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Review Article

Catalytic Conversion of Low Alcohol to Hydrocarbons: Challenges, Prospects, and Future Work Considerations

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Energy sources will contribute enormously to global economic development in the coming years. Global energy sectors mainly depend on fossil fuels, which contribute to greenhouse gas emissions. With the threat of declining oil supplies and the need to reduce CO_2 emissions, the development of viable substitutes for fossil fuels is high on the global priority list. Currently, there is an increased focus on using low alcohols as fuels and petrochemicals. Catalytic conversion is a viable approach for upgrading low alcohols to fuels and value-added chemicals. This review study shows that optimal catalyst modification improves catalytic performance in the volarization of bioethanol. Heterogeneous catalysts are widely used in bioethanol conversion due to their activity. However, further studies are needed to address the challenges of limited selectivity, catalyst deactivation, recovery, and regeneration for improved biofuel production.

1. Introduction

The declining oil resources attributed to high energy usage and global warming are two of the major issues facing the world in the twenty-first century. The growing concentration of CO_2 in the atmosphere is widely believed to be the most significant contributor to global warming. Lately, global warming has made it to the top of the social agenda, garnering international awareness and fostering a sense of unanimity that civilization should be modified to address the primary source of CO_2 generation and pollution-related challenges, including fine dust. Moreover, the overwhelming dependence on fossil fuels as our primary energy source is responsible for these issues. Petroleum is the most accessible fossil fuel for utilization in transportation; however, at the current significant level of consumption, existing oil reserves and natural gas are anticipated to diminish within 50 and 70 years, respectively [1]. The recognition of additional oil and natural gas sources may delay the complete depletion of these fossil fuels. Still, substantial fuel scarcity concerns are projected in the future. The annual utilization of petroleum and natural gas has risen by 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 [2]. Figures 1 and 2 depict the rising trend in global energy consumption and annual CO_2 emissions. Figure 1 shows that energy consumption will increase significantly from 2025 to 2050, attributed to an increase in energy demand.

From Figure 2, it can be deduced that CO_2 emission rates increased during the 21st century, resulting in a rise in atmospheric CO_2 content. 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 CO_2 emissions in the Asia region and 31 % of world CO_2 emissions. North America was the second most polluting location in the world in 2020, with 5.3 billion metric tonnes of CO_2 released in that location. CO_2 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

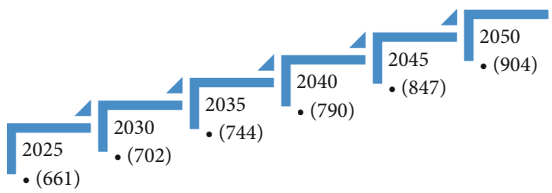


Figure 1: Global energy consumption (in quadrillion Btu) projection >2025. (source: EIA [3]).

continent. The emergence of COVID-19 in 2020 prompted the imposition of tight lockdowns and limitations to reduce the virus's transmission. As a result of the disruptions to travel and commercial activity, there was a significant drop in global emissions. Earlier in 2020, some of the most dramatic decreases were observed when many of the first lockdowns were implemented. By comparison, worldwide energy-related CO_2 emissions decreased by more than 14 % in April 2020 as contrasted to the similar month of the preceding year. According to EIA's International Energy Outlook 2016 (IEO2016) reference case, worldwide energy-associated CO_2 emissions are expected to rise by one-third from 2020 to 2040, primarily due to growing energy utilization in nonmember nations of the Organization for Economic Cooperation and Development (OECD).

Notwithstanding a significant drop in the CO_2 per unit of energy of the world's energy resources, global emissions have risen in recent years [4]. During the twentieth century, increased CO_2 emission rates resulted in a rise in the atmospheric CO_2 content from around 295 ppm to 380 ppm. Additionally, it has been claimed that the earth's temperature has risen by approximately 0.6°C over the same period [2–4]. The need to provide a sustainable substitute for fossil fuel becomes imperative to meet the high energy requirement for transportation and other areas of the economy.

In this period of limited fossil fuel resources and rising CO_2 emissions in the environment, meeting the transportation sector's energy requirements is becoming exceedingly challenging. The present global trend of shifting away from traditional liquid fuels such as gasoline and light oil and toward substitute clean gas and liquid fuels necessitates a vivid description of the role and place of low-alcohol fuels in the evolving scenario. Most recently, researchers raised awareness about environmental conservation and the application of low alcohol or alternative fuels in automobile engines, both of which benefit the environment. The use of alcohol fuels has the potential to lower carbon dioxide levels in the atmosphere, which has a substantial impact on the global warming potential of the environment. However, widespread utilization in the public transport sector requires further advancement since the practical application of such energy sources would necessitate the modification of current gasoline engines and the provision of infrastructure to supply and distribute suitable fuels. As a result, the quickest way to offer renewable energy for the automotive industry is to replace petroleum with liquid biofuels that can be used with existing engine configurations through a catalytic conversion process [7].

The review paper by Ezinkwo et al. [8] focused on issues related to the conversion of bioethanol to butadiene. Catalytic conversion and issues related to other petrochemicals produced from ethanol were not addressed in the review. Ennaert et al. [9] thoroughly reviewed zeolite chemistry, potentials, and challenges of catalytic conversion processes. Also, few studies focused on the catalytic upgrading of bioethanol and ethanol to butanol (and ethanol to butanol) [10, 11], while the effect of bioethanol impurities on steam reforming for hydrogen production was studied by Sanchez et al. [12]. The recent study by Kianfar et al. [13] provided a thorough overview of the many zeolite-based catalysts and the impact of modifying the surface or framework of the zeolite on the selectivity, stability, and conversion of methanol to gasoline. In addition, the effects of the operational reaction parameters were also investigated. The limitation of this review is that it focuses only on zeolite catalysts. The review work by Phung et al. [14] addressed the production of biopropylene from bioethanol and the factors affecting the conversion processes. These studies did not include the comprehensive evaluation and performance of different catalysts for low alcohol conversion. To this end, this insight concentrates on the catalytic conversion of low alcohol into fuels and petrochemicals. Rather than simply summarizing the present state of our understanding of such a process, our goal was to outline and engage in critical discussion about the potentials and limitations of low alcohol as fuel and a comprehensive review of different catalysts for low alcohol conversion. The study also presents challenges that need to be addressed and future work considerations for the effective conversion of low alcohols into fuels and petrochemicals. In this study, various works on the catalytic conversion of low alcohol were reviewed, focusing on the application of zeolite-, silicoaluminophosphate- (SAPO-), zirconium-, and alumina-based catalyst systems. A systematic literature search was conducted for information and works relevant to achieving the objectives.

1.1. Potentials and Limitations of Low Alcohols as Fuel and Petrochemicals. Low-alcohol fuels have recently gained a great deal of interest, and they have begun to substitute several compounds used as octane boosters, especially in car fuels. With the prohibition of tetraethyl lead as a fuel enhancer to increase the octane rating of gasoline fuel, MTBE and alcohols have been utilized 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 alcohol oxygen concentration, octane rating, and autoignition 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) are more than that of gasoline combustion, the combustion pressures produced by alcohol combustion in ICEs are greater than those produced by gasoline. Additionally, when 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 so far mainly relied on first-generation alcohols in the form

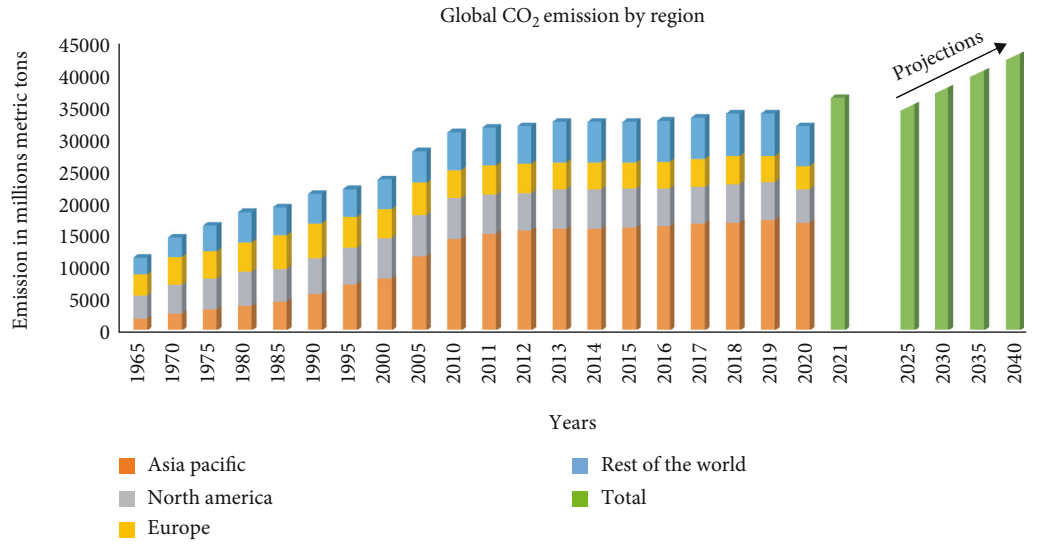


Figure 2: Global CO_2 emission by region (sources: EIA [4], IEO, 2016 with projections to 2040 [5], International Energy Agency (IEA) [3], and Short-Term Energy Outlook [6]).

of 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 a lot in common [15]. Unlike gasoline and diesel, alcohols contain oxygen; as a result, the addition of alcohols to petroleum-based products increases the performance of fuel combustion, which ultimately leads to a reduction in emissions into the atmosphere [16]. Furthermore, when it comes to employing low alcohol as a fuel, the solubility of low alcohol in water is crucial. Low alcohols (methanol, ethanol, and propanol) are all soluble 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 [17].

Low alcohols, such as ethanol, can be employed as fuel in vehicle engines because of their high-octane number; nevertheless, their utilization is fraught with difficulties. Ethanol has a calorific value of 27 MJ/kg, which is approximately 65% of that of gasoline (44 MJ/kg). As a result, ethanol fuel does not combust readily and requires significantly more fuel utilization than pure gasoline, which has a better heating value and energy efficiency than ethanol. The low flame speed of ethanol-blend gasoline, as a result, adds to a reduction in engine performance and poor cold-starting capabilities, making it challenging to use during winter. Consequently, the disparity between the lower calorific values of the two fuels results in a rise in the fuel utilization of the gasoline/ethanol blend with increasing ethanol concentration in the blends, resulting in a reduction in engine fuel economy [18]. When contrasted to gasoline, this feature describes why the engine will require a greater amount of ethanol or methanol mixes to produce the same amount of engine power. Moreover, because no passenger automobile is designed to run on 100% ethanol, utilizing 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, as well as any plastic parts that come into contact with fuel and the fuel injection system [19]. This appears to be a time-consuming task with substantial cost implications.

2. Review of Catalysts for Low Alcohol Conversion into Fuels and Petrochemicals

The catalytic conversion of low alcohols (methanol and ethanol), which occurs at an optimal temperature and in the presence of a catalyst, makes it easier for ethanol to be converted into olefins and then higher hydrocarbons (oligomers). Converting ethanol to ethylene through catalytic dehydration is the oldest process in the industry [20]. During the conversion process, ethanol undergoes dehydration to yield ethylene, which is subsequently oligomerized to produce olefins, paraffin, naphthenes, and aromatics. Due to the use of renewable biomass in transforming ethanol to propylene, the process is deemed carbon–neutral [21]. According to Harmsen et al. [22], ethylene is utilized in synthesizing plastics and rubbers, as well as ethylene glycol and vinyl chloride resin. It is also employed to make 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 into C_4 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 these processes [23–26]. In several acid-catalyzed conversions of olefins, olefin oligomerization is a deactivation or undesirable reaction process. Still, it can also be beneficial to carbon-carbon bond creation when the correct catalyst and parameters are used [27]. For more than 80 years, light olefins (C_2-C_5) have been oligomerized using

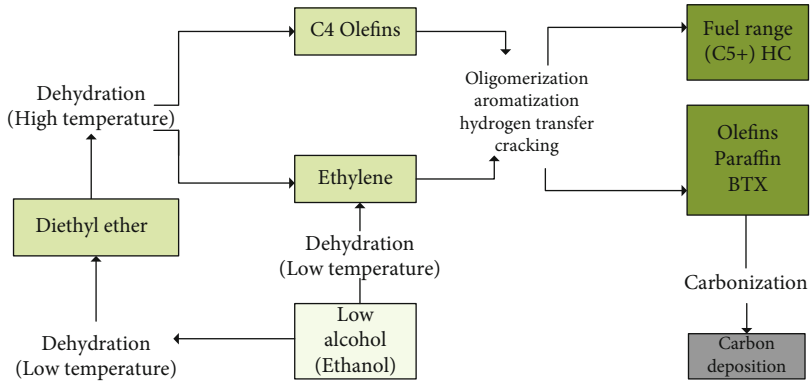


Figure 3: Pathway for the catalytic transformation of ethanol to hydrocarbon (HC) (adapted from [32] with modifications).

acid-based catalysts to form fuels, primarily gasoline; however, more lately to distillates and other products, 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 specific manufacture of linear and branched higher olefins have been developed and put into commercial production, with applications in the fields of fuel and chemicals. However, given significant research work and the ease with which heterogeneous catalysis are handled in petrochemical industries, and just a handful of oligomerization facilities throughout the globe are equipped to work with heterogeneous systems. The oligomerization of ethylene, propylene, and butene by solid acids occurs through unspecific cationic pathways [28], resulting in high-branching-indices oligomers that are mostly used in the production of gasoline and diesel [29–31]. The sections below present a review of different catalyst for low alcohol dehydration and olefins oligomerization. The conversion pathway for the transformation of ethanol into hydrocarbons is presented in Figure 3. The sections below present a review of different catalyst for low alcohol dehydration and olefins oligomerization.

2.1. Introduction to Zeolite-Based Catalyst. A unique category of silica-aluminas is the crystalline, microporous zeolites [33]. 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 [34–37]. The utilization of MFI zeolites in low alcohol dehydration and oligomerization of olefins is among the most extensively researched catalytic materials. This is partially attributed to their earlier industrial employment in the Mobil Olefins to Gasoline and Distillate (MOGD) and PetroSA for the conversion of olefins to distillate (COD) mechanisms. However, the versatility of this class of materials allowed scientists to select the appropriate pore volume, connectivity, and hence, shape specificity [38, 39]. To improve the catalytic activity, some catalyst fabrication techniques include incipient wetness impregnation (IWI) or ion-exchange procedures for metal or phosphorous doping, NaOH treatment, and specified temperature steaming are applied after the catalyst preparation. According to Rahimi and Karimzadeh [40], all of these postmodifications can provide further stability to thermal treatment, a reduction in catalyst deactivation, or an increase in the activity/selectivity of a specific product.

Numerous studies have been carried out in ethanol dehydration with zeolite catalysts, some of which have been described in more detail [41]. The study by Zhang et al. [42] using the HZSM-5 catalyst (Si/Al = 25) for the ethylene synthesis from ethanol evaluated the performance and stability of the zeolite employed in the process. The dehydration processes were conducted at $T = 250$ to 450°C, with an LHSV of $3\,h^{-1}$ and a pressure of 70 bar. At lower temperatures, the conversion process was unfavourable, but increasing the reaction temperature improved the ethanol conversion. At a temperature of 325°C, the maximum ethanol transformation was 97.3%, while the maximum ethylene specificity was 98.5% at 300°C. The HZSM-5 exhibited the most significant ethylene specificity when operated at a reduced temperature. When the HZSM-5 catalyst was tested after 60 hours, it was discovered that it had the greatest initial efficiency of 93.1%, reached after only 10 hours of process run time [42]. The study showed that the HZMS-5 catalyst was efficient; however, it deactivates with a more prolonged process time, reducing catalytic performance and efficiency. Furthermore, in addition to temperature, other parameters such as pressure, catalyst type, and metal doping influence catalytic activity (Figure 4) shows the influence of operating parameters in ethanol transformation to olefin and BTEX. According to Figure 4, the catalytic performance of different zeolite catalysts at $P = 1$ bar, $T = 569$ and 659°C, and catalyst weight of 0.15-0.3 g can be deduced that all the catalytic conversion process at operating conditions, $T = 659 \circ C$, $P = 1$ bar, recorded 100% conversion, the C_5+, and BTEX yield was low (13-36%), with appreciable yield of C_1-C_4 range hydrocarbon (59-74%). However, at $T = 569 \circ C$ and $P = 1$ bar with ethanol conversion rate below 100% (86.3-99.2%), more C_5+ and BTEX hydrocarbons were produced (44-68%) with 40-56% yield of C_1-C_4 hydrocarbon. This showed that the operating condition, $T = 569 \circ C$, and $P = 1$ bar, favours the production of fuel range (C_5+) hydrocarbons than $T = 659 \circ C$ and $P = 1$ bar.

The influence of metal doping on the catalytic activity of ZSM-5 was studied by Song et al. [44]. To improve the catalytic transformation of ethanol to propylene, the H-ZSM-

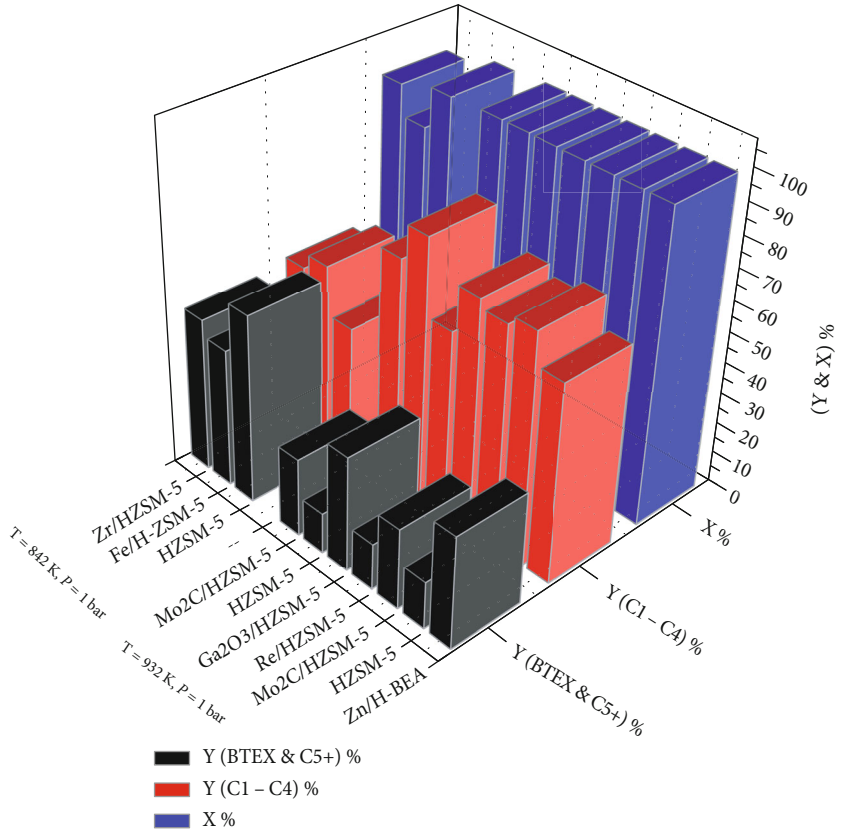


FIGURE 4: Conversion efficiency (X) and selectivity (Y) of C_1-C_4, BTEX, and fuel (C_5+) range hydrocarbons in catalytic conversion of bioethanol over different zeolite catalysts (adapted from [43]).

5(80) catalysts were modified by adding metal ions to the surface of the material. An ion-exchange technique was employed to incorporate the ions, magnesium, calcium, barium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, cerium, argon, and palladium while an impregnation method was used to introduce the ions, bismuth, titanium, vanadium, zirconium, molybdenum, and tungsten. As a result of this study, the hydrocarbons produced with the doped H-ZSM-5(80) show appreciable yield in comparison to the performance of the unmodified catalyst. When likened to unmodified catalysts, the alkaline earth metal- (magnesium, calcium, and barium) doped catalysts gave much higher ethylene yields, but propylene yields were significantly lower. However, the decline in the H-ZSM-5 acidity 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. [45] with Zr Catalyst modified with alkaline earth metals. However, NH_3-TPD did not provide any concrete evidence for a reduction in acidity, according to the study [44]. The catalytic performance of the H-ZSM-5(80) materials altered with manganese, iron, cobalt, copper, zinc, argon, bismuth, and vanadium was comparable to that of the unmodified H-ZSM-5(80). The introduction of nickel and gallium ions improved the synthesis of C_5+ 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. [46] and Makarfi et al. [36]. The addition of chromium, cerium, palladium, titanium, zirconium, molybdenum, and tungsten increased olefin yields (ethylene and propylene). The maximum propylene output (31%) was produced using Zr-doped H-ZSM-5(80) as a starting material. However, when H-ZSM-5(80) was employed for 5 hours, propylene production plummeted below 30% with an appreciable increase in ethylene yield [44]. The Zr-doped H-ZSM-5(80) exhibits improved stability than H-ZSM-5(80) in propylene production. This can be attributed to the ability of zirconium to successfully protect the zeolite framework from dealumination with water, thus increasing the hydrothermal stability. The ZSM-5 zeolites doped with Zr and Ti proved to be the most efficient catalysts for propylene synthesis.

Awareness of methanol-to-hydrocarbon (MTH) chemistry and its industrial potential has been widespread for some time. The energy crisis of the 1970s sparked new interest in methanol-to-gasoline (MTG) technology. In the late 1970s, the New Zealand government decided to build the world's first plant to produce gasoline from natural gas using methanol [47]. In 1986, a plant was commissioned with a targeted annual gasoline synthesis of 600,000 tonnes via an H-ZSM-5 catalyst. However, due to the subsequent decline in crude oil prices, only the methanol production step was commissioned after the plant was shut down. In the mid-1980s,

the Topsoe Integrated Gasoline Synthesis (TIGAS) process developed by Haldor Topsoe AS, which also relied on H-ZSM-5 as a catalyst, was demonstrated on a pilot scale [48].

The operating parameters strongly influence the methanol-to-hydrocarbon (MTH) process. To achieve the highest possible catalyst stability and selectivity in MTH, the most critical factor is the choice of the optimum temperature and pressure [13]. Since the conversion of methanol to hydrocarbons is an exothermic reaction, researchers have investigated a range of temperature trends. Extreme reaction temperatures directly affect the rate at which the catalyst particles lose their active state, and this rate increases linearly as the maximum temperature increases [49]. The study by Kianfar et al. [13] on the effect of operating parameters (space velocity, pressure, temperature, and feed supply) on MTG process shows that for specific modified catalysts, the conversion rate improves with the process parameters; however, the selectivity decreases with increasing temperature. These results are based on the fact that as the temperature increases, the selectivity decreases. The influence of pressure on the conversion of methanol has also been the subject of various studies [50–53]. According to studies conducted in a fixed-bed reactor, the transformation of methanol to hydrocarbons at high pressure resulted in the formation of more aromatic compounds [50–53]. This is due to the higher specificity of aromatics in the decomposition of C_5+ hydrocarbons under elevated pressure [54]. However, as the pressure increases, the mass of coke produced on the catalyst also increases. Introducing water into the feed stream of MTH process reduces coke formation and improves catalyst performance. In addition, water in the feedstock can promote olefin synthesis while reducing specificity in aromatics and paraffin production [55–57]. Moreover, studies conducted on the specified tubular reactor using methanol as feedstock show that the olefins' specificity improves as the feed stream's diluents decrease with the partial pressure of methanol [58–63].

The Si/Al ratio of ZSM-5 catalyst has been shown to directly affect the BrØnsted/Lewis ratio, which in turn affects the strength and distribution of acid sites and consequently the specificity for different products [64–66]. Benito et al. [64] investigates the relationship between the Si/Al ratio in ZSM-5 zeolite and the nature of the main hydrocarbon products in the MTG. The researchers found that light alkenes (such as ethene, propene, and butene) are the first reaction products and that increasing the Si/Al ratio leads to an increase in the BrØnsted/Lewis ratio. According to the analogous study by Gao et al. [65], increasing the Si/Al ratio in ZSM-5 zeolite from 20 to 60 resulted in a decrease in the total acid sites. On the other hand, the ratio of strongly acidic to weakly acidic sites increased during this process. Based on their results, increasing the Si/Al ratio seems to extend the catalyst lifetime by 87% and increase the number of C_4, C_5, and aromatics but decrease the amount of C_9+ hydrocarbons. The zeolite morphology is another factor that influences catalytic performance. Wang et al. [67] investigated the effect of zeolite morphology on the performance of the Zn-ZSM-5 zeolite in the conversion of methanol to aromatics. The Zn was incorporated into the zeolite in the form of different morphologies. The result shows that the morphology of the zeolite significantly affects the amount of BrØnsted and Lewis acid sites on the zeolite after impregnation and consequently on the overall performance of the catalyst in terms of conversion and selectivity towards aromatics. According to their findings, the catalytic activity of impregnated zeolite decreases in the order of catalyst morphologies: hollow > spherical > rod − shaped > coffin − shaped. Under typical reaction conditions (e.g., $T = 390 \circ C$, $P = 5$ bar, TOS: 12.5 h^{-1}, WHSV: 3.18 h^{-1}), the hollow structure showed the highest selectivity for aromatics during MTO process [67]. The review of zeolite catalyst for the conversion of low alcohols to hydrocarbons at varying process parameters is presented in Table 1.

The use of zeolites, highly porous crystallized minerals with pronounced catalytic activity and structural specificity, can improve adsorption/separation processes. With the discovery of amorphous aluminosilicates as Ni supports in ethylene oligomerization, Ni-doped zeolites have been recognized as viable alternatives for ethylene oligomerization. Among the transition metals for oligomerization, nickel's extensive and unusual reactivity with unsaturated chemicals has rendered it a huge breakthrough in olefin oligomerization, both in terms of research and commercial perspectives including heterogeneous and homogeneous catalytic processes. Nickel, unlike other metals predominant in oligomerization, including Ti and Cr, can be used for oligomerization of various olefins, including ethylene and the two traditionally difficult alkenes (propylene and butene), in terms of catalytic oligomerization. The microporous nickel zeolite catalysts (Ni-Y, Ni-Beta, and Ni-MCM-22) exhibited reasonable reactivity, while microporous and mesoporous solids such as Ni-Y and Ni/MCM-36 showed excellent performance with turnover frequencies, TOF = 10,500 h^{-1} and 16,000 h^{-1}, respectively. Ni-doped mesoporous MCM-41 and MCM-48 were the most effective catalysts with ethylene yields of 110 to 158 g.gcatal^{-1} h^{-1} and TOFs of 15,700 to 47,380 h^{-1} recorded in a batch process at 150°C and 35 bar [68, 69]. The oligomer's structure was influenced by the catalyst, the process technique, and conditions. Based on these indicators, the oligomerization of ethylene dimers (C_4) [70–72], intermediate olefins (C_6–C_{10}) ([73–77], or diesel range products can be controlled [78, 79]. These show that Ni doping can improve the catalytic performance of zeolite catalysts for effective olefin oligomerization. However, catalyst performance also depends on other operating parameters.

When it comes to selective oligomerization under moderate circumstances, nickel promotion is required, just as it is with amorphous aluminosilicates. The use of zeolites as prototype materials for discovering active Ni sites and kinetic or density functional theory research has been investigated. The application of bifunctional Ni–H–Beta for the oligomerization of olefins was investigated lately by Martínez et al. [78] and is an uncommon instance of this nanocrystalline zeolite being used for this purpose. Ion exchange or IWI of an industrial H-beta zeolite using a nickel nitrate precursor prepared the catalysts used in this study. The performance of the catalysts increases with nickel dosage up to a maximum of 2.5 wt.% before plateauing.

Table 1: Review on the application of zeolite catalyst for low alcohol conversion at different operating parameters.

Catalyst	Process	Catalyst synthesis methods	Operational Conditions	Results (%)			Inference	References
				X	S	Y		
Zr/HZSM-5	ETE	IM	$T = 450 \circ C$, $P = 1$ bar, $M_c = 0.2$ g	100	61	61	Addition of Zr to H-ZSM-5 zeolite results in an increase in the initial yield of C3+ olefins.	[160]
HZSM-5	ETP	COM	$T = 400 - 500 \circ$ C, $P = 1$ bar, $M_c = 0.2$ 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.	[161]
HZSM-5	ETE	HTM	$T = 450$ C, $P = 0.1$ bar, W/F = 0.01 – 0.4 g·min mL^{-1}	100	-	-	A process temperature above 300°C is required to produce C_5+ hydrocarbons, which correlate to the amount of gasoline generated.	[162]
HZSM-5	ETE	HTM	$T = 250 - 500 \circ$ C, $P = 0.5$ bar, $M_c = 0.3$ g, WHSV = 1 h^{-1}	100	100	100	There was a significant rise in the generation of ethene but a corresponding decline in the amounts of aromatics.	[163]
Fe/HZSM-5	ETE	IM	$T = 500 - 700$ C, $M_c = 0.2$ g	100	98	98	Metals, including Cr, Fe, and Ni, tend to be efficient for the synthesis of C3+ olefins and paraffin, which may be precursors to aromatics.	[32]
HZSM-5	ETE	COM	$T = 225 - 425 \circ$ 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.	[164]
HZSM-5	ETE	COM	$T = 350 \circ$ C, $P = 20$ bar, $M_c = 0.3$ 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.	[165]
HZSM-5	ETE	COM	$T = 350 \circ$ C, $P = 30$ bar, $M_c = 0.3$ 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.	[166]
HZSM-5	ETE	HTM	$T = 325 \circ C$, $P = 0.7$ 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.	[42]
ZSM-deSi	ETE	DST	$T = 200 \circ$ C, $P = 1$ bar, $M_c = 0.2$ 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.	[167]
HM90	ETE	COM	$T = 180 \circ$ C, $P = 1$ bar, W/F = 25 g · min mmol^{-1}	100	100	100	During dehydration, ethanol transformation and selectivity to C_2H_4 and $(C_2H_5)_2O$ remained nearly constant.	[168]
Fe/HZSM-5	ETE	IM	$T = 400 \circ$ C, $M_c = 0.2$ 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.	[169]

Table 1: Continued.

Catalyst	Process	Catalyst synthesis methods	Operational Conditions	Results (%)			Inference	References
				X	S	Y		
P-ZSM-5 (P/Al =0.5)	ETP	IM	$T = 550 \circ$ C, $P = 1$ bar, W/F = 0.01 g/cm^3 min^{-1}	100	31	31	The incorporation of P improved the hydrothermal stability of the ZSM-5, which in turn led to a considerable improvement in the catalyst's durability during the ethanol transformation.	[170]
Sc_2O_3-In_2O_3/Beta Zeolite	ETP	DEP	$T = 260 \circ$ C, $P = 1$ bar, $M_c = 0.8$ g, WHSV = 0.2 h^{-1}	100	52	52	The addition of Sc_2O_3 to In_2O_3/Beta improves the stability of the catalyst, owing to the prevention of the lowering of In_3+ to In_0 caused by Sc_2O_3 alteration.	[171]
HZSM-5	MTO(E+P)	COM	$T = 310 \circ$ C, WHSV = 7 h^{-1}, $P = 1.3$ bar, $M_c = 0.06$ g	5	18+33	-	Low methanol conversion can be attributed to low operating temperature.	[58]
HZSM-5	MTO(E+P)	COM	$T = 330 \circ$ C, WHSV = 7 h^{-1}, $P = 1.3$ bar, $M_c = 0.06$ g	52	14+30	-	Methanol conversion increases to 52% when the temperature is increased by 20°C (310 C).	[58]
HZSM-5	MTO(E+P)	COM	$T = 350 \circ$ C, WHSV = 7 h^{-1}, $P = 1.3$ bar, $M_c = 0.06$ g	73	10+30	-	Operating temperature affects methanol conversion and olefin yield.	[58]
HZSM-5	MTO(E+P)	COM	$T = 390 \circ$ C, WHSV = 7 h^{-1}, $P = 1.3$ bar, $M_c = 0.06$ g	91	5+35	-	Methanol conversion increases with an increase in temperature.	[58]
HZSM-5	MTH	HTM	$T = 380 \circ$ C, WHSV = 2 h^{-1}, $P = 10$ bar, $M_c = 1.40$ g	98	-	41	Methanol conversion and olefin yield increase with increasing temperature.	[53]
Hierarchical ZSM-5	MTH	HTM	$T = 350 \circ$ C, WHSV = 1.2 h^{-1}, $P = 11$ bar, $M_c = 0.7$ g	100	59	-	The hierarchical ZSM-5 zeolite exhibited less coke formation and deposition over a 24-hour period, significantly less than the conventional ZSM-5 zeolite.	[60]
ZSM-5/MCM-48	MTH	HTM	$T = 380 \circ$ C, WHSV = 1 h^{-1}, $P = 10$ bar, $M_c = 2$ g	97	-	42	The composite catalyst showed high performance and stability during the MTH reaction.	[53]
ZSM-5/MCM-48	MTH	HTM	$T = 420 \circ$ C, WHSV = 1 h^{-1}, $P = 10$ bar, $M_c = 2$ g	100	-	41	The catalyst results in increased methanol conversion at high temperature.	[53]

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: coprecipitation method; PM: precipitation nethod; IM: impregnation methods; DST: desilication treatment; DEP: deposition-precipitation. Results: X, S, and Y: conversion, selectivity, and yield, respectively. W/F and WHSV: space velocity; M_c: catalyst weight.

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 (Vmicro approx. 0.2 cm^3) was perceived during the examined parameters, even at reasonably significant ethylene transformations, including 60–80% at 10 hours TOS. However, it was not stated in the study whether the increased stability was due to the distinctive structural characteristics of Ni-H-Beta catalysts or modifications to the operating parameters. However, the same authors presented the idea of conducting a comparison assessment among these catalysts (industrial aluminosilicate (Siralox 30), mesoporous mesostructured Ni/Al-MCM-41, and nanocrystalline Ni–H–Beta) to evaluate their individual properties and performance at different operating conditions [80]. Moreover, when compared to other mesoporous MCM-41 support materials, the mesoporous Ni/Al-MCM-41 exhibits the highest efficiency under the same operational parameters as indicated above. Jan et al. [81] recently conducted a systematic investigation using a comparable Ni–Hβ catalyst in a continuous packed bed reactor. To prepare the catalyst used for this study, a $Ni(NO_3)_2$ solution was continuously dropped into a commercial zeolite (in the NH_4^- form, Si/Al = 25). In a long 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 catalytic activity which is low compared to the Ni–H–Beta catalysts [81, 82]. Table 2 shows a review of the ZSM-5 catalyst for olefin oligomerization.

2.2. 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 [83]. 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 AlPO4 and SAPO molecular sieves, the MeAPSO molecular sieves are somewhat inferior [84]. 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 [83]. Even the extreme silicon SAPOs have lower catalytic performance compared to zeolites such as USY, as reported by Martens et al. [85].

The study of ethanol transformation performed on SAPO-based catalysts (SAPO-34) at 500 °C recorded almost 100% conversion on all catalysts, as reported by Duan et al. [86]. 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 had a yield of 88% and 7% for C_2H_4 and C_3H_6, respectively [86]. 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 [44, 87, 88]. When compared to ZS-MM, the ZS-HS demonstrated significantly higher propylene yield as well as 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 [86].

The study by Wu et al. [89] on the effects of the SAPO-11 synthesis technique on ethanol dehydration to ethylene noted that the synthesize, 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 ethylene specificity of 99% and 96%, respectively [89]. According to the investigation's findings, the artificially produced SAPO-11 can compete favourably with the commercial type [89]. Similarly, the results of a study by Li et al. [90] showed the efficacy of the SAPO-based catalyst, SAPO-34, which recorded 9% higher ethanol conversion than ZSM-5 after 10 hours TOS. Futhermore, Potter et al. [91] reported that SAPO-5 and SAPO-34 frameworks could all convert ethanol to a significant extent; however, only the SAPO-34 catalysts efficiently catalyze 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 [91]. Compared to the SAPO-5 catalyst, which has larger pores, the SAPO-34 is a more effective catalyst due to its smaller pores. As a

Table 2: 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	[172]
Ethylene	Microsized HZSM-5 & nanosized HZSM-5	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}	With respect to activity (62.5% transformation) and deactivation resistance, nanosized HZSM-5 zeolites surpassed microsized HZSM-5 zeolites.	[173]
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	[172]
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	[172]
Propylene	Fentone-ZSM-5	T = 280 ∘ C, WHSV = 4.0 h^{-1}, P = 40 bar	C_5+	Propene conversion and diesel specificities were 98% and 92%, respectively	[174]
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	[172]
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	[172]
Propylene	Zr-ZSM-5	T = 260 ∘ C, P = 40 bar, WHSV = 1 h^{-1}	C_5+	Liquid yield of 88% and diesel selectivity of 61% was obtained	[175]
Ethylene	H-MCM-41/ZSM-S	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	[172]
Propylene	FeSO4-ZSM-5,	T = 280 ∘ C, WHSV = 4.0 h^{-1}, P = 40 bar	C_6+	98% propene conversion	[174]
Propylene	H2O2-ZSM-5	T = 280 ∘ C, WHSV = 4.0 h^{-1}, P = 40 bar	C_6+	97% propene conversion	[174]

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 [92].

The zeolite SAPO-34 proved to be more efficient in terms of specificity compared to ZSM-5 zeolite due to its smaller crystal size. Smaller crystal size resulted in less coke deposition during the methanol-to-olefin (MTO) process [93]. 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 [94], it can be inferred that the shape specificity of SAPO-34 has a significant impact on 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 [95, 96]. The use of 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 [97]. Using SAPO-34 and SAPO-5 catalysts with variable crystallite size, Hajfarajollah et al. [98] were able to investigate the effect of crystallite size on several parameters, including conversion, lifetime, and selectivity for 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) [98]. In addition, the hydrothermal synthesis conditions were found to have a significant effect on 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 the course of 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 [99]. In another study, Najafabadi et al. [100] 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 [101]. The review of SAPO-based catalysts for low alcohol conversion at varying process conditions is shown in Table 3.

2.3. Zirconia-Based Catalysts. Li et al. [102] describe ZrO_2 as a distinct mesoporous metal oxide with certain chemical characteristics (acid, base, and redox features) [103]. 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 [45]. Zirconia has demonstrated excellent performance in the ethanol dehydration process and has attracted much attention. Sato et al. [104] studied the effect of different catalysts (Cu/SiO_2, $Cu/Cu_2O/SiO_2$, and Cu/ZrO_2) on ethanol conversion into petrochemicals. All processes were carried out in a fixed bed reactor at $T = 473 - 548 \circ C$, $P = 1 - 10$ bar, and WHSV = 29.1 g_{cat}h/mo l_{EtOH}. It was found that the highest ethylene and acetaldehyde selectivities of 17% and 54%, respectively, with the highest conversion of ethanol (57%) were recorded at 498°C over Cu-modified zirconia. Acetaldehyde was the most abundant product generated in this experiment. When heated to 523°C, the Cu_2O/SiO_2 catalyst yielded acetaldehyde with complete selectivity and just 15% ethanol conversion [104]. Moreover, Phung et al. [105] studied the catalytic performance of some catalysts in ethanol conversion, including $MgO–Al_2O_3$, SiO_2, ZrO_2, TiO_2, Al_2O_3, $WO_3/MgO–Al_2O_3$, 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 $P = 1$ bar and $T = 150 - 500 \circ C$. It was observed that ethylene production improved to 99% with the WO_3/ZrO_2 catalyst at 350°C while the commercial WO_3/TiO_2 catalyst demonstrated a 93% ethylene production at 250°C. The generation of DEE plateaued at 150°C and then began to decline with a subsequent increase in temperature. Ethanol conversion on metal oxides occurred in the following order: $Al_2O_3 > TiO_2 > ZrO_2 > MgO - Al_2O_3 > SiO_2$. 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°C, which was the lowest temperature tested. Compared to the study of Sato et al. [104], Phung et al. [105] recorded considerable ethylene production due to the promotion of ZrO_2 with WO_3. Furthermore, the findings from Phung et al. [105] 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. [106] employed a coprecipitation approach to prepare a yttrium-modified zirconia catalyst. The operating parameters for ethanol conversion in a fluidized bed reactor were $T = 550 \circ C$, $P = 11.1$ bar, W/F = 0.05 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 5 wt.% Y. The production of propylene 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 [106]. Wang et al. [107] synthesized a Y-doped

Table 3: Review of SAPO-based catalyst for low alcohol conversion.

Catalyst	Process	Catalyst synthesis methods	Operational conditions	Results (%)			Inference	References
				X	S	Y		
SA (SAPO-34)	MTO (E+P)	DGC	$T = 450 \circ$ C, $P = 0.169$ bar, $M_c = 0.05$ g, W/F = 5 ghmol^{-1}, TOS = 40 mins	100	39 + 41	-	Coke formation led to the degradation of SAPO-34 catalyst	[176]
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) affects 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 treated SAPO-34 catalyst inhibited coke deposition	
NiAPSO-34	MTE	RCM	$T = 450 \circ$ C; GHSV = 1000 h^{-1}, $M_c = 0.325$ g, TOS = 1 hr	97	72		Compared to the other catalysts, the Ni-doped SAPO-34 showed the highest ethylene selectivity at 450°C	[177]
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 decreased in amount of acid site and particle size	
SAPO-34	MTE	RCM		100	59	-	Ethylene selectivity decreased with increase in TOS	
SAPO-34	ETE	HTM	T =400°C, WHSV = 3.5 h^{-1}, $M_c = 0.5$ g, TOS = 600 min	92	52	-	Lower conversion and selectivity than modified catalyst	
Cr/SAPO-34	ETE	IM		98	99	-	Improved ethylene selectivity compared unmodified SAPO-34 catalyst	
Co-Cr/SAPO-34	ETE	IM		100	100	-	Co-Cr loading provides suitable pore structure and moderate acid-base properties, resulting in increased catalytic performance.	
SAPO-11	ETE	HTM	$T = 340 \circ i$, 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	[178]
Mn/SAPO-11	ETE	HTM & IM		92	77	-		
Zn/SAPO-11	ETE	HTM & IM		87	69			

Table 3: Continued.

Catalyst	Process	Catalyst synthesis methods	Operational conditions	Results (%)			Inference	References
				X	S	Y		
HZSM-5/SAPO-34 (*Si/Al*.25:1 *wt*)	ETO (E + P)	HTM & MM	$T = 400 \circ$ C, $P = 1$ bar, $M_c = 0.5$ g	100	-	88 + 7	Synergistic catalysis of HZSM-5 and SAPO-35 occurred in HZSM-5/SAPO-35 catalyst. However, performance and olefin yield was affected by synthesis method and composition of HZSM-5/SAPO-35.	[21]
HZSM-5/SAPO-34 (*Si/Al*.25:4 *wt*.)	ETO (E + P)	HTM & MM		100	-	24 + 35		
HZSM-5/SAPO-34 (*Si/Al*.38:4 *wt*)	ETO (E +P)	HTM & MM		100	-	26 + 34		

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, and Y: conversion, selectivity, and yield, respectively. GHSV and WHSV: gas and weight hourly space velocity; W/F: catalyst weight/flowrate; M_c: catalyst weight.

zirconia catalyst for ethanol to propylene transformation by coprecipitation procedure with varied Y contents. This experiment was performed in a fluidized bed reactor with operating conditions similar to Xia et al. [106]. 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 ZrO2 leads to a decline in ethylene yield with increased propylene synthesis [107].

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 [108–110]. As a result of this modification, the SAPO-34 samples incorporated with metal often showed improved catalytic activity and longer lifetime [109]. 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°C and atmospheric pressure by Ali Zeinali et al. [108]. 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 the addition of Zr to SAPO-34 through the process of isomorphous substitution can potentially extend the catalytic lifetime of SAPO-34 in the MTO process. The weight losses that occurred due to the combustion of coke in SAPO-34, ZrAPSO-34, and Zr/SAPO-34 were about 15.91, 13.66, and 12.82%, respectively [108]. According to these results, the amount of coke formed on the Zr-doped SAPO-34 catalysts was lower than that formed 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 the rate of 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 [111]. The review of zirconia-based catalyst for low alcohol conversion at varying process conditions is shown in Table 4.

2.4. Alumina and Silica-Alumina Catalysts. The elevated internal surface area of 50–300 m^2g^{-1} of alumina catalyst and its excellent stability to thermal processing at 600°C make alumina catalyst a commercially essential catalyst [112, 113]. Unimolecular and bimolecular approaches to lower olefins are available for dehydration of alcohols, including ethanol over an Al_2O_3 catalyst [114], 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. [115]. The transformation of ethanol was conducted in a fixed bed catalytic reactor at 350°C and $P = 5$ 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 C_4-C_{10} alkanes as reported by Yandieva et al. [115]. Furthermore, contrary to Yandieva et al. [115], DeWilde et al.[116] demonstrated that ethanol dehydrates when it reacts with alumina at lower temperatures and pressure. The reaction which was performed at $T = 215 \circ C$ in a quartz tube-packed bed reactor recorded with 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°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 [116]. It can be deduced that Pt/alumina catalyst was not effective at high temperature 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. [117] 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 [117].

In the process of oligomerization, amorphous silica-aluminas (ASA) have been used for decades as acidic solid catalysts. This is primarily because, at elevated temperatures, these substances are more stable than acid resins or SPA and can be regenerated by using carbon burn [118, 119]. 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 process of oligomerization [120]. However, operating in the liquid phase at considerable temperatures (150 to 250°C), it is possible to achieve long run times of many months before renewal is required. de Klerk [118] 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, NH_3, and H_2S [121, 122]. 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

Table 4: Review of zirconia-based catalyst for low alcohol conversion.

Catalyst	Process	Catalyst synthesis methods	Operational conditions	Results (%)			Inference	References
				X	S	Y		
$Zr_{0.05}$APSO-34	MTO (E + P)	HTM	$T = 400 \circ$ 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	[179]
Sulfated Zr (S-Zr)	MTO (E + P)	PIM	$T = 160 \circ$ C, $M_c = 2$ g	41	94 + 0	-	Formation of C_3H_6 requires the participation of a third carbon atom (*-CH_X) which is not offered by S-Zr catalyst. (*: surface site)	[180]
Si-doped S/Zr	MTO (E + P)	PIM	$T = 160 \circ$ 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	$T = 450 \circ$ 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, which can be ascribed to the increased presence of strong acid sites.	[181]
La-ZrO_2	ETP	CPM	$T = 450 \circ$ 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/ZrO2 catalysts can be attributed to the coordination of redox and acid-base characteristics.	[182]
ZrO_2	ETP	PM	$T = 450 \circ$ C, $P = 11.1$ bar, $M_c = 0.7$ g , W/F = 0.01 − 0.08 g · min mL^{-1}	98	36	35	ZrO2 improved the efficiency of ETP conversion.	[45]
Y-ZrO_2	ETP	CPM	$T = 450 \circ$ 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.	[106]
Y-ZrO_2	ETP	CPM	$T = 450 \circ$ 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.	[107]
WO_3-ZrO_2	ETE	IM	$T = 500 \circ$ 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.	[105]
Cu_2O-ZrO_2	ETE	IM	$T = 200 - 275 \circ$ C, $P = 1$ bar, W/F = 29g · 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.	[104]
HPW-$Ce_{0.8}Zr_{0.2}O_2$	ETE	IM	$T = 300 \circ$ C, WHSV = 17 h^{-1}	100	100	100	Catalysts have been shown to produce less coke deposit and have a longer lifespan.	[183]

Table 4: Continued.

Catalyst	Process	Catalyst synthesis methods	Operational conditions	Results (%)			Inference	References
				X	S	Y		
MoO_3-ZrO_2	ETE	IM	$T = 380 \circ C$	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}.	[184]
SiO_2-ZrO_2	ETE	IM	$T = 380 \circ C$, $P = 11.1$ bar	100	96	96	The incorporation of Si leads to a considerable increase in the surface area as well as the total number of acidic sites.	[185]

Processes: ETE: ethanol to ethylene; ETP: ethanol to propylene; MTO (E + P): methanol to olefin (ethylene and propylene). Catalyst synthesis methods: CPM: coprecipitation method; PM: precipitation method; IM: impregnation method; HTM: hydrothermal method; PIM: precipitation-impregnation method. Results: X, S, and Y: conversion, selectivity, and yield, respectively. W/F and WHSV: space velocity; M_c: catalyst weight.

and 30) [118, 123]. The blended octane values of olefins obtained by these procedures are exceptionally high [124, 125], and the research octane number (RON) of olefins achieved by these methods is usually in the range of 92–94 [119]. 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 the combination of alumina (as a binder) with ZSM-5 zeolite can increase the amount of DME produced from methanol [126]. 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 [127]. 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 [128]. 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, the use of zeolite on alumina resulted in a decrease in both the micropore area and surface area of BET compared to pure ZSM-5 [127]. 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 particular case, water prevents methanol from being consumed by the catalyst because its adsorption on the surface of the catalyst competes with that of methanol [129]. 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. [126]. 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 [126]. The review of alumina-based catalysts for low alcohol conversion at varying process parameters is presented in Table 5.

3. Challenges in the Catalytic Conversion Processes

3.1. The Influence of Low Alcohol Water Content on the Catalytic Conversion Process. Numerous studies [130–132] have shown that water and pollutants that may be present in lower alcohols can affect the efficiency and stability of catalysts in the conversion of bioalcohols to hydrocarbons. When employing bioethanol (10 wt.% ethanol in water) as a feedstock, it was shown that water considerably influenced the ethanol conversion over alumina catalysts. The study by Kochar and AS [133] reported that high water concentrations significantly slowed ethanol transformation efficiency. The researchers recorded a 21% decrease in the initial ethanol conversion efficiency at $T = 380 \circ C$ with an 85 wt.% increase in water content over TiO_2/-Al_2O_3; however, the specificity of DEE improved at the cost of ethylene conversion. Moreover, the application of extremely high temperatures (>420°C) can potentially eliminate water's influence. In addition, some catalysts, including alumina-based catalysts, are often operated at high temperatures (>400°C) [134, 135], if the bioethanol water concentration is high to prevent the generation of DEE and increase ethylene production [133, 134, 136].

Zeolite catalysts (H-ZSM-5) have a peculiar pore structure and acidic characteristic that make them viable catalysts for transforming ethanol into gasoline. However, coke formation (which prevents the entry of active sites) and dealumination, on the other hand, trigger the immediate deactivation (i.e., reduction in acidity) of H-ZSM-5. There is a convoluted relationship between catalyst deactivation and water content during the catalytic process. The hydration of BrØnsted acid sites reduces the acidic strength of the catalyst. However, during the generation of coke, water and coke precursors compete for adsorption on the acid sites; hence, water has the potential to inhibit coke formation even at temperatures that are relatively low [137]. However, the dealumination of zeolites can occur in the presence of water at $T > 450 \circ C$, leading to a significant decrease in the number of active sites on the catalyst [138, 139]. 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 and the introduction of metal promoters, especially for catalysts with great specificity and hydrothermal stability at tolerable temperatures [130].

3.2. Catalyst Deactivation of Carbon and Coke Deposition onto the Catalyst Surface. In catalytic processes, there is the deposition of various components on the surface of the catalyst, which results in catalyst deactivation and a reduction in catalytic performance due to clogging of sites and pores on the catalyst. The sintering process is the most critical component in catalyst deactivation. Catalyst deactivation is characterized by a considerable reduction in the active surface area. 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. A fouling activity 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 recently garnered considerable awareness. It should be noted that the perception of carbon and coke deposition is relatively ambiguous

Table 5: Review of alumina catalyst for low alcohol conversion to olefins.

Catalyst	Process	Operational condition	Results (%)			Inference	References
			X	S	Y		
γ-χ Al_2O_3/B (M-Al-B)	ETE	$T = 400 \circ C$, $P = 1$ bar, $M_c = 0.05$ g,	100	92	92	Increasing temperatures, from 200 to 400°C, led to a surge in ethanol transformation.	[186]
CS2/AMA	ETE	$T = 400 \circ C$, $P = 1$ bar	94	93	88	The catalyst boosts the catalytic performance, increasing the amount of ethylene produced.	[187]
ZAl (alumina-based ZSM-5)	MTH	$T = 350 \circ C$, TOS = 10 h, WSHV = 2.55 h^{-1}	100	73	-	P in the binder for increased specificity of C_2-C_4 olefins, especially C_3H_6. HC yield improved up to a P/Al value of 0.8 and then decreased at 1.2.	[188]
ZAlPO (P/Al = 0.4)	MTH		100	77	-		
ZAlPO (P/Al=0.6)	MTH		100	83	-		
ZAlPO (P/Al = 0.8)	MTH		100	85	-		
ZAlPO (P/Al = 1.0)	MTH		100	83	-		
ZAlPO (P/Al = 1.2)	MTH		98	74	-		
PTH	ETE	$T = 500 \circ C$, $P = 1$ 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.	[189]
γ-Al_2O_3	ETE	$T = 215 \circ C$, $P = 0.02$ 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	[116]
H-USY zeolite	ETE	$T = 350 \circ C$, $P = 1$ 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	[190]
Pt/γ-Al_2O_3	ETE	$T = 250 \circ C$, $P = 8$ bar	60	50	30	Ethylene may go through oligomerization at acid sites, eventually leading to the predominance of the synthesis of normal alkanes.	[115]
Al-SV	ETE	$T = 350 \circ C$, $P = 1$ 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 ratio of weak to strong acid strength.	[117]
Al_2O_3	ETE	$T = 450 \circ C$, $P = 1$ bar	99	90	89	With an increase in temperature, ethylene specificity improved for all the evaluated catalysts.	[191]
γ-Al_2O_3	ETE	$T = 450 \circ C$, $P = 0.005$	100	97	97	At $T = 350 - 450 \circ C$, the catalyst was effective in the specific ethanol conversion to ethylene.	[192]

Processes: ETE: ethanol to ethylene; ETP: ethanol to propylene; MTH: methanol to hydrocarbons.

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 a distinctive 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 [140].

Much research on ethylene oligomerization has looked at catalyst deactivation (a serious concern in heterogeneous catalysis). Catalyst deactivation is due to pore blockage by heavy hydrocarbons and significant product adsorption on active sites. As a result, the pore size and process conditions influence the catalyst deactivation and lifespan. For instance, microporous nickel–modified zeolites (Ni–Y and Ni–MCM-22) experienced increased deactivation during conversion [74, 76]. It was reported that at a process temperature of 50 and 70°C, NiY lost around half of its initial reactivity after 120–180 mins TOS while the Ni–Beta nanocrystalline zeolite with a substantial exterior surface area was an exception [78]. Under process parameters (120°C and 35 bar), this catalyst, Ni–Beta, showed no evidence of deactivation. Catalysts having mesopores, including nickel–amorphous silica-alumina, nickel–mesostructured silica-alumina, and nickel-sulphated alumina, on the other hand, demonstrated extremely strong deactivation resistance. The degree of catalyst deactivation (around 50 and 70% during 100-hour TOS) was unaffected by the WHSV, although it improved with pressure and temperature. According to Scurrell [77], Ni-exchanged silica-alumina showed just a slight deactivation under more extreme situations (35 bar and 120–180°C) during 900-hour TOS tests [77]. 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 3.5 MPa for 170-hour TOS according to Lallemand et al. [141].

3.3. 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 [142]. Zeolites take centre stage in this discussion since they are used in many acid-catalyzed processes. Another fundamental aspect that makes catalyst recovery a difficult task is that in catalytic processes, the bonds between metal and ligand are frequently broken and reestablished. 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 in conjunction with a continuous flow of liquid, the "leaching" process causes the catalyst to lose its activity [143]. However, when the catalyst was embedded inside the pores of zeolites or mesoporous materials, there was a significant reduction in leaching. Despite these benefits, reactions in which ultrafiltration has been performed have, in most cases, demonstrated a decline in activity following recycling [144].

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. It is possible that the catalyst, solvent, or procedure are highly costly, that the leaching rate of the catalyst is too high, that the cost of the solvent or ligand is exorbitant, or that 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 fluorous and ionic liquids) have on the surrounding environment are not yet fully understood [143].

3.4. 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 bimetallic 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) [31], accompanied by zeolites having additional transition metals (especially Ti or Fe in little quantity) in place of Al in their framework or sometimes extraframework positions (Cu-zeolites). Despite recent advances, basic-type zeolites [145] and also bigger pore zeolites and mesoporous materials have restricted uses. Zeotype materials, such as silicoaluminaphosphate (SAPO) [146], 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 [84]. 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 [147]. 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 are 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 synthesized with OSDAs. However, the cost and inability to recycle OSDAs due to the postsynthesis calcination required to remove the entrapped molecules are highly costly and limit their broader application in commercial settings [148]. 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 [149].

4. 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 increases in 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 the fabrication of a diverse variety of commodity chemicals. In a wide range of methods, liquid fuel can be produced by utilizing fundamental and applied techniques that are now readily available commercially. To design both financially sustainable and promising approaches when commercializing, 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 themselves, it is more about problem-solving for low-cost approaches than the mechanism itself. It is necessary to adopt 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. 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 [150]. Due to the intrinsic restrictions of applying low-energy-density biomass and the sophisticated nature of the transformation procedure into alcohol fuels, the actual cost of plant construction proves to be prohibitively high. Furthermore, the climates and soils of a large portion of Africa are strikingly comparable to Brazil's [151]. 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 et al.'s early discoveries [152]. 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 centre on addressing the following questions and concerns which include but are not limited to: (i) Does oligomerization with a catalyst that has both a 10MR and a 12MR route yields 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 unidimensional zeolite's product? These problems require attention, generally involving shape selection, but which will almost always necessitate material identification before they can be answered. The capacity to evaluate the product generated by the new acid catalyst has been a bottleneck in the establishment of 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 C_8 fractions. Since these data are sometimes unavailable for the C_9 and C_{10} hydrocarbons, it is assumed that the product distribution of the C_9 and C_{10} fractions is identical to the C_8. This may be valid for a specific catalyst, or it may begin to disintegrate, as Exxon investigators have reported for some catalysts like MFI [153]. 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 need to be considered and tackled correctly. Catalysts are highly efficient when it comes to 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. At the moment, an activated Al_2O_3-based catalyst is the most commonly used catalyst in the industrial plant for low alcohol conversion, such as ethanol to ethylene. Moreover, some by-products 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 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 is still 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 to facilitate the development of a catalytic low-alcohol conversion system and to offer robust assistance for the market competitiveness of the overall process. This will necessitate more systematic research to fine-tune the coexisting 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 which should 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 [154]. 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 the enhancement of the reactor, process simulation, and optimization, among other operating conditions.

Separation of the organic products and recovery of the catalyst 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 is different for the catalyst and the organic product, is another possible approach to enhance product separation and catalyst recovery. In this case, structural adjustments often need to be made to the catalyst [155]. 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. In an effort to restore the lost catalytic performance of zeolite, an oxidation regeneration strategy has been employed by burning coke at elevated temperatures in the air [156–158]. To prevent the irreversible loss of acidity, the temperature at which the catalysts are regenerated should not be higher than the temperature 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 [156]. However, Valle et al. [157] noted that the regenerated Ni/HZSM-5 catalysts retained similar activities for a total of 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 [159]. 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 [158]. The stability of the catalyst may be due to the fact that some metal species catalyzed the oligomerization of intermediates. This was done by promoting the migration of hydrogen atoms through C-H activation. These intermediates prevent coke from forming on the catalyst's surface during the reaction [158].

Ionic liquids (IL) have only recently been proposed as an alternative method for separating and recycling spent catalysts [155]. In these solvents, catalysts with polar or ionic behaviour can be immobilised so that they can 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 [155]. Therefore, the existing catalyst system needs to be further developed to achieve the more significant preferential activity, extended durability, and flexible regeneration properties and procedures without substantial loss of activity before testing in a commercial-scale biofuel production plant can be completed [159]. 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.

5. Conclusion

Due to the dwindling supply of fossil fuels and the increasing accessibility of low-alcohol conversion technologies in recent years, low alcohols have become a fundamental feedstock for the synthesis of fuels and petrochemicals. It is expected that diversification of biomass feedstocks and improvement in the efficiency of low alcohol production will lead to the synthesis of abundant, comparatively cost-effective low alcohol that can produce a wide range of value-added chemicals. Moreover, the decision on the potential products is usually based on the local market and the timely assessment of their long-term profitability. Due to the limitations of low alcohols as a viable transportation fuel, catalytic conversion offers the potential to transform low alcohol into gasoline equivalents and speciality chemicals. Because low alcohol contains a significant amount of water, extreme caution must be exercised when considering the effects water may have on the framework and activity of catalysts and other processes that rely on catalysis.

Research and development work on the modification of aluminosilicates from amorphous to microporous/mesoporous zeolites and then to mesoporous aluminosilicates have provided important information on the fundamental factors governing performance and stability in low alcohol conversion. For the effective transformation of low alcohol to fuels and petrochemicals, some critical parameters are acidity, average pore size, porosity distribution, and precursor-to-acid site ratio. Mesoporous materials offer a promising remedy in prospective industrialization potential: a workable balance between efficiency and stability. This is due to the flexibility of siliceous material synthesis employing various alumination techniques. As a result, amorphous aluminosilicates (such as zeolites) and more recently mesoporous and mesostructured aluminosilicates have shown significant performance in catalytic conversion processes and as supports for metal oxides such as nickel and zirconium oxide in the conversion of low alcohols. The unique pore structure and acidic character of the ZSM-5 zeolite catalyst make it one of the most desirable 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. Coke formation and dealumination trigger the readily deactivation of ZSM-5. Furthermore, alumina-based catalysts have lower acidity, and they usually exhibit mesoporosity. In this regard, there has been increased academic and industrial interest in developing viable and stable catalysts for the effective transformation of low alcohol to fuels and petrochemicals.

Although extensive research has been conducted to improve low alcohol conversion, selectivity toward a preferred product, and catalyst stability, additional studies on the correlations between the catalyst framework/activity and the appropriate process conditions are considered necessary to logically design catalysts and effectively valorize low alcohols into fuels and petrochemicals. In addition, the economic consequences of valorizing low alcohols compared to alternative synthetic routes need to be studied and evaluated to facilitate the commercialization of the newly developed low alcohol conversion processes.

Data Availability

The data are available upon request from the authors.

Conflicts of Interest

All authors declare that they have no conflicts of interest.

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