



Synthesis and Performance Evaluation of Co/H-ZSM-5 Bi-functional Catalyst for Fischer-Tropsch Synthesis

MSc Dissertation

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ABSTRACT

The motivation behind this study is the need to manage and reduce wastes, in particular waste tyre and biomass, while in turn recovering energy from these carbonaceous materials. These wastes were gasified to produce synthetic gas which served as a feed to the Fischer-Tropsch Synthesis process to produce hydrocarbons. The formed hydrocarbons can be used as fuels for different purpose like transportation, domestic and industrial heating systems. Cobalt supported on zeolite catalysts are used because of their high acidic sites present in the zeolite that can break the Anderson-Schultz-Flory polymerization kinetics and also because cobalt-based catalysts are preferred for low temperature Fischer-Tropsch (LTFT) synthesis process due to their negligible water and carbon dioxide formation as well as stability and life span.

In this research, a bi-functional Co/H-ZSM-5 catalyst was synthesized, characterized and evaluated for direct production of hydrocarbons at different process conditions. The bi-functional catalyst was prepared by incipient wetness impregnation method of an aqueous cobalt solution as the source of cobalt metal onto an H-ZSM-5 zeolite support, thereafter dried at 120 °C and calcined at 400 °C to obtain the finished Co/H-ZSM-5 catalyst. Physicochemical analyses performed included, Nitrogen Physisorption at 77 K to determine the surface area, pore volume and size of the synthesized catalyst. Also the N₂ adsorption was used to determine the adsorptive properties of the catalyst. X-ray diffraction at 2θ region between 10 to 90 ° by using Co-Kα radiation ($\lambda=1.79026 \text{ \AA}$) was used to determine the material crystallinity, structure and composition. For the morphology and elemental composition of the catalyst, a Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Spectroscopy was used. Thermal stability of the catalyst was checked using a Thermal Gravimetric Analyzer to determine how the catalyst degraded with time when temperature was increased uniformly. Reducibility of the catalyst was determined by using Temperature Programmed Reduction equipment in a hydrogen environment from room temperature to 900 °C. Transmission Electron Microscopy was used to check the catalyst morphology, and the dispersion of the metal-oxide particles within the catalyst support.

The bi-functional zeolite supported catalyst was found to possess a surface area of 292 m²/g, pore volume of 0.18 cm³/g and pore size of 2.83 nm. The catalyst morphology was found to be irregular and aggregated-circular shape with a particle size of about 2.5 ± 0.5 μm. The embedded

cobalt-oxide particles were obtained to be about 8 ± 3 nm located closer to the surface of the support and were reduced to metallic cobalt of 25% composition, at 330 °C in a hydrogen rich environment with an expected hydrogen consumption of 133 %.

The process conditions under study involved flow rate, pressure and temperature and synthetic gas of different H₂/CO ratio. The Synthetic gas mixture was purchased from Afrox and prepared in a way to mimic or simulate the syngas mixture expected from gasification of the waste tyre and biomass. However the study mainly focused on Hydrogen, Carbon Monoxide and Carbon dioxide as the dominant constituents of a waste tyre produced syngas. The bi-functional, Co/H-ZSM-5 performance evaluation was compared to commercial Co/SiO₂ catalyst under similar conditions. The performance evaluation and comparison was made based on conversion and selectivity at different conditions. The process conditions considered were a flow rate of 1200, 2400 and 3600 GHSV (ml/gcat.hr), a pressure of 2, 8 and 15 bar, Low Temperature Fischer-Tropsch (LTFT) process at 220 and 250 °C was used, with a syngas composition that included H₂/CO ratio of 1.5, 2.5 and 2.5 with 5 % of CO₂ present in the reactant feed.

The combination of 2 bar, 1200 GHSV and temperature of 220 °C and 1.5 of ratio was considered as low process conditions. While the combination of 15 bar, 1200 GHSV, 250 °C and ratio of 2.5 was considered as high process condition. Three pre-calibrated GCs (two online and one offline) were used to analyze the reaction products and the feed and the integrated peak-data analyses was captured by the use of a Data Apex Chromatograph software package known as Clarity ® (v. 2.5). The captured and analyzed data was used to calculate conversion and selectivity according to the methods reported in literature.

With regard to the effect of process conditions, at low process conditions, the bi-functional catalyst, Co/H-ZSM-5, resulted in a 3 % CO conversion, while the commercial Co/SiO₂ catalyst, resulted in 15 % of CO conversion. However the bi-functional catalyst was more selective to gasoline range products and 16 % selectivity to C₅ hydrocarbons was obtained and 79 % to C₆₊, as compared to selectivities of 4 and 75 % for C₅ and C₆₊ respectively, for Co/SiO₂ catalyst. Also Co/SiO₂ was found to be more selective to Olefins, the undesired products, with a selectivity of about 91 % to C₆₊ hydrocarbons as compared to a selectivity of 87 % for C₆₊ hydrocarbon obtained by using the bi-functional Co/H-ZSM-5 catalyst. Methane production was high for the Co/SiO₂ catalyzed reaction, (about 13 % selectivity) with some quantity of water produced, as

compared to 3 % methane selectivity for Co/H-ZSM-5 catalyst with no water produced during the reaction. At low process condition, both catalysts were less prone to middle distillates hydrocarbon production.

At high process conditions, a CO conversion of about 54 and 68 % was obtained by Co/H-ZSM-5 and Co/SiO₂ catalyst respectively. At these conditions the H-ZSM-5 supported catalyst was observed to produce more methane, about 53 % selectivity while for Co/SiO₂ catalyst it was obtained to be 35 % selective to methane, with 66 and 7 % of C₆₊ olefin and paraffin selectivity respectively. Co/H-ZSM-5 offered 9 % selectivity to C₆₊ per olefin and paraffin hydrocarbons. The commercial catalyst showed an orderly manner of distributing products at these conditions while the bi-functional catalyst randomly distributed the formed products with a high selectivity to middle olefin distillates.

In terms of CO₂ co-feeding in the reactant feed, both CO and CO₂ were hydrogenated to hydrocarbons. A CO conversion of about 73 % was obtained by Co/H-ZSM-5 catalyzed reaction while for Co/SiO₂ catalyzed reaction a conversion of 70 % was obtained. About 63 and 75 % of CO₂ conversion was obtained by H-ZSM-5 and SiO₂ supported catalyst. These results were obtained at high process conditions. No change in paraffin selectivity was observed when comparing a state in which CO₂ was present and absent, however olefin selectivity is significantly affected by the presence of CO₂. Thus, an increase in olefin selectivity is observed with Co/SiO₂, achieving 76 % of C₆₊ Olefin from 66 % and Co/H-ZSM-5 increasing middle olefin distilled from 25 to about 30 % of selectivity.

Based on the performance evaluation the bi-functional catalyst was proven to yield higher hydrocarbons from a simulated waste-tyre synthetic gas with no requirement of downstream hydrocracking, since the bi-functional catalyst cut-off higher hydrocarbons due to its acidic sites. While the metallic sites of the catalyst, catalyzes the reaction of synthetic gas to hydrocarbons. This type of catalyst with both metallic sites and acidic sites is a hybrid-catalyst commonly known as bi-functional catalyst (Kang *et al.*, 2014).

At low process conditions the bi-functional Co/H-ZSM-5 catalyst is found to be more preferred while at higher process conditions the commercial catalyst was found to be more preferred,

however in the presence of CO₂ co-feeding, either catalyst can be used, but if water elimination is required the bi-functional catalyst is more suitable for the process.