evaluated according to (Hannon et al., 2020). This encompasses various aspects, including farming activities, feedstock collection and transportation, and ethanol manufacturing. The second section of the investigation focused on converting ethanol to hydrocarbons, covering catalytic operations, product recovery, and HC transportation, distribution, and storage. The end-of-life combustion of the CADO product, specifically for gasoline fuel, was also included in the system boundary. More detailed information about the LCA inputs can be found in the Appendix. LCA input details are shown in Appx. Figure 5

8.3 Results and Discussion

8.3.1 CADO-ETH Process Result

Figure 8.2a present the result for the CADO-ETH, along with the phase selectivity of the catalyst for gaseous and liquid products for the first and second (after catalyst regeneration) cycle. The primary liquid products included aromatics (BTX: benzene, toluene, and xylenes), C₅+ hydrocarbons (C₅-C₁₂ – gasoline range HCs (GRH) and C₁₀-C₂₀ – diesel range HCs (DRH), and their selectivity changed over time. The NiZ catalyst from the first cycle showed appreciable stability but experienced a decrease in ethanol conversion after 48 hours on stream. The Ni-doped catalyst (NiZ) recorded a gradual reduction in ETH conversion from its initial

value of 100% to 62.4% after 40 hours on stream. This decrease in conversion can be attributed to increased oligomerization of ethylene resulting from the early stages of ethanol dehydration reaction (Guisnet and Magnoux, 1994). Additionally, the selectivities of the NiZ catalyst towards C₅-C₁₂ and BTX declined after 32 and 40 hours on stream, respectively, shifting towards selectivity for C₁₀-C₂₀. However, the ETH conversion rate gradually increased and reached approximately 100% after 56 hours on stream, followed by a decrease of 39.5% after 80 hours. After 64 hours on stream, the selectivity towards GRH exhibited a significant increase, likely due to the weakening of acid sites during deactivation. Gaseous hydrocarbons (C₁-C₄) decreased with increasing time on stream, particularly after 64 hours for the catalyst. The NiZ recorded the highest selectivity for C₅-C₁₂ (89.9%), BTX (10.6 %), and C₁₀-C₂₀ (21.8 %) at 72, 88, and 96 hours on stream. NiZ demonstrated significant average selectivity towards C₅-C₁₂ (79.2 %) and C₁₀-C₂₀ (7.4 %), BTX (4.5 %).

Following NiZ deactivation after the initial cycle, the catalysts underwent a five-hour regeneration process at 550 °C, with an 80 mL/min airflow rate. The regenerated catalyst is denoted NiZ/R. The results of the regeneration procedure indicated an improvement in the catalytic performance of the used and deactivated catalysts. After regeneration following deactivation, the NiZ/R catalyst exhibited enhanced catalytic activity, like the behaviour observed with the deactivated catalyst. These findings align with previous studies by Yung et al. (2019). The NiZ/R catalyst, like the fresh catalyst, maintained a consistent CADO-ETH conversion of around 100% up to 48 hours on stream. However, a drop to 60.6% was observed after that point, followed by a progressive decline after 56 hours on stream (Figure 8.2b). In contrast to the pure catalyst, the NiZ/R catalyst showed an increase in the synthesis of GRH, resulting in a decrease in selectivity towards DRH fractions. With an increase in time on stream (TOS), the selectivity of the regenerated catalyst exhibited a significant decrease in their ability to favour gaseous HCs. The regeneration and application of regenerated catalysts demonstrated that they retained their catalytic activity after the regeneration cycle. This indicates that the catalyst did not undergo irreversible dealumination during the extended TOS required for the CADO-ETH process (Wang et al., 2017, Li et al., 2022b). The product distribution analysis of the second cycle CADO-ETH conversion demonstrated that the regenerated catalyst displayed comparable catalytic performance to NiZ, exhibiting a significant preference for GRH (80.7 %) over DRH (4.3 %) and BTX (5.1%). This discovery aligns with the product distribution observed in the first cycle.

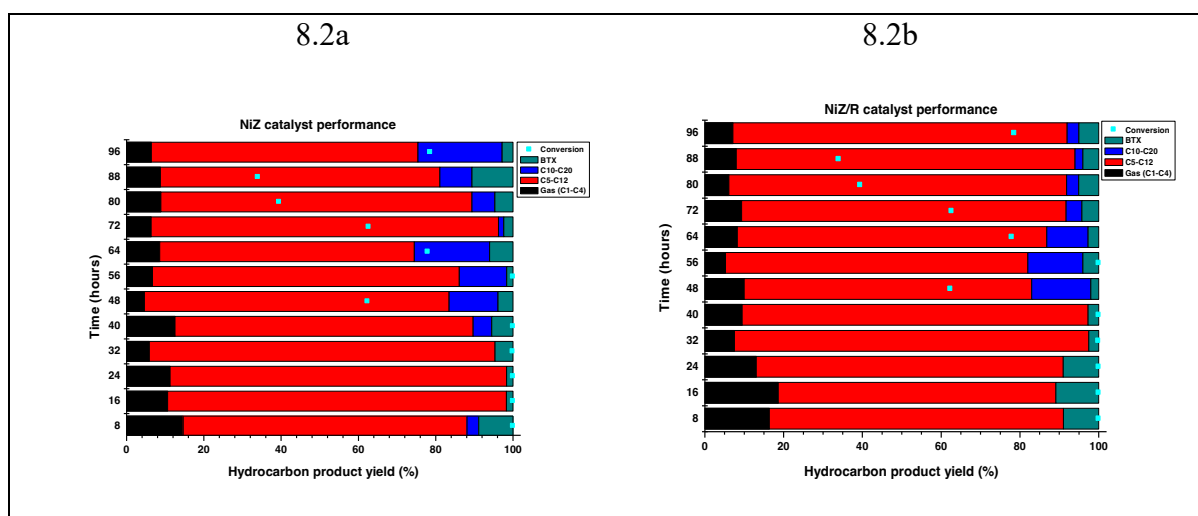


Figure 8-2a & b. Product distribution (GRH, DRH, & BTX) of NiZ and regenerated catalyst (NiZ/R)

8.3.2 Cost Estimation of Catalyst using CatCost

The cost estimation of catalysts was efficiently carried out using CatCost, available as a spreadsheet or web-based application that can be easily launched in any modern web browser. Both versions of CatCost can be downloaded from the website <https://catcost.chemcatbio.org>. The tool is designed with modular components encompassing the essential aspects of catalyst cost analysis. The web-based software and the spreadsheet version of CatCost follow a similar workflow, ensuring consistency in the estimation process. In CatCost, various inputs are considered, including the pricing year, the unit for mass calculations (e.g., USD per kilogram of catalyst), raw material costs, processing costs, the value of the spent catalyst, and desired outputs. The module in CatCost dedicated to managing raw material expenses plays a crucial role as they typically constitute a significant portion of the total catalyst cost. This module allows easy and quick entry of synthesis recipes from laboratory notebooks or publications. It features automated unit conversions, synthesis yield calculations, and the ability to query libraries for relevant information. Additionally, CatCost enables manual entry of raw material prices and provides guidance on obtaining appropriate pricing information for bulk quantities (above 1,000 kilograms). It provides access to various price databases, including free options (e.g., Alibaba), proprietary resources (e.g., IHS Process Economics Programme), vendor websites, and quotes. CatCost employs log-log extrapolation techniques, as described by (Qi et al., 2015b), for smaller purchasing sizes based on laboratory chemical suppliers' prices.

Furthermore, CatCost incorporates a built-in library with freely available data on price trends for different items. Lastly, the tool includes a component to account for inevitable losses of raw materials during production due to spoilage and waste. With its comprehensive functionality, CatCost simplifies and streamlines the estimation of catalyst costs, making it a valuable resource for cost analysis in research and development endeavours.

8.3.2.1 *Effects of Scale on the Cost of the Catalyst*

The cost of Ni/HZSM-5 catalyst in a process plant is significantly influenced by the quantity of catalyst purchased. Increasing the production scale (using the baseline catalyst requirement) and purchasing are expected to result in cost savings due to economies of scale and volume-buying. Despite being a well-known association, there are limited tools available for academics to measure the consequences of scale on catalyst cost. CatCost addresses this using its built-in scaling logic, which adjusts catalyst cost estimates based on the entered production scale. This automatic adjustment includes modifying equipment sizes and quantities to ensure they remain within the valid range for each cost estimate function. Equipment with unit sizes below the lower limit is priced based on its minimum size, while equipment with units above the upper limit has its quantity increased until the unit size falls within the range. ZSM-5 may be relatively expensive per GGE (gallon of gasoline-equivalent) due to its higher utilization rate than next-generation catalysts. The costs displayed in Figure 8.3a represent the net costs associated with the catalyst, including the projected SCVs (scale-up costs) for Ni/HZSM-5 catalyst. Discrepancies in price may be observed when compared to reducing the scale of production (for instance, 50 % of baseline scale production (BSP) requirement) showed an increase in net catalyst cost from \$31.42/kg to \$69.96/kg (\$31.31/kg and \$69.85/kg after deducting the projected SCVs) (SI Figs. 1j & k) which can also be attributed to jumps between synthesis scales, primarily due to contract manufacturers having equipment at predetermined scales. In practice, these discrepancies would likely be smoothed out by mixing equipment with varying scales and making discretionary adjustments to the selling margin. According to the data presented in Table 8.1, the cost of catalysts obtained from the current study is comparable to that of commercial vendors for large-volume production. This finding demonstrates the efficiency of purchasing from a contract manufacturer when catalysts are required in smaller quantities, i.e., less than a few kilotons per year. In this case, the contract manufacturer is responsible for procuring the necessary raw materials and managing all aspects of capital and operating costs, waste disposal, and related activities according to the buyer's requirements. A

study conducted by Baddour et al. (2018) found that estimating the cost of catalysts synthesised by a contract manufacturer using an all-in hourly cost method for specific equipment yielded results within 20% of market prices for various catalyst materials. On the other hand, catalysts that are produced in large quantities, such as fluid catalytic cracking catalysts (with a global production volume of 650 kilotons) (Van Allsburg et al., 2022), and those that must meet standardized specifications, are typically produced in dedicated facilities. Figure 8.3b & c illustrates how the components of catalyst purchase cost, including direct labour, overhead, maintenance, and repair, change as materials progress through two distinct purchasing scales. This is consistent with Van Allsburg et al. (2022) study. The tabular representation of this information can be found in the Appx. Table 1.

When investigating the influence of scale on CADO catalysts using CatCost, significant discrepancies are observed among different material types. The intricate and resource-intensive synthesis process of Ni/HZSM-5 catalyst results in a substantial reliance on the purchase scale for its net cost when starting with the commercially available Ni/HZSM-5 catalyst. The scale-dependent cost breakdown shown in Figures 8.3b & c reveals that processing costs dominate at 50 % BLSP due to their proportionality with the amount of Ni/HZSM-5 produced compared to 100 % BSP. This aligns with the high-consumption, low-cost approach to catalysts in recirculating bed applications, where Ni/HZSM-5 has a relatively lower contribution from raw materials cost. It is evident that in the case of 100 % BSP of catalyst, processing and overhead costs decrease proportionally with increasing scale, making raw materials the primary targets for additional cost reduction at larger production scales. This is further explained by the Donut chart in Appx. Figures 2a & b. The findings of this study showed that the cost of the catalyst and its components are significantly influenced by the operation's magnitude, material type and application. By examining cost and impact, catalyst developers can identify the primary cost factors that offer the most significant opportunities for targeted research and development. CatCost web-based application provides interactive visualizations of catalyst cost to facilitate the decision-making process in R&D. These visualizations offer more detailed breakdowns than shown in Figure 8.3b & c. As demonstrated in Figure 8.4 using CatCost-generated Sankey diagrams, the cost breakdowns for Ni/ZSM-5 catalysts exhibit a balanced composition, unlike other catalysts in that a single material may dominate cost contributor (Appx. Figure 3 presents the Sankey plot for the 50% BSP). The well-balanced cost breakdown for Ni/HZSM-5 reflects its status as an established, commercially available material that has undergone optimization throughout the scale-up process to minimize costs. Consequently, Ni-doped HZSM-5 may

exhibit a lower total cost than other materials. Overall, understanding the effects of scale on catalyst costs and identifying the significant cost factors contribute to informed decision-making and optimization in catalyst development and purchasing.

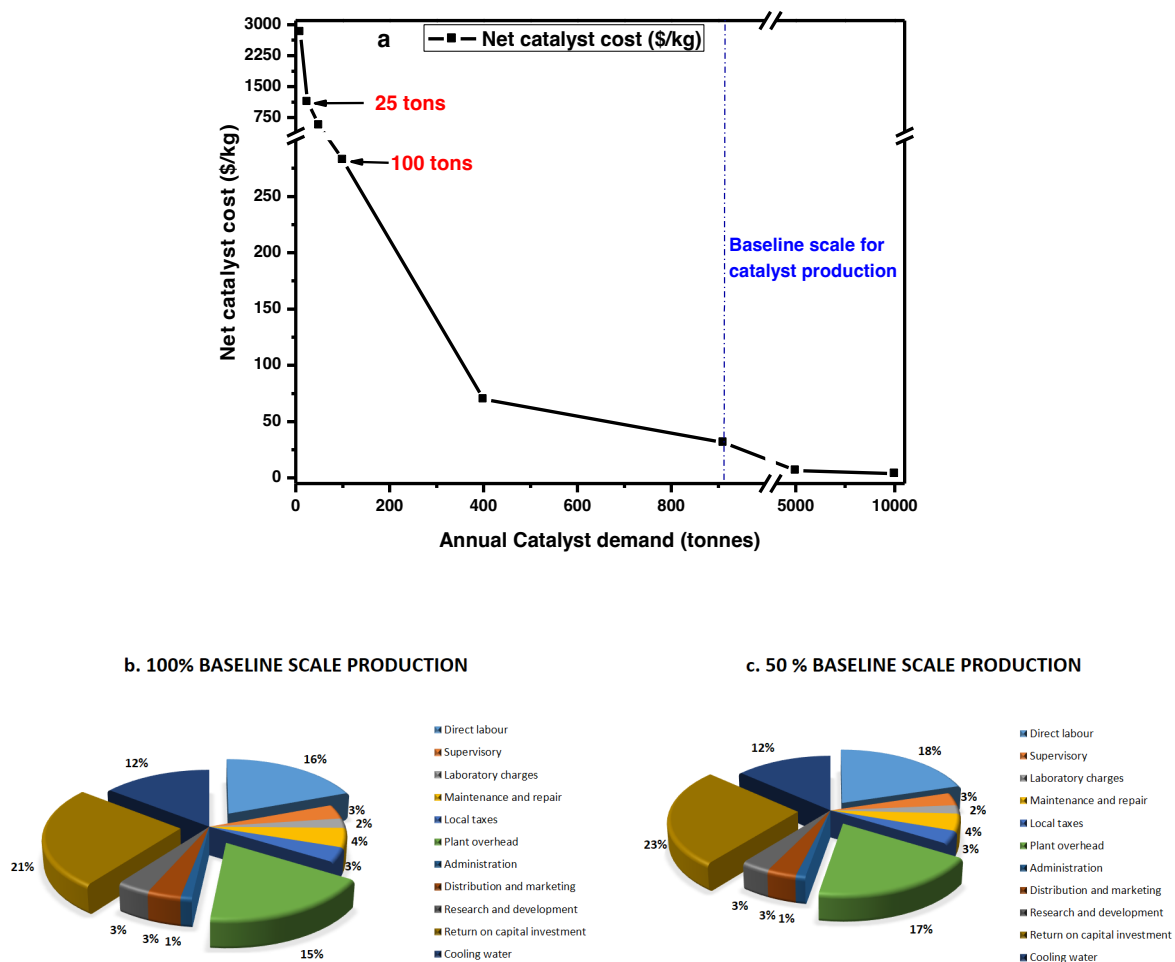


Figure 8-3. (a) Effect of scale on the net cost of catalyst. Cost estimated from the CatCost model, (b & c). Catalyst purchase cost breakdown for 100 and 50 % BSP using CapEx and OpEx method

Table 8-1. Price Comparison (present study and commercial vendors)

Catalysts	Price (\$/kg)	Vendor	Source
Ni/HZSM-5 (1000 tons)	28.7	Present study	Present study
Ni/HZSM-5 (100 % BSP)	31.4		
Ni/HZSM-5 (50 % BSP)	69.9		
Ni/HZSM-5 (25 % BSP)	121.5		
ZSM-5	40	Made in China	https://pingxiangnaike.en.made-in-china.com/product/zdCTiOXGrLRK/China-Zeolite-Zsm-5-Used-for-Hydrocarbon-Interconversion.html
ZSM-5	25-30	Alibaba	https://www.alibaba.com/product-detail/Hot-Sale-Synthetic-Zeolite-ZSM-5_1600449192511.html?spm=a2700.7724857.0.0.4ac97f55SF3Iq4
ZSM-5	50-200	Alibaba	https://www.alibaba.com/product-detail/ZSM-5-zeolite-for-FCC-catalyst_62208192183.html?spm=a2700.7724857.0.0.4ac97f55SF3Iq4

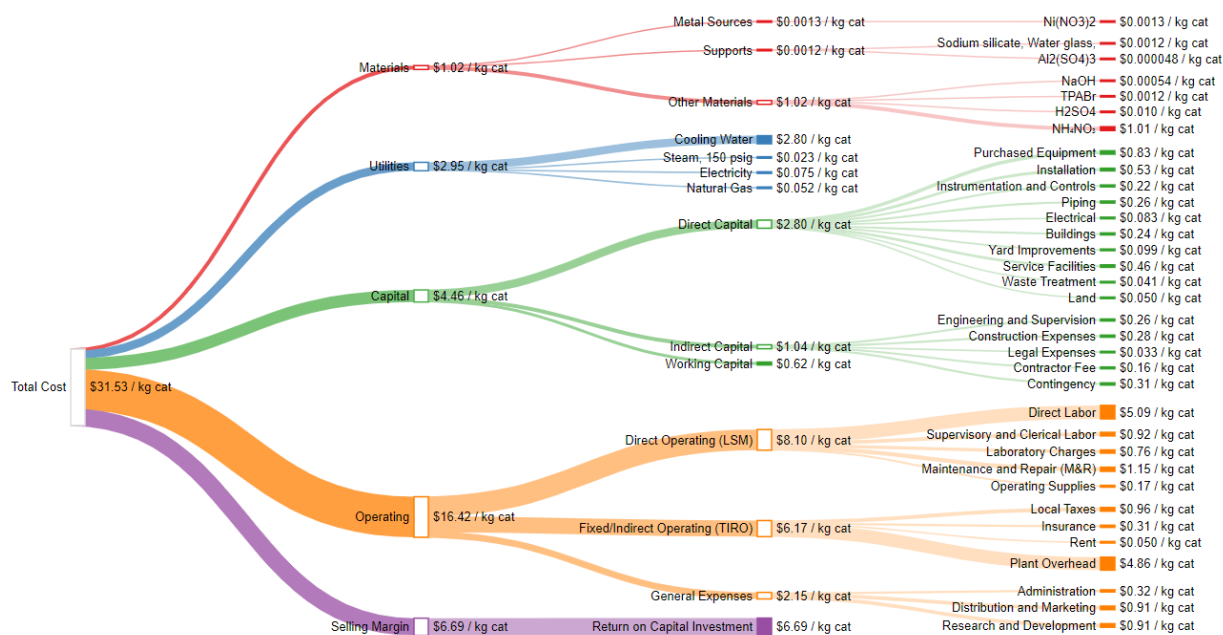


Figure 8-4. Sankey diagram for catalyst cost showing a detailed breakdown of contributors to the net catalyst cost (purchase cost) for Ni/HZSM-5 catalyst

Lines and width correlate to the cost contribution. The Sankey diagram is an example of visualization in the Catcost web-based software version. LSM – Laboratory supplies and maintenance; TIRO – Taxes insurance, rent and overhead

8.3.2.2 Sensitivity analysis

Sensitivity analysis is crucial in evaluating the ambiguity associated with catalyst costs. It goes beyond simple cost analysis and provides valuable insights into the risks and rewards involved for catalyst researchers. CatCost offers a quantitative approach for analysing the impact of

various input variables, providing developers with valuable information. In Figure 8.5, a tornado plot visually depicts the influence of different cost inputs on the net cost of producing Ni/HZSM-5 in a dedicated factory. A combination of literature resources and price surveys was utilised to determine each category's high and low inputs. This approach ensured accurate identification of the upper and lower bounds of the inputs. As previously demonstrated (Figure 8.3a & b), the production scale and raw material prices have the greatest impact on cost uncertainty, which is unsurprising given that the precursor cost contributes significantly to the total catalyst purchasing cost at this scale. Figure 8.5 further highlights some intermediate contributors to the uncertainty. These include the utilization and pricing of process gas, the number of direct labour operators in the production facility (indicating the potential for process intensification), the capacity factor (accounting for planned vs actual productivity discrepancies), and the factor for distribution and marketing charges. Additionally, several minor factors have a smaller impact on catalyst cost, each affecting it by <\$3/kg. These factors include synthesis yield, metal losses during catalyst use and refining, utility expenses, and various capital and operational expenditures components. Appx. Figures 4 and 5a-c present the Tornado plot for 50 % BSP and a detailed breakdown of the plot for 100 % BSP. CatCost, as a web-based application, incorporates sensitivity analysis to assist researchers in identifying the areas of the manufacturing process, materials, and market factors that provide the greatest potential for future advancement. Sensitivity analysis plays a crucial role in evaluating cost ambiguity associated with catalysts. CatCost provides researchers with a comprehensive tool for quantitatively assessing the impact of different inputs, facilitating informed decision-making, and identifying areas for cost optimization and process improvement.

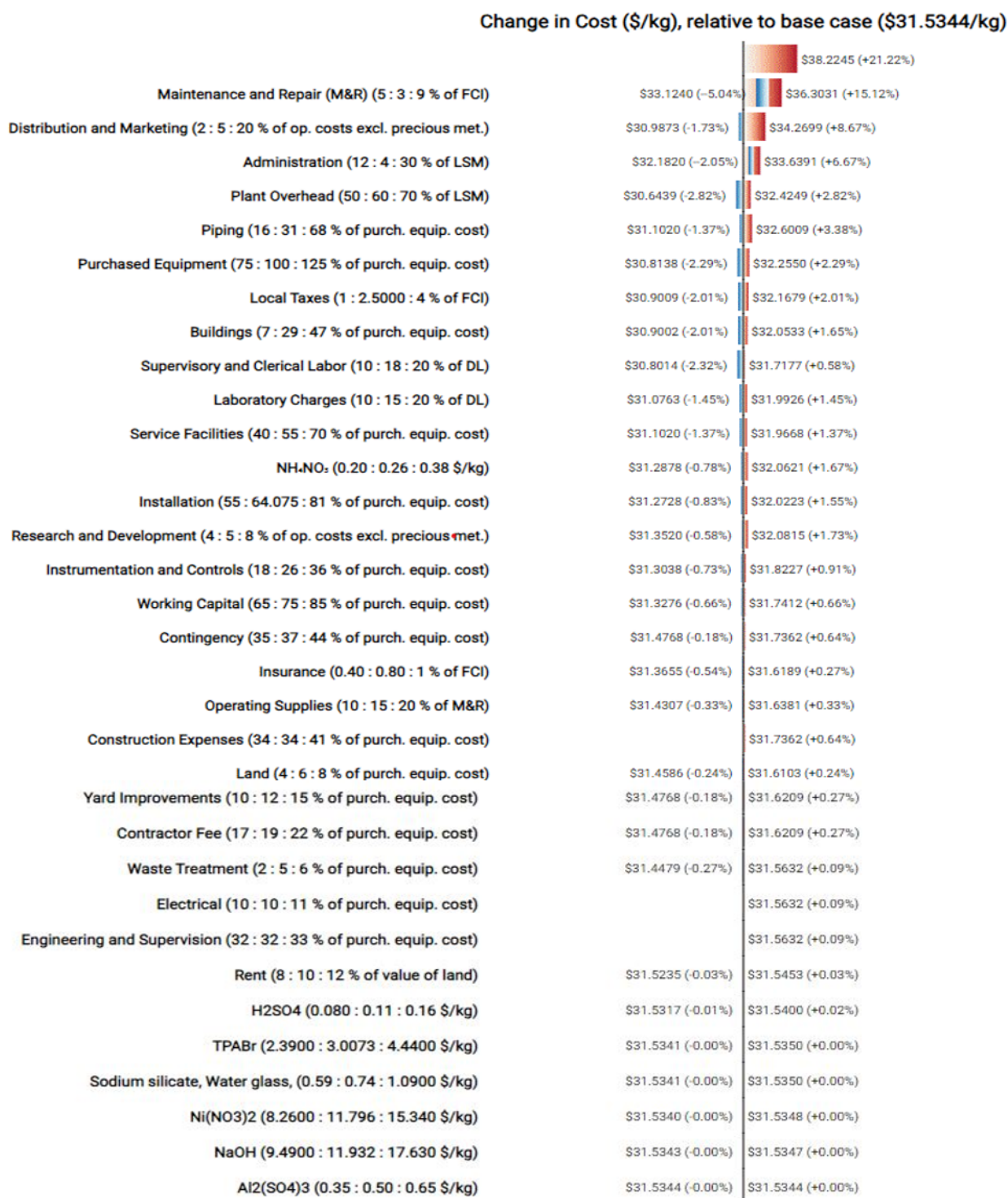


Figure 8-5. Sensitivity analysis results are illustrated in a tornado plot, depicting the impact of crucial input variables on the net catalyst cost for Ni/HZSM-5 in a dedicated plant operating at an annual production scale of 911 tons (100% BSP). This scale aligns with the biorefinery baseline of processing 2,000 dry tonnes of biomass per day. Appx. Figure 4 presents the tornado plot for 50 % BSP.

8.3.3 CADO-ETH - Conversion of Wet Ethanol to Anhydrous Ethanol and Fuel blendstocks

In an industrial facility that produces ethanol, a beer column separates the ethanol-containing broth from fermentation into wet ethanol vapour, water, and any solid residues (Figure 8.6). For this analysis. We assume a second-generation ethanol production process (moist vapour conc. of 40 wt%), equivalent to a liquid feed concentration of 6.4% by weight (8.1% by volume). The sensitivity of cost estimates varies for the two processes being examined. For the conversion of wet ethanol vapour to anhydrous ethanol (referred to as CADO), the impact on capital costs (CapEx) is expected to be low, while to produce anhydrous ethanol from 40% ethanol vapour, both operating costs (OpEx) and capital costs (CapEx), especially for distillation steam, are affected. Both processes involve ethanol, and we will analyze the costs associated with each conversion pathway. The comparison is based on the process configurations shown in Figure 7 and assumes an annual ethanol production rate of 61 million gallons (231 million litres), typical for small ethanol plants in the US and Brazil (Hannon et al., 2020). This production rate was used in the TEA conducted by the NREL for cellulosic ethanol production. In producing anhydrous ethanol, the wet ethanol vapour undergoes rectification in a column, followed by molecular sieves dehydration. On the other hand, the CADO process involves introducing moist ethanol vapour into a catalytic reactor, where it is converted into liquid hydrocarbons, light gases (excluding ethylene), and water. This mixture is then cooled to the ambient temperature and passed through a three-phase separator. Water is separated from the bottom, less dense liquid HCs are extracted from the middle, and incompressible gases are collected from the top. Most of the gas, approximately 73% by mass, is burned to reduce the demand for natural gas in the heat process, while the remaining gas is recycled back into the reactor to be converted into liquid fuels (Hannon et al., 2020).

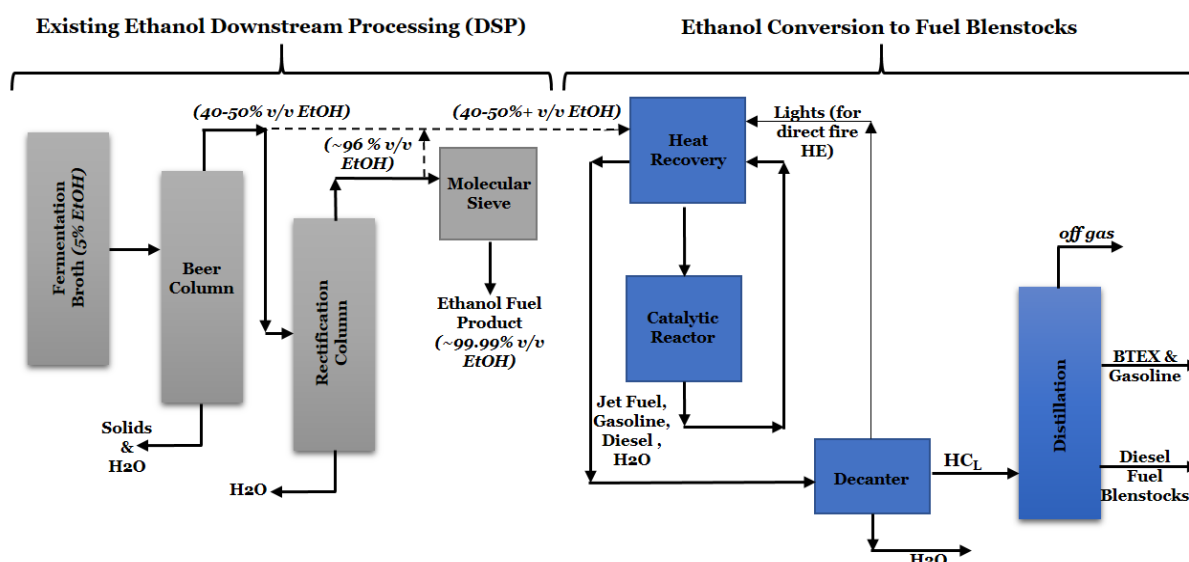


Figure 8-6. Catalytic conversion of bioethanol to fuel blendstocks via CADO-ETH

8.3.3.1 Economics of CADO-ETH Process

The estimation of manufacturing fuel-grade hydrocarbons from moist ethanol vapour is based on the NREL model from 2011 (Humbird, 2011). Given that stoichiometric yields, market prices, and price supports are comparable for gasoline, aviation fuel, and diesel (as shown in SI, Table 2), this analysis is presented in relation to HC fuel blendstocks. Costs associated with the operation of the process can be found in the Appendix. The current and future catalyst purchase prices for converting wet ethanol into fuel blendstocks are estimated at \$70/kg and \$31.42/kg, respectively (Appx. Tables 3a & b). These prices were determined using the NREL catalyst cost estimator, CatCost, and compared and verified through consultation with a commercial catalyst manufacturer (Baddour and Snowden-swan, 2019). The lifespan of the catalysts is expected to be 6 months for laboratory powder and pilot pellets catalysts, and this is extended to 9 months for present commercial catalysts and future catalysts, based on extrapolation estimates from 200-hour ageing investigations, according to (Hannon et al., 2020). Conducting studies on ageing over longer periods would enhance these estimates' reliability. The electricity cost was \$0.05/kWh, a typical rate for the midwestern region of the US (Hannon et al., 2020). Approximately 60 % of the operating expenses can be attributed to replacing catalysts and energy consumption. Additionally, the use of chemical wastewater treatment additives for removing dissolved hydrocarbons results in an additional cost of \$1.85 per 1,000 litres of treated water, which is considered. The cost of returning used catalysts to the provider is factored into the overall cost of catalyst disposal, with a unit cost of \$2,000 per

tonne of catalyst. Insurance, taxes, and maintenance costs are included in consistency with the NREL anhydrous ethanol model (Humbird, 2011). It is anticipated that the labour requirements for converting blendstocks to ethanol will be similar to those for ethanol dehydration, as the unit operations involved are of similar complexity. Despite the unlikely need for additional personnel, the labour cost is accounted for, and the labour costs are comparable in Appx. Tables 3b & c. The capital costs are presented in SI, Table 3d. The NREL model is converted to 2023 dollars, according to (Hannon et al., 2020), resulting in an estimated capital expenditure of \$25.14 million for manufacturing anhydrous ethanol from wet ethanol vapour. To annualize the expenses related to capital expenditures, they are multiplied by 0.18 (average inflation rate for the past 10 years), adjusted value for inflation (0.03 increase from 2019 (Hannon et al., 2020)), representing a 10-year amortization period with a 12% interest rate. Following this approach, the annualized cost of capital contributes \$0.037/L of anhydrous ethanol, equivalent to a reduction of \$1.74 per gigajoule (GJ) lower heating value (LHV).

The key equipment required to produce fuel blendstocks from wet ethanol vapour in the CADO process includes two catalytic reactors capable of catalyst regeneration, a three-phase decanter, four heat exchangers, pumps, and load-out systems. It is assumed that the storage tank requirements for fuel blendstock and H₂O-product are the same as those for ethanol. The dissolved hydrocarbons remaining in the H₂O after decanting are typically between 600 and 1,500 ppm and are removed and transferred to wastewater treatment (Hannon et al., 2020). A compressor is installed to generate the required pressure of 0.417 MPa for moving wet ethanol through the reactor, and another compressor is used for gas recycling. It should be noted that compressors may not be necessary if distillation is performed under pressure. Although including a compressor in the design is precautionary, a back pressure-controlled flash system may be used in practice for a Greenfield facility. The anticipated total installed capital expenditure is approximately \$18.1 million (\$15.3 million in 2019), equivalent to \$0.079 per litre of ethanol feed or \$0.143 per litre of fuel blendstocks (~15.5 % increase compared to the cost in 2019 attributed to the 0.03 % increase in average inflation for the past 10 years). It is assumed that the CADO processing capital expenditures will remain consistent regardless of the underlying technology. Applying the same capital recovery factor of 0.18 to anhydrous ethanol, the annualized cost contribution for ethanol transformation to fuel blendstocks via CADO is estimated at \$0.022 per litre (\$1.03/GJ LHV). With expected advancements in the future, the overall expenses associated with producing fuel blendstock from wet ethanol vapour

using CADO technology are expected to be ~ 3% away from the costs involved in ethanol distillation and dehydration to meet fuel grade standards (Hannon et al., 2020, Narula et al., 2015).

8.3.3.2 Comparative Evaluation of CADO-ETH using Feedstock from Different Sources

We conducted a comprehensive economic analysis to evaluate the competitiveness of producing fuel blendstocks using both current and projected CADO-ETH technologies. These technologies utilize ethanol derived from corn (from the US) and sugar cane juice (from Brazil) through present and future cellulose conversion techniques, including the combined conversion of sugar cane juice and cellulosic feedstocks like bagasse and leaves. Figures 8.7a & b showed global ethanol production from 2007 to 2023 (projected) from different sources: corn (US), sugarcane (Brazil) and sugar beet (EU) (Fig. 8.7a), while Fig. 8.7b showed a comparison of costs between ethanol (corn and sugarcane), and gasoline, covering the period from 2007 to 2023. With a significant global production, it is evident that there is a readily available and sustainable supply of ethanol feedstock for CADO-ETH, indicating the feasibility of producing ethanol from these feedstocks. To determine the projected costs of ethanol production, we considered estimates of operating expenses obtained from reliable sources and an annualized capital cost derived by multiplying the total capital by 0.18, as mentioned earlier. Although most corn ethanol plants in the US have fully amortized their investments, we used average feedstock prices and treated the processes as new facilities. This approach was necessary due to the unpredictable nature of biomass feedstock pricing, particularly in the case of corn. The costs associated with producing 40 % ethanol vapour, as outlined in Appx. Table 3c, was calculated by subtracting the costs of distillation and dehydration from the overall cost of producing fuel-grade ethanol, according to (Hannon et al., 2020). The cost of ethanol, the mass yield of blendstock fuel per unit of ethanol, and the conversion cost from ethanol to fuel blendstocks were considered in determining the minimum blendstock product selling price (MBSP). The MBSP was compared to the historical wholesale pricing of gasoline fuel when the price of petroleum ranged from \$60 to \$100/bbl. Our analysis revealed that the price of gasoline fuel from CADO-ETH is higher than that of petroleum on a volumetric basis. For instance, when the wholesale crude oil price was \$75 per barrel, the wholesale gasoline fuel price was \$2.64/gal, representing a ~10.3% lower than the price of gasoline fuel (\$2.95/gal). This finding is consistent with the research conducted by (Hannon et al., 2020), which reveals that the cost of hydrocarbon fuel derived from ethanol is higher (~19 %) than that obtained

from petroleum. At a crude oil price of \$100/bbl, ethanol conversion to HC blendstock fuels can be competitive across various ethanol production platforms, including current cane sugar (Table 8.2). However, without some form of price support and government subsidy, it is not economically viable at lower oil prices.

Table 8-2. Approximate operating and annualized capital costs associated with fuel blendstocks produced by CADO-ETH using ethanol derived from various sources.

Biomass Feedstocks	Technological Maturity		Ethanol Selling price (\$/L)	ETG conversion			MBSL (\$/L)		
							From ethanol: Market ^a	From petroleum ^s	
	Ethanol Production	Ethanol to Blendstock	5 y: 2018-2023 (current: MESP)	Yield (L blend/ L ethanol)	Cost (\$/L blend) 2019	Cost (\$/L blend) current*	5y and Current price	5y (\$64/bbl): 2018-2023 & current ((\$75/bbl)	\$100/bbl
Corn starch (1G)[‡]	Current	Current	0.55 (0.37)	0.487	0.065	0.077	1.17 (0.78)	0.54 (0.70)	1.28
		Projected	0.55 (0.37)				1.17 (0.78)		
Sugar cane (1G)[‡]	Current	Current	0.60 (0.48)	0.548	0.065	0.077	1.25 (1.00)		
		Projected	0.60 (0.48)	0.487					
SCB (2G)[‡]	Current	Current	-	0.487		0.077			
		Projected		0.548		0.055			

[‡]1G: First-generation corn starch and sugarcane prices are based on average market values over past 5 y (US Energy Information Administration, 2021). MESP EtOH price based on (Hannon et al., 2020) (inflated by 1.8% average inflation to obtain 2023\$).

[‡]2G: Second-generation sugarcane bagasse (SCB) (estimate of MESP from respective sources updated to 2023\$ (Regis et al., 2023, Hannon et al., 2020). OpEx includes feedstock and coproducts. Sugarcane (current and projected) (Humbird, 2011, Hannon et al., 2020).

*Conversion costs from SI Table 3a & b, plus annualized capital costs.

[§]HC price from EtOH based on MESP/yield + conversion cost.

^sHC price from fossil fuel based on oil cost/L. Adapted from Energy Information administration (EIA) (US Energy Information Administration, 2022).

<https://www.macrotrends.net/1369/crude-oil-price-history-chart>https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=p&s=f0000000_3&f=m

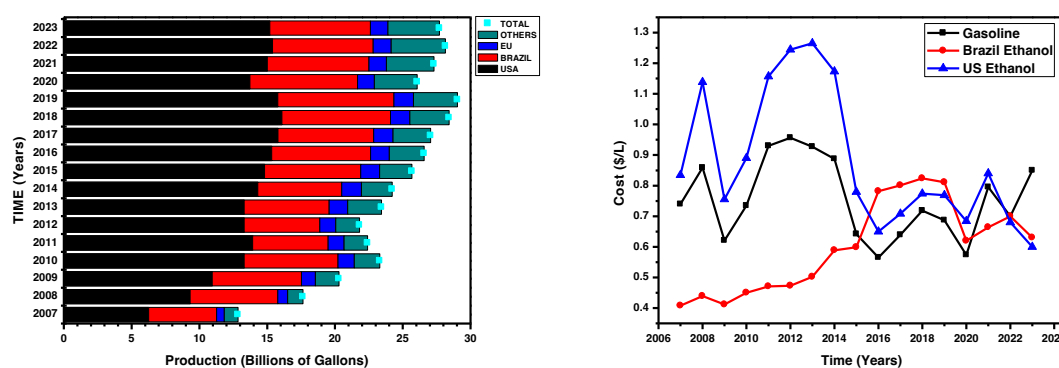


Figure 8-7 (a). Global EtOH production (2007-2023), (b). Cost comparison between (corn and sugarcane) EtOH and gasoline (2007 – Jan 2023)

8.3.4 Life Cycle Analysis (LCA) of CADO-ETH Technology

Figures 8.8 provide a comprehensive breakdown of GHG emissions throughout the entire life cycle, from well-to-wheel, for the synthesis of ethanol using CADO from different feedstocks such as corn, cane sugar, corn stover, and cane cellulosic material, while Figure 8.9 represents the life cycle analysis for the conversion of petroleum to gasoline. The CO₂ emission, well-to-wheel, WTW (which comprises of wheel-to-pump, WTP and pump-to-wheel, PTW) result from these processes in Figures 8.8 & 8.9 is presented in Table 8.3. When ethanol is generated using "first-generation" techniques that employ easily fermentable feedstocks and established technology, overall GHG emissions for gasoline fuel production (used as a reference) are reduced by 25 % for corn starch ethanol and 53 % for sugarcane juice ethanol. These reductions highlight the environmental benefits of ethanol produced through "first-generation" technologies. The combined conversion of sugarcane juice and cellulosic material, utilizing current or future CADO technologies, leads to appreciable emissions reductions of approximately 63 %. Compared to ethanol produced through "second-generation" processes involving lignocellulosic conversion using emerging technologies, these numbers show a favourable outcome. It is worth noting that applying CADO to corn starch ethanol results in slightly higher greenhouse gas emissions compared to sugar cane ethanol. This discrepancy arises from the lower emissions associated with farming sugar cane and the ability to utilize lignin for steam and electricity generation in CADO. On the other hand, CADO applied to corn starch ethanol depends on fossil energy. The inclusion of credit in Table 2 (specifically 73 gCO₂e/MJ for HC fuel in this scenario) to account for the CO₂ recaptured through the growth of new plants (biogenic carbon) had a notable effect on maintaining low life cycle GHG emissions for fuels derived from biomass, in contrast to fuels produced from fossil sources.

Using ethanol from sugarcane, a vehicle running on 6.4 cm³ of ethanol produced from one hectare of sugarcane can cover a total distance of 65,280 km. In contrast, to travel the same distance of 65,280 km, 4.67 cm³ of gasohol would be required, emitting 10.2 MT of carbon dioxide throughout the manufacturing, distribution, and combustion processes. To cover the same 24,400 km achievable with 3.58 cubic meters of E85, the reference vehicle would need 2.73 cm³ of gasoline. This would generate 7.43 MT of CO₂ due to the manufacturing, distribution, and burning of such a volume of petrol (Oliveira, 2008). The numbers presented in Table 2 were computed using the default information from the Greenhouse gases, Regulated Emissions, and Energy usage in Transportation (GREET) model for corn-based scenarios and

the Virtual Sugarcane Biorefinery for sugarcane-based scenarios. However, adjustments were made to account for the energy savings from using 40% ethanol as the feedstock for CADO instead of anhydrous ethanol. Specifically, credits were given for eliminating the energy required for distillation when producing anhydrous ethanol from 40% ethanol. This elimination of energy corresponds to 25 GJ/h (23.5 MMBtu/h, 0.0016 GJ/L) of natural gas and 2.6 GJ/h (710 kW, 0.00017 GJ/L) of electricity (Hannon et al., 2020).

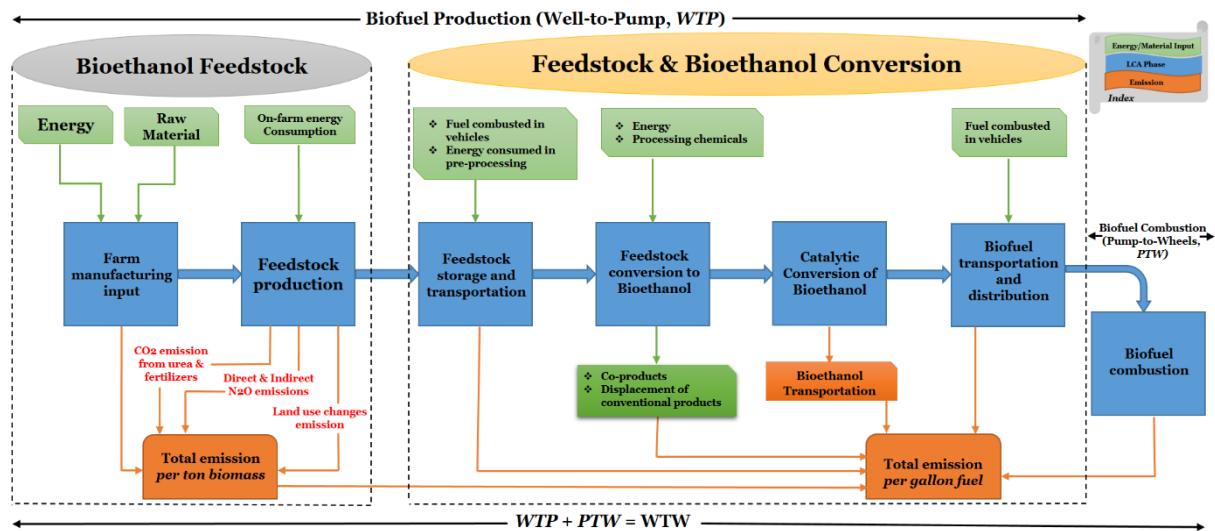


Figure 8-8. Life cycle analysis: Bioethanol to gasoline (*Well-to-Wheel*)

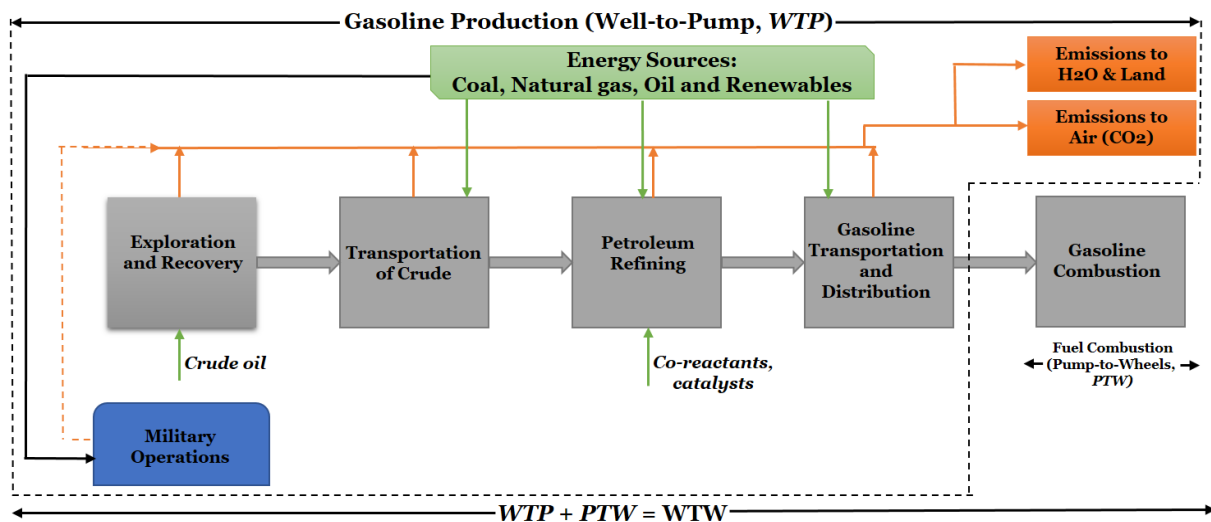


Figure 8-9. Life cycle analysis: Petroleum to gasoline (*Well-to-Wheel*)

Table 8-3. Comparative Evaluation of greenhouse gas (GHG) emissions generated during the production of gasoline fuel using two approaches: utilizing the CADO process with ethanol obtained from various sources and the conventional petroleum-based production method.

Bioethanol Source						Petroleum Source	
Bioethanol Biomass	Technology	Emission (gCO ₂ e/MJ of fuel blendstock				PTW _{gp}	WTW _{gp}
		Feedstock Synthesis Ethanol Transformation	CADO- and ETH	Gasoline use (PTW _{gb})	WTW _{gb} ^β		
#Corn starch	Current	45.46	6.67	15.5	67.7 -25%		
*Sugar cane	Current	23.75	3.15	15.5	42.5 -53%	73.4	90.2
**Cane cellulosic	Current	14.46	3.15	15.5	33.2 -63%		
**Cane cellulosic	Projected	13.87	3.15	15.5	32.6 -64%		

PTW (gb, gp) - fuel utilization in a gasoline system (gb: gasoline from ethanol & gp: gasoline from petroleum).

WTW - full supply, production, and use chain. CO₂ emission of gasoline (derived from ethanol (Ternel et al., 2021) and fossil fuel (Bauen et al., 2022)).

The calculation of catalytic conversion values incorporates emissions resulting from the transportation and distribution of EtOH, with an estimated value of 0.85 gCO₂e/MJ (Hannon et al., 2020).

^βWhen expressed as negative percentages, the values indicate the reduction in greenhouse gas (GHG) emissions in contrast to petroleum gasoline fuel.

[†]Provided by Argonne National Laboratory for corn starch ethanol case (Hannon et al., 2020) & (Moreira et al., 2022).

^{*}Provided by (Dias et al., 2016)

[‡]Cane cellulosic (Hannon et al., 2020)

According to Hannon et al. (2020), biomass conversion into ethanol through fermentation and the subsequent catalytic conversion into hydrocarbon blendstocks using a dehydration mechanism (CADO) achieve considerable energy efficiencies. Combined, the overall energy efficiency exceeds 93% when these two steps are combined. The potential for high energy efficiency has been demonstrated in practice (Hannon et al., 2020). However, the primary challenge lies in addressing the cost aspect. Previous studies estimated that a three-step process would increase the cost of ethanol by \$3.38 to \$7.98 per gigajoule (Regis et al., 2023, McAloon et al., 2000). In contrast, in its current state of development, the CADO technology described in this article is projected to increase the cost of ethanol and is expected to incur no additional cost compared to anhydrous ethanol in the future. When comparing the selling prices of ethanol produced by existing and expected techniques, including both 1G and 2G biomass feedstocks,

to the selling price of petroleum-derived gasoline fuel, the prices are approximately equal to or greater than gasoline fuel on a USD/GJ basis. This holds regardless of whether 1G or 2G feedstocks are used. Therefore, even with high efficiency and low conversion costs, the selling price of gasoline or diesel fuel derived from ethanol will at most be equal to or slightly higher than conventional gasoline fuel due to varying operating costs demonstrated by these two processes. The production of fuel blendstocks using CADO from various biomass feedstocks and processes can be cost-competitive due to existing production incentives. Some regions have a strong market demand for low-carbon blendstocks, and this demand is expected to increase over time, driven by the transportation industries' goals of reducing greenhouse gas emissions.

The study by Hannon et al. (2020) reported that the operational results of CADO cover a scale of up to 0.12 L of ethanol processed per hour, with a potential scaling up to 2.0 L/h currently underway. These scales fall within the validated range for commercialising processes based on gas-phase heterogeneous catalysis (Hirschmann, 1964, Pangarkar, 2014, Bisio and Kabel, 1985). To support commercial application in the next stage, further scaling up by a factor of around 1,000 is necessary to process 15×10^6 L per year of ethanol (Hannon et al., 2020). The distribution of products derived from CADO resembles gasoline blendstocks. Still, modifying the catalyst or developing additional methods to achieve ranges more typical of other fuels, including aviation fuel and diesel, is possible. These modifications and developments also have the potential to decrease the aromatics content, which is important for accessing alternative fuel and engine types. In its present stage of development and considering the limits on aromatic content, CADO-derived blendstocks could be blended at 20-40% with petroleum-derived gasoline fuel. However, verification and certification are still required. Further utilization or blending of low-carbon, biomass-derived HCs at higher levels could be enabled by advancing CADO catalysts and technologies, blending with fuels from other processes with lower aromatic content, separating CADO-derived products into fractions suitable for various applications, or a combination of these approaches.

The economics of adding CADO as a bolt-on to current ethanol production facilities are slightly less favourable compared to adding CADO as part of an integrated Greenfield plant that produces partially purified ethanol as an intermediary for further transformation to fuel blendstocks. This is due to the additional cost of producing anhydrous ethanol in existing facilities. However, CADO has a low capital cost, making adding CADO-mediated fuel

blendstock production to existing ethanol plants feasible. This allows for the rapid establishment of low-carbon gasoline fuel production capacity, attractive investment returns, and increased product diversity for biofuel producers. The anticipated cost reduction for future CADO-derived fuel blendstocks is projected to be over 30%, bringing the estimated cost down to \$0.03/L compared to the current process (\$0.05/L). However, this reduction is comparatively lower than the historical cost reductions observed for industrial processes, particularly those based on gas-phase heterogeneous catalysis (Enos, 1958, Cunningham, 1980). It should be noted that the projected cost reduction for future CADO-derived fuel blendstocks falls short of the post-commercialization cost reductions typically seen in industrial processes. It is important to recognize that the actual costs of CADO may differ from expected costs due to various factors such as location, time and equipment costs. Therefore, cost estimates are always subject to possible fluctuations. Should it be possible to produce HC blendstocks at a comparable cost to anhydrous ethanol, this would be a significant improvement and an opportunity to direct biofuel synthesis towards applications critical to stabilising the climate.

As previously mentioned, the amortization of investments in corn ethanol plants in the United States can be partially due to government subsidies, which could contribute to the future competitiveness of corn ethanol. The production of corn ethanol in the US receives significant government subsidies. According to Shapouri et al. (2002), the federal excise tax exemption for ethanol blends amounts to \$0.53/gal. This tax exemption brings the prices of conventional gasoline and ethanol to a comparable level, promoting ethanol as an alternative to gasoline. However, in Brazil, ethanol producers have been eligible for financial support since the program's initiation, and the government sets the prices consumers pay at the pump. However, as of 1999, prices were allowed to become more competitive, rendering this support unnecessary (Goldemberg, 2006).

8.4 Conclusion

The potential of biofuels in addressing carbon emissions in the transport sector is significant. With biofuels derived from biomass, there is an opportunity to reduce the reliance on fossil carbon and transition to a more sustainable and environmentally friendly transportation system. However, it is crucial to continue advancing technologies and processes to optimize biofuel production, improve their properties to closely resemble traditional fossil fuels, and explore their compatibility with various engines and transport modes. The catalyst (Ni/HZSM-5) cost was estimated to be \$31.4 and \$69.9/kg for 100 and 50 % baseline scale production using the

CatCost model. The quantity of catalyst purchased by a process plant significantly impacts its cost. Increasing the scale of production and purchasing can lead to cost savings due to economies of scale and volume buying. Discrepancies in price arise from jumps between synthesis scales, which can be addressed by mixing equipment of varying scales and making discretionary adjustments to the selling margin. The cost breakdown of catalyst purchases, including materials, processing, overhead, and margin, varies with different purchasing scales. When analyzing the influence of scale on CADO catalysts, significant discrepancies are observed among different material types, with the Ni/HZSM-5 showing a notable reliance on purchase scale due to its intricate synthesis process. Processing and overhead costs decrease proportionally with increasing scale, making raw materials the primary focus for cost reduction at larger production scales.

The production of biofuels from renewable biomass sources is gaining increased attention to address the depletion of crude oil reserves and mitigate the environmental impact of traditional fuels. Ethanol, as the predominant biofuel, has limitations for use as a standalone transportation fuel, but research is underway to improve its properties and explore alternative biofuel molecules. The transport sector requires further advancements in biofuel technologies to reduce carbon emissions. Catalysts such as HZSM-5 zeolite promise to convert alcohols and oxygenates into hydrocarbon fuels. Continued research, development, and investment in biofuel production are necessary to unlock the full potential of biofuels in achieving a sustainable and low-carbon transportation system. The current estimated cost of converting wet ethanol to fuel blends includes operating and annual capital expenditures of \$0.05 per liter. These costs are expected to decrease to \$0.03/L in future periods. This cost is comparable to the unit energy production cost of producing anhydrous ethanol from wet ethanol, which is \$0.02/L. The cost of producing biofuel from CADO was more competitive with the crude oil price of \$100/bbl, while at the current oil price, the selling price of CADO gasoline is not competitive with gasoline from petroleum. The single-step catalytic conversion of ethanol into hydrocarbons is a promising avenue for renewable fuel production. Both the traditional three-step processes and the innovative CADO strategy offer potential solutions, however, the CADO technology showed potential in GHG emission reduction (by >25%) and carbon balance. Continued research and development are crucial for optimizing these processes, improving liquid fuel yields, and conducting comprehensive assessments of their economic viability and environmental sustainability. These analyses and methodologies offer valuable

insights into cost estimation, manufacturing processes of catalysts and biofuels, and life cycle assessment (LCA), thereby facilitating decision-making and optimization within the industry.

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CHAPTER 9

CONCLUSION AND RECOMMENDATION

This chapter presents the major findings obtained in this work based on the following specific objectives: (i) Synthesis and characterisation of a newly developed tunable ZSM-5 catalyst active in low alcohol conversion, (ii) Investigate the effects of metal modification on the ZSM-5 catalyst and activities as a function of its properties, (iii) Study the effects of operating conditions on low alcohol catalytic conversion and product distributions, (iv) Evaluate the performance of transition metal doped catalysts in the conversion of low alcohols to fuel range hydrocarbons, (v) Investigation of the deactivation, stability, regeneration, and reusability of the synthesised catalyst, (vi) Perform a techno-economic analysis of the catalytic conversion of low alcohols into fuel blendstocks, (vii) Conduct an environmental analysis on the variability of catalytic upgrading and utilisation of low alcohol fuels.

9.1 Overall Results and Conclusion

The novelty of the work presented in this thesis focused on the development of a tunable mesoporous ZSM-5 zeolite catalyst and modification with transition metals (Co, Fe, and Ni) for effective conversion of low alcohols to fuel-range hydrocarbons and petrochemicals. The extent to which the above objectives are met and their main findings are summarised below:

A tunable mesoporous ZSM-5 with Si/Al of 40 was successfully synthesised and modified with different concentrations (0.5-10 wt%) of transition metals (Co, Fe, and Ni). Comprehensive characterisation techniques (XRD, FTIR, SEM, EDS, PSD, BET, NH₃-TPD) were employed to analyse the catalysts and reveal changes in properties such as crystallinity, surface area, pore volume, particle size, and acidity. The synthesised catalysts exhibited a remarkable surface area of 397.5 m²/g, a pore diameter of 2.22 nm, and a total pore size of 0.706 cm³/g (0.678 and 0.029 meso- and macropores, respectively).

- I. Modifying ZSM-5 zeolite with transition metals affected the catalysts' physicochemical properties and catalytic activities. The presence of metals affected the crystallinity, surface area, acidity, and selectivity of the catalyst toward various hydrocarbon products. Increased metal concentration >1 wt% significantly decreases crystallinity, surface area and total pore volume. Compared to other studies from the literature, our catalyst exhibited a large surface area, demonstrating

its suitability for catalysis. Among the metal-doped catalysts, the 1 wt% Ni-doped catalyst increased the surface area by 9.7 % (440.3 m²/g) with reference to the pure ZSM-5, which could be due to the development of additional pores during the metal incorporation process or the formation of NiO species outside the zeolite pores. Furthermore, further increase (in metal content) leads to decreased surface area, suggesting that 1 wt% is the optimum Ni concentration required to achieve greater surface area. However, metal doping improved catalytic performance, product selectivity and distribution but also increased coke formation, which affected catalyst deactivation. The catalysts with low metal doping (0.5 wt%) showed better potential for converting lower alcohols to hydrocarbons than catalysts with high metal concentration (10 wt%), indicating their suitability for producing sustainable fuel-range hydrocarbons.

- II. The effects of operating conditions, such as metal loading, temperature, and weight hourly space velocity (WHSV), on the conversion of ethanol to hydrocarbons were investigated. The catalysts exhibited different selectivities for various product ranges depending on the reaction conditions. Low metal doping (0.5 and 1 wt%) favoured liquid hydrocarbon selectivity, while higher concentrations (5 wt%) shifted towards gaseous hydrocarbons. Increasing WHSV (5 to 12 h⁻¹) and temperature (350 to 400 °C) promoted liquid hydrocarbon production. The selectivity for the different products varies with the change in reaction conditions, such as temperature and WHSV. The unmodified catalyst exhibited the highest selectivity for gaseous hydrocarbons and the lowest for liquid hydrocarbons, while metal-doped catalysts exhibited higher selectivity for liquid hydrocarbons. Among the catalysts tested, the Ni-doped catalysts exhibited considerable selectivity for C₉-C₁₂ and liquid hydrocarbon production, the Co-doped preferred C₅-C₈ and benzene, while the Fe-doped catalysts enhanced benzene production. The thermal stability study of the spent catalyst showed that catalyst coking increased with metal doping from 0.5 to 5 wt%, leading to catalyst deactivation. Moreover, with increasing temperature and WHSV, coke deposition increased as most consist of hard coke (400-600 °C). Co-doped catalyst recorded the lowest weight loss (1.3 and 1.4 mg for 1 and 5 wt% Co-doping) compared to Fe- (1.4 and 1.5 mg) and Ni-doped catalysts (1.6 and 1.7 mg). Analysis of the spent catalysts showed that the catalyst

framework was preserved despite coke deposition, with reduced crystallinity, surface area, and mesoporous volume due to coke deposition. Consistent with the TGA results, the decrease in crystallinity and textural properties including a decrease in surface area from 306 - 440 m²g⁻¹ to 18 - 113 m²g⁻¹, and reduction in mesopore volume correspond to increased coke deposition and metal doping. Overall, the results conclude that the catalytic performance of ZSM-5 can be enhanced by doping with transition metals and optimising the reaction conditions can lead to desired product selectivity while reducing catalyst deactivation.

- III. The catalytic performance of catalysts doped with transition metals in the conversion of low alcohols (methanol, ethanol and propanol) to hydrocarbons (LATH) was evaluated. The catalysts showed selectivity towards different hydrocarbon products, and their performance was influenced by factors such as metal concentration, reaction temperature and WHSV. The TGA-DTA study showed that Ni/HZSM-5 exhibited excellent stability with the least coke deposition, while Co/HZSM-5 had a higher tendency for coke deposition and deactivation attributed to significant weight loss (9.6 and 8.5 wt%) in MTH and ETH conversion. In the PTH process, Co/HZSM-5 displayed the lowest weight loss (5.0 wt%), and Fe/HZSM-5 exhibited the least stability. Among the catalyst tested, Ni/HZSM catalyst exhibited appreciable stability and catalytic performance in LATH conversion.
- IV. The stability and regeneration of HZSM-5 and Ni/HZSM-5 zeolite catalysts in ethanol conversion were investigated. The catalysts demonstrated stability over multiple conversion cycles, with varying selectivity towards different hydrocarbon products. Regeneration processes improved catalytic performance and restored the catalysts' properties with ~99.9 % ethanol conversion, indicating their potential for sustainable application. While the unmodified catalyst favoured aromatics (BTX) and gasoline range hydrocarbons, the Ni-doped catalysts showed a broad product distribution, producing gasoline and diesel fuel blendstocks. The unmodified HZSM-5 demonstrated greater stability than Ni/HZSM-5, while the regeneration process improved the catalytic activity of the spent and deactivated catalysts, indicating the potential for catalyst reuse and sustainability. The study on

regenerated catalysts revealed that the structural and functional groups of the catalysts remained unchanged, retaining the MFI framework of zeolite catalyst after the regeneration process. This explains the ability of the regenerated catalysts to exhibit comparable catalytic performance to that of the original catalysts. The Ni/HZSM-5 catalyst showed higher coke deposition (with 2.8 wt% weight loss attributed to hard coke) than the unmodified HZSM-5 catalyst (2.1 wt%), attributed to the presence of nickel on the Ni/HZSM-5 catalyst promoting coke formation and enhanced its combustion, resulting in increased selectivity for long-chain hydrocarbons and faster deactivation.

- V. The techno-economic analysis of the one-step conversion of low alcohol to fuel blends, also known as consolidated alcohol dehydration and oligomerisation (CADO), showed the process's commercialisation potential. The cost implications of catalyst purchase were analysed, with considerations for scale and synthesis. The catalyst (Ni/HZSM-5) cost was estimated to be \$31.4 and \$69.9/kg for 100 and 50 % baseline scale production using the CatCost model. Catalyst manufacturing costs can be reduced through economies of scale and volume purchases, and the cost breakdown varies depending on purchase size. For larger production volumes, cost reduction focuses on raw materials. The analysis of catalyst costs has therefore shown that buying catalysts from commercial suppliers or distributors is more effective when they are needed in a few tonnes for small-scale use. The current estimated cost of converting wet ethanol to fuel blends includes operating and annual capital expenditures of \$0.05 per liter. These costs are expected to decrease to \$0.03/L in future periods. This cost is comparable to the unit energy production cost of producing anhydrous ethanol from wet ethanol, which is \$0.02/L. The cost of producing biofuel from CADO was more competitive with the crude oil price of \$100/bbl, while at the current oil price, the selling price of CADO gasoline is not competitive with gasoline from petroleum. However, it is expected that CADO biofuel will be on par with conventional gasoline with the help of government incentives and support. Life cycle analysis has shown that the production and use of CADO biofuel results in lower greenhouse gas emissions than conventional gasoline. This shows that biofuel produced using our current CADO process can reduce greenhouse gas emissions by >25%. The study highlights the potential of

biofuels derived from renewable biomass sources in addressing carbon emissions and transitioning to a sustainable transportation system.

9.2 Implications:

The findings from this study have several implications:

- I. The incorporation of transition metals into mesoporous ZSM-5 zeolite catalysts can enhance their catalytic performance and selectivity. Optimisation of metal loading and reaction conditions can lead to desired product selectivity and improved catalyst stability.
- II. The conversion of low alcohols to hydrocarbons offers a potential pathway for producing sustainable fuel-range hydrocarbons. Using mesoporous ZSM-5 zeolite catalysts shows promise in achieving efficient conversion and desired product distributions.
- III. The presence of transition metals in catalysts can increase coke formation, which affects catalyst deactivation. Understanding and mitigating coke formation are crucial for developing industrial-scale catalysts with improved longevity and stability.
- IV. The successful regeneration of spent catalysts can restore their catalytic activity and properties, allowing for reuse and promoting sustainability in catalytic processes.

Conclusively, these results provide insight into the synthesis and applicability of a newly developed tunable mesoporous ZSM-5 zeolite catalyst for the conversion of low alcohol to fuel-range hydrocarbons as well as the stability and regeneration of the catalyst, demonstrating its reusability and great potential for industrial application. The characteristic feature of meso-macroporous hierarchical structure exhibited by the catalysts plays a crucial role in improving the catalyst's overall performance and catalytic efficiency. The significant mesoporous structure also facilitates better mass transport and accessibility for the reactants, which positions these catalysts as extremely promising for various applications. The techno-economic and life cycle assessment showed the process's economic viability and environmental sustainability.

9.3 Recommendations and Future Work Considerations:

Based on the milestones and findings of this study, the following recommendations and considerations are necessary for future work to achieve a successful CADO process and improved biofuel production:

- I. Further investigate the effects of different metal concentrations and combinations on catalyst performance, selectivity, and stability. Evaluate the potential of other transition metals for doping.
- II. Focus on developing strategies to minimise coke formation and enhance catalyst regeneration processes, including catalyst surface modification, reaction conditions optimisation, and the use of additives or promoters.
- III. Investigate opportunities for process intensification, such as reactor design optimisation, catalyst bed configuration, and process integration, to improve conversion efficiency and selectivity.
- IV. Investigate the factors affecting catalyst regeneration (reaction, temperature, time, and WHSV) and determine the optimal regeneration conditions based on the initial parameters to which the spent catalysts were exposed.
- V. Explore other catalyst materials and structures beyond ZSM-5 zeolite to enhance catalytic performance and selectivity in low alcohol to hydrocarbon conversion processes.

These recommendations and future work considerations aim to advance the understanding and application of catalysts in low alcohol to hydrocarbon conversion processes, optimise biofuel production, and contribute to the development of sustainable and environmentally friendly transportation systems.

Appendices

1a

Global Inputs		Processing Cost Estimation Inputs	
Estimate Name NIH2SM-5		Processing Cost Estimation Methods CatCost includes two methods for estimation of processing costs: > The Step Method (3a only) Uses costs in \$/hr for synthesis steps run at a contract manufacturer. > The CapEx & OpEx Factors method (3b-3e) Uses process design literature for a dedicated, new-build catalyst plant.	
Economics Basis Year 2016 ? Currency USD (\$) ? Currency Symbol \$		When compiling a catalyst estimate, the user may choose either method, complete both to compare them, or combine the two (e.g., if the user wants to estimate some steps of a synthesis using one method and some steps using the other). The 5a Outputs sheet displays separate outputs from each method, as well as a combined display for estimates that use both methods.	
Output Units Mass Unit kg ?			
Step Method Inputs			
Synthesis Campaign Size Base			
Order size (1-1000 tons)	911 ton	BASELINE GLOBAL PLANT REQUIREMENT	
Equipment size	Large (150 ton/day)		
Synthesis time	3.0 days		
Cleaning time	1.0 days		
Total: Synthesis campaign length	4.0 days		
Overhead and Selling Margin			
G&A Overhead	5 %	?	
S&P&D Overhead	5 %	?	
Selling Margin	8.7 %	?	
CapEx & OpEx Factors Inputs			
Production Capacity - Catalyst Base			
Design Production, Annual	8.26E+05 kg	?	CONVERSION OF GLOBAL REQUIREMENT KG
Capacity Factor	100 %	?	
Actual Production, Annual	8.26E+05 kg	?	
Production Capacity - Operating Hours			
Operating Hours (Labor)	8760 hours	?	
On-Stream Factor	90 %	?	
Operating Hours (Production)	7884 hours	?	
Design Production Rate	1.05E+02 kg/hr	?	
Plant Life			
Plant Life (for depreciation)	10 years	?	
Selling Margin			
Calculate using (select):	ROI		
Return on capital invested (pre-tax)	15 %/year	?	
Flat margin (% of costs)	%	?	

[illegible]

CapEx & OpEx Factors: Equipment Costs	
Select a Process Template or User-Entered Custom Process	
Zeolite ZSM-5 (25%)	
Equipment Cost Totals for Selected Template	
Purchase Cost	\$ 6,984,950
Installed Cost	\$ 11,480,661
Labor Factor (# of operators)	3.9

CapEx & OpEx Factors Equipment Lists: Custom Process and Process Templates	
<i>Show/Hide Individual Process Templates Using +/- at left (Show all using "2" at top left, hide all</i>	
User Entry: Custom Process	
~ show/hide User Entry: Custom Process	
Process Template: FCC Catalyst (USY w/ RE)	
~ show/hide Process Template: FCC Catalyst (USY w/ RE)	
Process Template: Metal Carbide (Bulk)	
~ show/hide Process Template: Metal Carbide (Bulk)	
Process Template: Metal Carbide on Metal Oxide	
~ show/hide Process Template: Metal Carbide on Metal Oxide	
Process Template: Metal on Metal Oxide – Incipient Wetness	
~ show/hide Process Template: Metal on Metal Oxide – Incipient Wetness	
Process Template: Metal on Metal Oxide – Strong Electrostatic Adsorption	
~ show/hide Process Template: Metal on Metal Oxide – Strong Electrostatic Adsorption	
Process Template: Nanoparticles – Flow Synthesis	
~ show/hide Process Template: Nanoparticles – Flow Synthesis	
Process Template: Zeolite ZSM-5 (25%)	

CapEx & OpEx Factors Template Name	
Zeolite ZSM-5 (25%)	
Description	
Derived from the design for FCC Catalyst (USY w/ RE). 25% ZSM-5, 37.5% matrix, and 37.5% clay. More crystallizers than for FCC because of longer crystallization time of ZSM-5 vs. USY. The process is semi-batch and is valid from approximately 10 million lb/year up to 500 million lb/year.	

Scaling Inputs: Zeolite ZSM-5 (25%)	
Scaling Input Specific to this Process Design/Template	
THIS PROCESS Design Production Rate	1.00E+08 lb < select mass unit ?
	catalyst < select catalyst or AF ?
	year < select time unit ?
THIS PROCESS Design Production Rate, in Estimate U	5.75E+03 kg catalyst/hour ?

From CatCost "1 Inputs" Sheet (Specific to this Estimate)	
ESTIMATE Design Production Rate	1.05E+02 kg catalyst/hour ?

1d

[illegible]

(- show/hide Process Template: Zeolite ZSM-5 (25%))

1e

CapEx & OpEx Factors: Utilities Costs

Selected Process Template

Zeolite ZSM-5 (25%)

Note: ordinarily this is set by the entry on 3b Equip but can be overridden

Process Utilities Consumption and Cost for Selected Template

Utility	Consumption per kg catalyst	Units	Unit Cost	Units	Cost (\$/kg catalyst)	Cost (\$/year)	
Cooling Water	0.341142686	kgal	0.14	\$/kgal	0.0478	39,471	
Process Water	0	kgal	1.3	\$/kgal	-	-	
Steam, 150 psig	0.00462253	ton	5	\$/ton	0.0231	19,101	
Steam, 600 psig	0	ton	5.7	\$/ton	-	-	
Electricity	0.499002073	kWh	0.055	\$/kWh	0.0274	22,682	
Natural Gas	0.017334486	MMBtu	3	\$/MMBtu	0.0520	42,978	
					Totals	0.1503	124,232

1f

Utilities Process Templates		
Zeolite ZSM-5 (25%)		
Scaling Inputs: Consumption for 1 <unit> of catalyst/AP		
Select unit	lb	? ?
Catalyst or AP?	catalyst	
In CatCost units	0.45359237 kg catalyst	
Utility	Consumption per lb catalyst	Units
Cooling Water	0.15473972	kgal
Process Water	0	kgal
Steam, 150 psig	0.002096744	ton
Steam, 600 psig	0	ton
Electricity	0.226343533	kWh
Natural Gas	0.007862791	MMBtu

1g

CapEx & OpEx Factors: Factored Capital Expenditures			
Cost Item	Base	Units	Total Cost (\$)
Direct Capital			
Purchased Equipment	100 % of purchased equipment cost		6,984,950
Installation	64 % of purchased equipment cost		4,495,711
Instrumentation and Controls	26 % of purchased equipment cost		1,816,087
Piping	31 % of purchased equipment cost		2,165,335
Electrical	10 % of purchased equipment cost		698,495
Buildings	29 % of purchased equipment cost		2,025,636
Yard Improvements	12 % of purchased equipment cost		838,194
Service Facilities	55 % of purchased equipment cost		3,841,723
Waste Treatment	5 % of purchased equipment cost		349,248
Land	6 % of purchased equipment cost		419,097
Total Direct	338 % of purchased equipment cost		23,634,474
Indirect Capital			
Engineering and Supervision	32 % of purchased equipment cost		2,235,184
Construction Expenses	34 % of purchased equipment cost		2,374,883
Legal Expenses	4 % of purchased equipment cost		279,398
Contractor's Fee	19 % of purchased equipment cost		1,327,141
Contingency	37 % of purchased equipment cost		2,584,432
Total Indirect	126 % of purchased equipment cost		8,801,037
Total Fixed Capital Investment (FCI)	464 % of purchased equipment cost		32,435,511
Working Capital	75 % of purchased equipment cost		5,238,713
Total Capital Investment (TCI)	539 % of purchased equipment cost		37,674,224

CapEx & OpEx Factors: Factored Operating Expenditures				
Cost Item	Base	Units	Cost (\$/year)	Cost (\$/kg catalyst)
Direct Labor				
Direct Labor Operators (rounded up)	10 operators			
Direct Labor Hours per Year	87,600 hr/yr			
Direct Labor Rate	48 \$/hr			
Direct Labor Cost (DL)			4,204,800	5.0878
Direct Operating Costs				
Supervisory and Clerical Labor	18 % of DL		756,864	0.9158
Laboratory Charges	15 % of DL		630,720	0.7632
Maintenance and Repair (M&R)	5 % of FCI		1,621,776	1.9624
Operating Supplies	15 % of M&R		243,266	0.2944
Total: Labor, Supplies, Maintenance, Lab (LSM)			7,457,426	9.0235
Fixed/Indirect Operating Costs				
Local Taxes	2.5 % of FCI		810,888	0.9812
Insurance	0.8 % of FCI		259,484	0.3140
Rent	10 % of value of land		41,910	0.0507
Plant Overhead	60 % of LSM		4,474,456	5.4141
Total: Taxes, Insurance, Rent, Overhead			5,586,737	6.7600
General Expenses				
Administration	20 % of LSM		1,491,485	1.8047
Distribution and Marketing	10 % of op. costs excluding precious metals content		1,316,840	1.5934
Research and Development	5 % of op. costs excluding precious metals content		658,420	0.7967
Total: Admin, Dist., Mkting., R&D			3,466,744	4.1948

Spent Catalyst Value			
Inputs		Units	
Metal to recover	Nickel		
Support	SiO2		?
Metal wt. % of AP	3 %		?
Catalyst bulk density	356 kg/m3		?
Planned reactor configuration	Fixed Bed		?
Has trace Sn, Cu, Fe > 2% of AP?	No		?
Classification for Sale or Landfill	Zeolite, Silica, Alumina		?
Catalyst Attrition During Use			
	Base	Units	
Active Phase Losses			
AP mass in fresh catalyst	0.5000	kg/kg catalyst	?
Metal mass in fresh catalyst	0.0150	kg/kg catalyst	
AP losses during use (typical)	3 %		?
AP mass after use	0.4850	kg/kg catalyst	
Metal mass after use	0.0146	kg/kg catalyst	
Support Losses			
Support mass in fresh catalyst	0.5000	kg/kg catalyst	
Support losses during use (typical)	2 %		?
Support mass after use	0.4900	kg/kg catalyst	
Total Catalyst Solids			
Catalyst mass after use	0.9750	kg/kg catalyst	
Catalyst volume after use	0.0967	ft3/kg catalyst	
Metals Recovery Value and Fees			
	Base	Units	
Value of Metal Content			
Metal losses during refining (typical)	70 %		
Recoverable metal	0.0044	kg/kg catalyst	
Recoverable metal, troy ounces	0.1403	oz t/kg catalyst	
Spot price escalated to basis year	12.34	\$/kg metal	?
Recoverable metal value	0.05	\$/kg catalyst	
Costs of Recovery			
Incoming fee	11.17	\$/kg catalyst	?
Thermal oxidation fee	0.30	\$/kg catalyst	?
Refining fee	-	\$/kg catalyst	?
Metal contaminant fee (Sn, Cu, Fe)	-	\$/kg catalyst	?
Total recovery fees	11.47	\$/kg catalyst	
Landfill Fees and Sale Value			
Landfill cost	(0.38)	\$/kg catalyst	
Sale value, if any	0.11	\$/kg catalyst	
Best Choice for this Spent Catalyst:	Sale		
Total Spent Catalyst Value/(Cost)	0.11	\$/kg catalyst	

**CatCost CapEx & OpEx Factors Estimate:
Ni/HZSM-5**

Basis Year	2016	
Design Production, Annual	826,445 kg	
Actual Production, Annual	826,445 kg	
Cost Item	Unit Cost \$/kg catalyst	Annual Cost \$/year
Capital Costs (10-year plant life)		
Fixed Capital Investment	3.9247	3,243,551
Working Capital	0.6339	523,871
Total Capital Investment	4.5586	3,767,422
Operating Costs		
Direct Operating Costs		
Raw Materials	-	-
Process Utilities	0.1503	124,232
Labor, Supplies, Maintenance, Lab	9.0235	7,457,426
Indirect Operating Costs		
Taxes, Insurance, Rent, Overhead	6.7600	5,586,737
General Expenses		
Admin, Dist., Mkting., R&D	4.1948	3,466,744
Total Operating Costs	20.1285	16,635,140
Selling Margin		
Return on Capital Investment (15%/yr of total capital invested)	6.8379	5,651,134
Flat Margin (disabled)	-	-
Total Margin	6.8379	5,651,134
Catalyst Purchase Cost	31.5250	26,053,696
Spent Catalyst Value (SCV)	0.1075	88,823
Net Catalyst Cost	31.4175	25,964,873

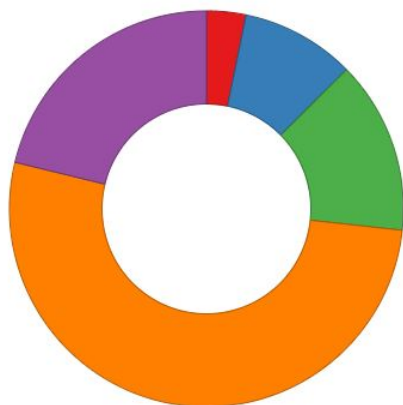
CatCost CapEx & OpEx Factors Estimate: Ni/HZSM-5		
Basis Year	2016	
Design Production, Annual	362,874 kg	
Actual Production, Annual	362,874 kg	
<u>Cost Item</u>	<u>Unit Cost</u> \$/kg catalyst	<u>Annual Cost</u> \$/year
<u>Capital Costs (10-year plant life)</u>		
Fixed Capital Investment	8.6008	3,120,992
Working Capital	1.3907	504,667
Total Capital Investment	9.9915	3,625,659
<u>Operating Costs</u>		
Direct Operating Costs		
Raw Materials	-	-
Process Utilities	0.1503	54,548
Labor, Supplies, Maintenance, Lab	20.3568	7,386,954
Indirect Operating Costs		
Taxes, Insurance, Rent, Overhead	15.1636	5,502,473
General Expenses		
Admin, Dist., Mkting., R&D	9.4220	3,418,987
Total Operating Costs	45.0927	16,362,962
<u>Selling Margin</u>		
Return on Capital Investment (15%/yr of total capital invested)	14.9873	5,438,488
Flat Margin (disabled)	-	-
Total Margin	14.9873	5,438,488
Catalyst Purchase Cost	70.0715	25,427,108
Spent Catalyst Value (SCV)	0.1075	39,000
Net Catalyst Cost	69.9640	25,388,108

Figures (1a-i). CatCost model catalyst cost estimation for 100% Baseline Scale Production BSP, (1j & k) Summary of cost estimation for 100% 50% BSP using the CapEx and OpEx method

Catalyst Purchase Cost By Category: Donut Chart

« <

Total Cost

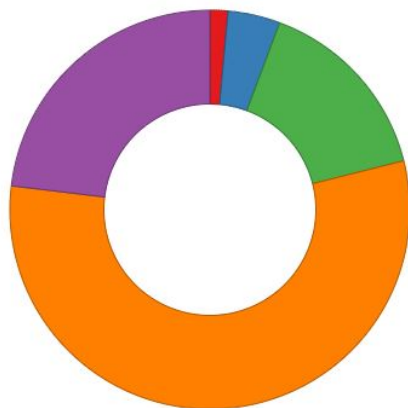


Category	Unit Cost	Percent of Current Chart
Materials	\$1.02 / kg catalyst	3.23%
Utilities	\$2.95 / kg catalyst	9.35%
Capital	\$4.46 / kg catalyst	14.14%
Operating	\$16.42 / kg catalyst	52.06%
Selling Margin	\$6.69 / kg catalyst	21.21%
Total	\$31.54 / kg catalyst	

Catalyst Purchase Cost By Category: Donut Chart

« <

Total Cost



Category	Unit Cost	Percent of Current Chart
Materials	\$1.02 / kg catalyst	1.46%
Utilities	\$2.95 / kg catalyst	4.21%
Capital	\$10.77 / kg catalyst	15.39%
Operating	\$39.09 / kg catalyst	55.85%
Selling Margin	\$16.16 / kg catalyst	23.09%
Total	\$69.99 / kg catalyst	

Figure 2 a & b. Donut chart (100 and 50 % BSP respectively) showing a summary of the cost contributors

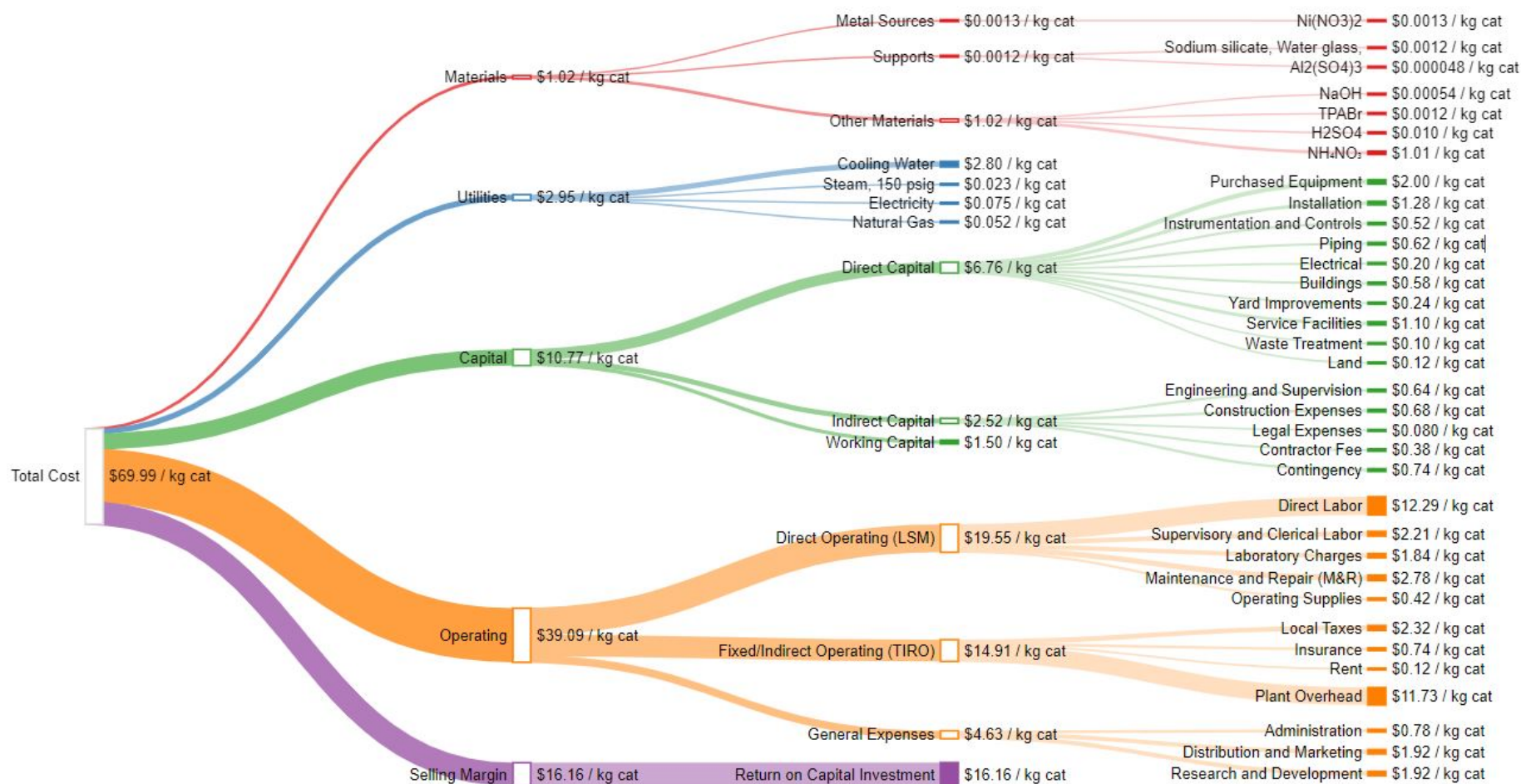


Figure 3. Sankey plot for 50% Baseline scale production (BSP)

Catalyst Purchase Cost Sensitivity: Tornado Plot

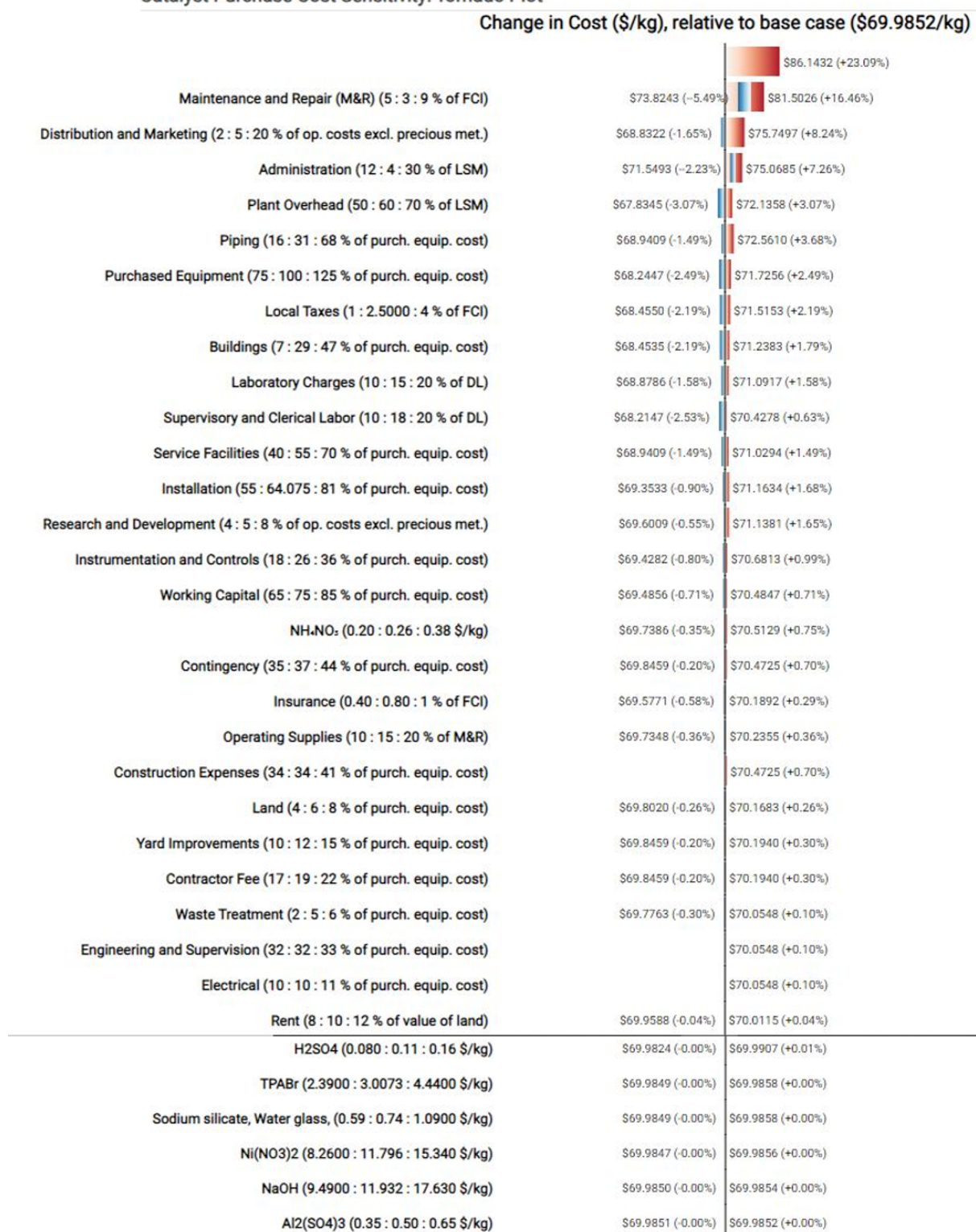


Figure 4. Tornado plot (Sensitivity analysis) for 50% BSP

1 Inputs

Production Capacity

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Design Production, Annual	Missing Inputs / No Change from Baseline
Capacity Factor	Missing Inputs / No Change from Baseline
Operating Hours (Labor)	Missing Inputs / No Change from Baseline

2 Materials

Calculation Inputs

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Finished Catalyst Mass Yield	Missing Inputs / No Change from Baseline
Active Phase Weight Percent	Missing Inputs / No Change from Baseline
Losses Due to Waste/Spoilage	Missing Inputs / No Change from Baseline

Metal Sources - Unit Cost

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Ni(NO3)2 (8.2600 : 11.796 : 15.340 \$/kg)	\$31.5340 (-0.00%)	\$31.5348 (+0.00%)
---	--------------------	--------------------

Metal Sources - Quantity

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Ni(NO3)2	Missing Inputs / No Change from Baseline
----------	--

Supports - Unit Cost

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Sodium silicate, Water glass, (0.59 : 0.74 : 1.0900 \$/kg)	\$31.5341 (-0.00%)	\$31.5350 (+0.00%)
Al2(SO4)3 (0.35 : 0.50 : 0.65 \$/kg)	\$31.5344 (-0.00%)	\$31.5344 (+0.00%)

Supports - Quantity

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Sodium silicate, Water glass,	Missing Inputs / No Change from Baseline
Al2(SO4)3	Missing Inputs / No Change from Baseline

Other Materials - Unit Cost

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

NaOH (9.4900 : 11.932 : 17.630 \$/kg)	\$31.5343 (-0.00%)	\$31.5347 (+0.00%)
TPABr (2.3900 : 3.0073 : 4.4400 \$/kg)	\$31.5341 (-0.00%)	\$31.5350 (+0.00%)
H2SO4 (0.080 : 0.11 : 0.16 \$/kg)	\$31.5317 (-0.01%)	\$31.5400 (+0.02%)
NH4NO3 (0.20 : 0.26 : 0.38 \$/kg)	\$31.2878 (-0.78%)	\$32.0621 (+1.67%)

Other Materials - Quantity

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

NaOH	Missing Inputs / No Change from Baseline
TPABr	Missing Inputs / No Change from Baseline
H2SO4	Missing Inputs / No Change from Baseline
NH4NO3	Missing Inputs / No Change from Baseline

3c Utilities

Consumption

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Cooling Water	Missing Inputs / No Change from Baseline
Process Water	Missing Inputs / No Change from Baseline
Steam, 150 psig	Missing Inputs / No Change from Baseline
Steam, 600 psig	Missing Inputs / No Change from Baseline
Electricity	Missing Inputs / No Change from Baseline
Natural Gas	Missing Inputs / No Change from Baseline

Unit Cost

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Cooling Water	Missing Inputs / No Change from Baseline
Process Water	Missing Inputs / No Change from Baseline
Steam, 150 psig	Missing Inputs / No Change from Baseline
Steam, 600 psig	Missing Inputs / No Change from Baseline
Electricity	Missing Inputs / No Change from Baseline
Natural Gas	Missing Inputs / No Change from Baseline

3d CapEx

Direct Capital Factors

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Purchased Equipment (75 : 100 : 125 % of purch. equip. cost)	\$30.8138 (-2.29%)	\$32.2550 (+2.29%)
Installation (55 : 64.075 : 81 % of purch. equip. cost)	\$31.2728 (-0.83%)	\$32.0223 (+1.55%)
Instrumentation and Controls (18 : 26 : 36 % of purch. equip. cost)	\$31.3038 (-0.73%)	\$31.8227 (+0.91%)
Piping (16 : 31 : 68 % of purch. equip. cost)	\$31.1020 (-1.37%)	\$32.6009 (+3.38%)
Electrical (10 : 10 : 11 % of purch. equip. cost)		\$31.5632 (+0.09%)
Buildings (7 : 29 : 47 % of purch. equip. cost)	\$30.9002 (-2.01%)	\$32.0533 (+1.65%)
Yard Improvements (10 : 12 : 15 % of purch. equip. cost)	\$31.4768 (-0.18%)	\$31.6209 (+0.27%)
Service Facilities (40 : 55 : 70 % of purch. equip. cost)	\$31.1020 (-1.37%)	\$31.9668 (+1.37%)
Waste Treatment (2 : 5 : 6 % of purch. equip. cost)	\$31.4479 (-0.27%)	\$31.5632 (+0.09%)
Land (4 : 6 : 8 % of purch. equip. cost)	\$31.4586 (-0.24%)	\$31.6103 (+0.24%)

Indirect Capital Factors

Change in Cost (\$/kg), relative to base case (\$31.5344/kg)

Engineering and Supervision (32 : 32 : 33 % of purch. equip. cost)		\$31.5632 (+0.09%)
Construction Expenses (34 : 34 : 41 % of purch. equip. cost)		\$31.7362 (+0.64%)
Contractor Fee (17 : 19 : 22 % of purch. equip. cost)	\$31.4768 (-0.18%)	\$31.6209 (+0.27%)
Contingency (35 : 37 : 44 % of purch. equip. cost)	\$31.4768 (-0.18%)	\$31.7362 (+0.64%)

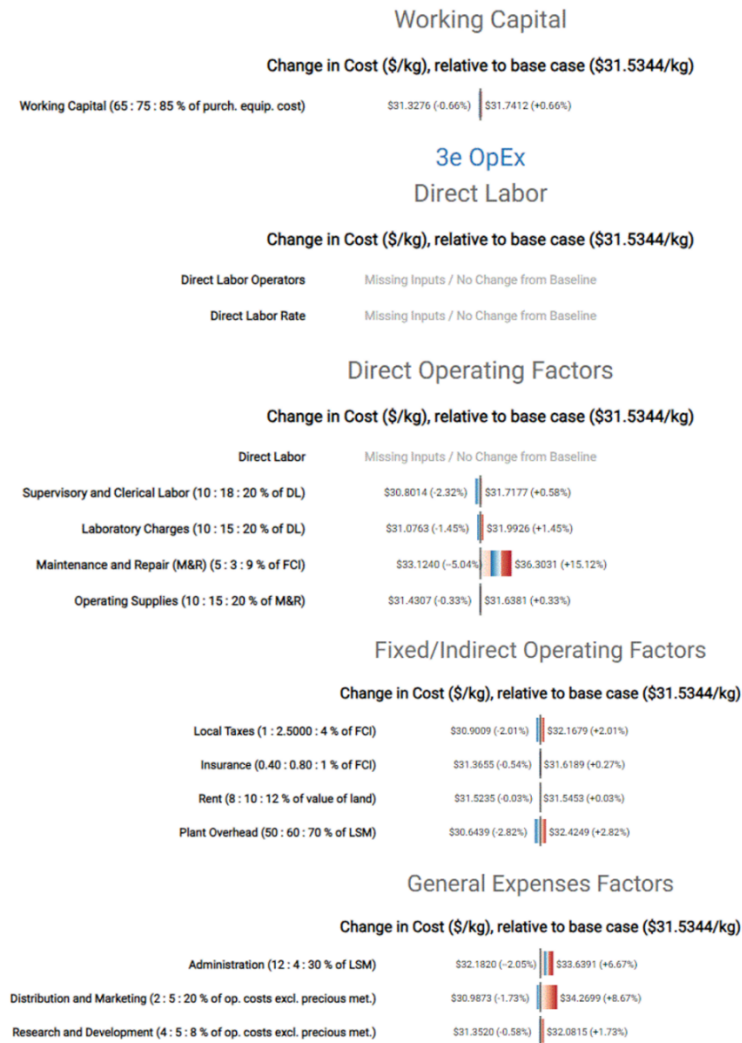


Figure 5 (a-c) Tornado (Detailed sensitivity analysis) by category for 100% BSP

Table 1. Effect of scale production on the contributors of net catalyst cost at different baseline scale production (100 and 50 %)

Components	100% BLSP	50% BLSP
Direct labour	16%	18%
Supervisory	3%	3%
Laboratory charges	2%	2%
Maintenance and repair	4%	4%
Local taxes	3%	3%
Plant overhead	15%	17%
Administration	1%	1%
Distribution and marketing	3%	3%
Research and development	3%	3%
Return on capital investment	21%	23%
Cooling water	12%	12%

2.0 TEA - Ethanol Conversion to Fuel Blendstock

Table 2. Current (2023) fuel prices adjusted from 2019 (Hannon et al., 2020). Stoichiometric yield is assumed to be the molecular weight (average) of the hydrocarbon product (C_2H_4 average formula, 28.05 g/mol) divided by ethanol C_2H_5OH molecular weight (46.07 g/mol)

Fuel	*Price (2019)		Price (current)		Stoichiometric Yield From Ethanol (g/g)
	\$/GJ	\$/L	\$/GJ	\$/L	
Gasoline	11.7	0.4	15.4	0.5	
Diesel	13.7	0.5	18.0	0.6	0.609
Jet fuel	14.5	0.5	19.1	0.6	

Table 3a. Estimated current conversion costs for converting 61 million gallons/year of 40% ethanol into fuel blendstocks in CADO-ETH (adjusted annually by average inflation over 10 years (1.8%) to account for 2023 dollars)

CADO ETHANOL TO HYDROCARBONS CURRENT PROCESS								
Operating Parameter	Size	Units	Cost	Units	*Costs \$ (2019)	Cost \$ (current)	Costs \$/L (HC)	Costs \$/L (HC) (current)
Wastewater	158	kgal/day	7.00	\$/kgal	383,000	451,940	0.0034	0.0053
Catalyst (Reactor)	34,656	kg/yr	70.00	\$/kg	2,426,000	2,862,680	0.0216	0.034
Electricity	2,816	kW	0.05	\$/kWhr	1,173,000	1,384,140	0.0105	0.016
Waste Disposal	34,657	kg/yr	2.00	\$/kg	69,000	81,420	0.0006	0.00093
Insurance & Taxes			2.0%	TIC	335,000	395,300	0.0030	0.0047
Maintenance			3.0%	TIC	502,000	592,360	0.0045	0.0070
Labour			1.0%	TIC	167,000	197,060	0.0015	0.0023
Contingency	0%				0	0	0.0000	0
					5,055,000	5,964,900	0.0451	0.0532
Total Conversion Costs (current) = \$5,964,900								

*Cost (\$) 2019 (Hannon et al., 2020)

Table 3b. Future CADO ethanol to gasoline fuel blendstock process

Operating Parameter	Size	Units	Cost	Units	Costs \$ (2019)	Costs \$ (current)	Costs \$/L (HC) (2019)	Costs \$/L (HC) (current)
Waste Water	157,5	kgal/day	7	\$/kgal	383,000	451,940	0,003	0,0036
Catalyst (Reactor)	34,655	kg/yr	30	\$/kg	1,040,000	1,227,200	0,0082	0,0097
Electricity	2,817	kW	0,05	\$/kWhr	1,173,000	1,384,140	0,0093	0,011
Waste Disposal	34,655	kg/yr	2	\$/kg	69,000	81,420	0,0005	0,00059
Insurance & Taxes			2,00%	TIC	335,000	395,300	0,0027	0,0032
Maintenance			3,00%	TIC	502,000	592,360	0,004	0,0047
Labor			1,00%	TIC	167,000	197,060	0,0013	0,0015
Contingency	0%				0	0	0	0
Total Conversion Cost					3,669,000	4,329,420	0.0291	0,03422

Table 3c. Cost estimation for producing anhydrous ethanol from a 40% ethanol feed using the current technology (sourced from NREL TP 47764 (Humbird, 2011), adjusted annually by 1.8% to account for 2023 dollars)

ESTIMATED CONVERSION COSTS HYDROUS TO ANHYDROUS ETHANOL								
Operating Parameter	Size	Units	Cost	Units	Costs \$ (2019)	Costs \$ (current)	*Costs \$/L (2019)	Costs \$/L (current)
Natural Gas	26.11	MMB TU/hr	4.00	\$/MMB TU	869,794	1,026,357	0.0038	0.0045
Waste Water	258.3	kgal/day	7.0	\$/kgal	627,405	740,338	0.0027	0.0031
Catalyst (Mole Sieve)	3,465	kg/yr	10	\$/kg	35,000	41,300	0.0002	0.00024
Electricity	710	kW	0.05	\$/kWhr	295,644	348,860	0.0013	0.0015
Waste Disposal	3,465	kg/yr	2.0	\$/kg	7,000	8,260	0.0000	0
Insurance & Taxes			2.0%	TIC	394,000	464,920	0.0034	0.0040
Maintenance			3.0%	TIC	591,000	697,380	0.0051	0.0060
Labor			1.0%	TIC	197,000	232,460	0.0017	0.0020
Contingency	0%				0	0	0.0000	0
Total Estimated Operating Costs					3,016,843	3,559,875	0.0182	0.022
Total Estimated Operating Costs. = \$3,016,843 = \$3,559,875 (current) Capital Costs (Rectification, Molecular Sieves) = \$19,695,596 = \$23,240,803 (current) Production Costs (OpEx + 0.15*CapEx) = \$0.0310. = \$0.0366 (current)								

Values used to calculate the conversion below include a development period of 0 - 22 months; Liquid fluid yield (% theoretical) of 36 - 80%, catalyst cost of 600 – 30 \$/kg (current and future cost) and catalyst lifetime of 6 - 9 months (Hannon et al., 2020). *Cost (\$) 2019 (Hannon et al., 2020).

Table 3d. Capital costs associated with the CADO process for converting 61 million gallons/year of 40% ethanol into hydrocarbons (Capital costs are assumed to be the same for both the current technology and the future process)

Equipment	Size	Units	Number	*Cost each	Install Factor	*Total Cost (2019)	Total Cost (current)
Reactor Preheater (HE1)	9.52	MMBTU/hr	1	\$360,732	3.00	\$1,082,000	\$1,276,760
Direct Fired Heater (HE2)	16.7	MMBTU/hr	1	\$489,033	3.00	\$1,467,000	\$1,731,060
Catalytic Reactor	9,521	gallons	2	\$387,707	3.25	\$2,520,000	\$2,973,600
Condenser (HE3)	105.7	MMBTU/hr	1	\$1,612,801	2.40	\$3,871,000	\$4,567,780
Decanter	12,000	Gallons	1	\$163,506	2.00	\$327,000	\$385,860
Product Storage	750,000	Gallons	0	\$844,259	1.50	\$0	\$0
Water Storage	50,000	Gallons	0	\$196,913	1.50	\$0	\$0
Water Pumps	183	gpm	4	\$47,176	1.57	\$295,000	\$348,100
Product Pumps	53	gpm	4	\$22,526	1.57	\$141,000	\$166,380
Compressor	2,388	kW	2	\$640,305	1.49	\$1,908,000	\$2,251,440
Stripper	557,963	Gallons	1	\$975,801	2.00	\$1,952,000	\$2,303,360
Flare System	5%					\$678,000	\$800,040
Product Load Out	8%					\$1,085,000	\$1,280,300
Capital Contingency	0%					\$0	\$0
Total installed Costs (TIC)						\$15,326,000	\$18,084,680

*Cost (\$) 2019 (Hannon et al., 2020).

Table 4. Conventional ethanol to hydrocarbon fuel blendstock technologies: NREL Report (NREL (Hannon et al., 2020))

Feedstock	Ethanol Yield		Gasoline Fuel Yield		Gasoline Fuel Yield Gal gasoline/gal EtOH	MISP (\$/gal)	MISP \$/L (\$/GJ)	Est Conv Cost (2019) \$/L gasoline (\$/GJ gasoline)	Est Conv Cost \$/L gasoline (\$/GJ gasoline): current
	gal/BDT	GGE/BDT	gal/BDT GGE/BDT	Gal gasoline/gal EtOH					
Corn Grain	118	78	52	53	0.440	\$2.80	\$0.74 (21.6)		
Corn Stover	79	52	35	35	0.440	\$2.80	\$0.74 (21.6)		
Corn Stover	72	47	32	32	0.440	\$2.30	\$0.61 (17.8)	0.112 (3.423)	0.132 (4.039)
Sugarcane	24	16	11	11	0.441	\$2.00	\$0.53 (15.5)		
High				0.579	4.2	1.11	32.5		
Low				0.439	2.0	0.37	18.8		

Average				0.509	3.1	0.74	21.6		
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Gasoline fuel LHV is 0.0342 GJ/L, while ethanol LHV is 0.0213 GJ/L. NR (not reported)

<https://hextobinary.com/unit/energy>

The data presented in Table S1 was obtained from the NREL (NREL 2016) and (Hannon et al., 2020) and adjusted to 2023 \$) study focused on conventional ethanol to gasoline fuel technologies. The table includes information on Minimum Intermediate (Ethanol) Selling Price (MISP) and Bone Dry Ton (BDT).

3.0 LCA - Energy Use in ethanol production and conversion to fuel blendstocks (Wang et al., 2012, Dias et al., 2016, Hannon et al., 2020)

The following tables provide a concise overview of the main input data for GHG emissions for the different pathways analysed in this article. Information on corn can be obtained from GREET (GREET 2018), while data on sugar cane can be found in the study by (Dias et al., 2016). Table 5a, for example, provides information on fertilisers used in corn, corn stover and sugarcane production. It also contains data on the energy used to cultivate corn, corn stover and sugar cane. Table 5b and Table 5c pertain to the conversion process of producing ethanol from corn and sugarcane. The information in Table 5c relates to the fuel produced and utilized in the United States for corn and corn stover ethanol, while the data on sugar cane is specific to fuel produced and used in Brazil (Dias et al., 2016). Table 5d details feedstock transportation (corn, corn stover, and sugar cane), ethanol and the final product (gasoline). Specifically, it includes information on the movement of corn from the farm to the collection stack and from the collection stack to the ethanol plant. The table considers a round trip, which involves transporting the product from its origin to the destination and returning to the origin (back-haul).

Within GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model, various types of corn Ethanol Plant Types are considered. However, in this study, the default values provided in GREET were used, which represent the industry average ethanol production. These values include 18% for Dry Milling Plant without Corn Oil extraction, 71% for Dry Milling Plant with Corn Oil extraction, and 11% for Wet Milling Plant (GREET, 2018) (3) and (Hannon et al., 2020).

Table 5a. Farming energy and nutrient input for ethanol production

Feedstock	Process Fuels - % input					*Total Nutrient Input
	Diesel + Gasoline fuel	Natural gas + Liquefied petroleum gas	Liquefied petroleum gas	Electricity	Total energy input	
Corn	70%	27%	15%	4%	6,502.65 (btu/bushel)	1655.6 (gr/bushel)
Corn stover	70%	27%	15%	4%	290,042.57 (Btu/dry ton transported)	72634.43 (gr nutrient/dry ton transported)
Sugar cane	100%	-	-	-	75,974.80 (Btu/ton)	8225 (gr/ton)

*Total nutrient input consists of: Nitrogen, P₂O₅, K₂O, CaCO₃, insecticide, herbicide, Urea.
 Units: corn farming (grams/bushel), corn stover (grams of nutrient/dry ton transported), and sugar cane (grams/ton)

Table 5b. Material and energy input of corn ethanol production

Feedstock	Corn- Dry Mill EtOH Production w/o Corn Oil Extraction	Corn - Dry Mill EtOH Production w/ Corn Oil Extraction	Wet Mill EtOH Production	Corn stover**
Material	gr/gal EtOH	gr/gal EtOH	gr/gal EtOH	gr/gal EtOH
Enzymes	7.9	7.9	8.5	
Yeast	2.7	2.7	2.9	2.7
Chemicals (H₂SO₄, NH₃, NaOH, CaO)	55.6	55.1	59.4	582
Cellulase	0	0	0	107
Corn steep liquor	0	0	0	132
DAP	0	0	0	14
Urea	0	0	0	21
Lime	0	0	0	0
Energy input	Btu/ gal	Btu/ gal	Btu/ gal	Btu/ gal
Electricity	2,220*	2,220*	0	
Coal	1,950	1,910	13,040	
Natural gas	19,341*	18,920*	31,330*	
Diesel		0		180
Biomass	0	0	0	0.012
Ethanol yield	2.9	2.9	2.7	78
	(gal/bushel of corn)	(gal/bushel of corn)	(gal/bushel of corn)	(gal/ dry ton)

*These values reflect the energy saving for the production 40% ethanol

** Based on NREL base case presented by (Dias et al., 2016).

Table 5c. Material and energy input of sugarcane ethanol production, per ton of sugarcane (70% wt. moist)

<i>Feedstock</i>	Cane juice		Cane cellulosic
	Current	Current	Projected
Sugarcane (ton)	1.0	1.0	1.0
Lime (kg)	0.6	0.6	0.6
Acids (H2SO4 and H3PO4) (kg)	0.7	0.7	0.7
Polymer flocculants (g)	2.7	2.6	2.6
Antibiotics (g)	1.1	1.4	1.6
Enzyme (cellulase) (kg)	0.0	0.5	0.4
Lubricating oil (g)	13	13	13
Product (Anhydrous ethanol (kg))	67	85	98
<i>Energy</i>			
Bagasse/straw (kg)	125	137	116
Electricity (kWh)	0	59	40

Table 5d. Transportation of Feedstock, EtOH and final product (Gasoline fuel or HC)

		Transportation method	Fuel type	Payload (tons)	Energy consumption (Btu/mile)	Distance (Miles, one way)
<i>Transportation of Gasoline</i>	Gasoline fuel transportation	B: 33% R: 7% P: 60%	B: Residual oil R: 50% diesel, 50%FTD	B: 20,000	B: 423 (Btu/ton-mile) ¹ R: 274 (Btu/ton-mile) P: 404 (Btu/ton-mile)	B: 520 R: 800 P: 400
	Gasoline fuel distribution	100% Truck	Diesel	25	17,596	30
<i>Transportation of Feedstock</i>	Corn (From farm to collection stack to EtOH plant)	Truck (MH + HH duty)	Diesel	8 + 15	15,476 + 17,596	10 + 40
	Corn Stover	Truck (HH –duty)	Diesel	25	17,596	53
	Sugarcane (From farm to EtOH plant)	Truck (HH - duty)	Diesel	60	65,137	22
<i>Transportation of EtOH</i>	Sugarcane (From farm to EtOH plant)	Truck (HH - duty)	Diesel	60	65,137	22
	Sugarcane (From farm to EtOH plant)	Truck (HH - duty)	Diesel	60	65,137	22
	Corn and Corn Stover (EtOH transportation)	B: 13% R: 79% T: 8%	B: Residual oil R & T: Diesel	B: 20,000 T: 25	B: 423 (Btu/ton-mile) ¹ R: 274 (Btu/ton-mile) T: 17,596	B: 520 R: 800 T: 80
	Corn and Corn Stover (EtOH Distribution)	100% Truck	Diesel	25	17,596	80
	Sugarcane (EtOH transportation)	100% Truck	Diesel	33	17,596	350

Sugarcane (EtOH distribution)	100% Truck	Diesel	25	17,596	30
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B: Barge, R: Rail, T: Truck, P: Pipeline, MH – Medium heavy; HH – Heavy heavy.
 For barge and truck we considered round trip. While the energy consumed for back-haul truck is the same as shown in the table, for barge is 312 (Btu/ton-mile). FTD: FischerTropsch Diesel.

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