CATALYTIC CONVERSION OF SYNTHESIS GAS TO FUEL OVER Cu-K PROMOTED AND SiO_2/Al_2O_3 SUPPORTED Fe CATALYSTS

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by

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Submitted in fulfillment of

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DEDICATED

TO

MY BELOVED FAMILY

CERTIFICATE

This is to certify that the thesis entitled, **"CATALYTIC CONVERSION OF SYNTHESIS GAS TO FUEL OVER Cu-K PROMOTED AND SiO_2/Al_2O_3 SUPPORTED Fe CATALYSTS"** being submitted by **Mr. Satyen Kumar Das** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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(Satyen Kumar Das)

ABSTRACT

Fischer–Tropsch synthesis (FTS) for converting syngas to hydrocarbons is receiving renewed attention, driven by the global need to convert non-petroleum based energy resources into gaseous & liquid fuels, waxes and chemicals. It is well recognized that the research and the development of catalysts play a vital role in all process of catalysis reaction. In the present investigation, different K and Cu promoted Fe/SiO_2 and Fe/Al_2O_3 catalyst formulations were prepared by varying Fe/Cu/K loading using a combination of co-precipitation and impregnation techniques. The characterization of fresh, reduced and spent catalysts was performed to identify their textural properties, surface morphologies and chemisorptions properties. The characterization was done by inductively coupled plasma analyzer, N_2 adsorption/desorption isotherm, BET surface area, pore volume, BJH pore size distribution measurements, temperature programmed reduction, H_2-chemisorptions, NH_3-temperature programmed desorption, X-ray diffraction; fourier transform infrared spectroscopy, thermogravimetric analysis, carbon hydrogen nitrogen sulphur analyzer, scanning electron microscope, energy dispersive X-ray (quantity & X-ray mapping), transmission electron microscopy techniques. The initial FT synthesis experiments were designed to evaluate each catalyst under fixed and representative conditions from which the most promising catalyst was selected for further study. Their catalytic performance of each catalyst was compared. The screening tests were carried out in a fixed bed reactor. Before screening test, each catalyst was reduced in situ with a flow of high purity hydrogen at $220^{O}C$ for 6 h under atmospheric pressure. The flow rate of H_2 was maintained at 200 ml/g Fe /min in the fresh catalysts. Screening test of each catalyst was carried out at temperature of $245^{o}C$, pressure of 15 bar at space velocity of syngas, 33 ml/g cat/min. and H_2/CO inlet molar ratio = 2:1. Effects of metal loading, support, promoter on carbon monoxide conversion, product selectivity (distribution) were studied. The results of the various characterization techniques were used to relate the observed catalytic performance and stability to the catalyst property. The catalytic activity during FTS for SiO_2 support is higher than Al_2O_3, because of higher degree of reduction. Water gas shift activity of SiO_2 supported catalyst is lower than Al_2O_3 supported catalyst due to decreased Fe/K contact owing to the high catalyst surface area of silica supported catalyst. Branched hydrocarbon, olefin and the aromatic content in liquid products, in the presence of Al_2O_3 is higher due to higher acidity of Al_2O_3 supported catalyst. It has been observed that incorporation of K to Fe/SiO_2 catalyst resulted in enhancement of metallic active sites due to higher dispersion. Incorporation of K and Cu favors the reducibility of the catalyst. Increase in active components (Cu-K) in catalyst had a diminishing effect of surface acidity. Also higher K loading had diminishing effect on textural properties. Increasing silica content, the metal support interaction increased.

During FTS, the CO conversion increased significantly with an increase in potassium loading up to 1 wt.% and passed through the maximum at the potassium loading near to 1 wt.%. Further increasing or decreasing potassium loading, a monotonic decline in catalyst activity is observed. Catalyst with ~1% K loading shows the uppermost CO conversion (56.3 wt%). Water Gas Shift activity increased with increase in K loading in the catalyst. The selectivity of C_5+ hydrocarbons increased and lighter hydrocarbons (methane & C_2-C_4) decreased with increase in K-content as well as decrease in silica content in the catalyst. Also increasing K content in the catalyst, olefin selectivity increased and olefin isomerization activity decreased. Catalyst with higher K content showed higher carbon range products as compared to less K promoted catalysts. Higher K content in the catalyst increases the secondary reaction due to which coke on spent catalyst as well as olefinicity nature of coke increased. Increasing K loading, decrease in acidity of the catalysts, increases immovable coke on the spent catalyst. Based on the above studies, silica supported catalyst with 1% K loading (Catalyst Cat-1K, Fe/Cu/K, wt%: 35.5/3/1) was selected for parameter study.

Parameter studies were conducted in a fixed bed reactor with mixture of H_2 and CO in a temperature range from 215 to 245^{O}C, the pressure range of 5-25 bar, the space velocity range of 1000-4000 cc/g cat/h and a H_2/CO feed ratio of 0.7/1–3/1 (mol/mol) to investigate the influence of the above process parameters on the performance of selected Cu-K promoted silica supported Fe based catalyst in terms of its %CO conversion, product selectivity, rate, liquid hydrocarbon product distribution and composition.

Increasing reaction temperature from 215^{o}C to 245^{o}C, higher yields of once-through hydrocarbon products are produced, whereas the content of CO_2, light hydrocarbon gases and olefins is higher. Increase of reaction temperature, the Anderson Schulz Flory (ASF) chain growth probability decreased. Reactor pressure has a significant effect on CO conversion and liquid hydrocarbon yields in the range investigated. With increase in pressure from 5 to 25 bar, the selectivity to the liquid hydrocarbons (C_5+) increased substantially, while the selectivity to methane, C_2-C_4 gaseous product & CO_2 decreased. Increase of reaction pressure, the chain growth probability increased. Increase in space velocity from 1000 to 4000 cc/g cat/hr, CO conversion decreased, selectivity of CH_4, C_2-C_4 and CO_2 is enhanced. CO conversion passed through maxima with the increase of the H_2/CO molar feed ratios from 0.7/1 to 3/1. Increasing H_2/CO ratios in the reactor result in higher amount of lighter hydrocarbons, lower selectivity of C_5+ and olefins. Chain growth probability decreased with increasing H_2/CO ratio. With increase of temperature and space velocity, selectivity of olefins to paraffins increased while

the reversed was observed with increase in pressure and H_2/CO molar ratio. The identification of different key components present in liquid products formed was done by GC-MS Method.

The effects of reaction conditions on the reaction rates are also studied. It was observed that FTS reaction rate (hydrocarbon formation rate) increased with increase in temperature, pressure and GHSV. However, FTS rate passed through optimum with increase in H_2/CO feed ratio from 0.7/1–3/1 (mol/mol). Water Gas Shift activity rate (CO_2 formation rate) increased with increase in temperature and GHSV, while decreased with increase in pressure, H_2/CO molar ratio. From the rate analysis, the optimum operating condition (T= 225 ^{0}C, P= 25 bar, H_2/CO ratio = ~ 1.2 and GHSV-2000 cc/g cat/h) for FT synthesis of selected silica supported Fe based catalyst (Catalyst Cat-1K: Fe/Cu/K, wt%: 35.5/3/1Cat-1K) was selected. The selected catalyst was tested at the above optimum operating conditions. At optimized operating condition, CO conversion was 45.9 wt.% once through mode operation and C_5+ selectivity for selected catalyst was 77.4 %.

To study the effect of run time on catalyst performance, stability measurement for the selected silica supported Fe based catalyst (Catalyst Cat-1K: Fe/Cu/K, wt%: 35.5/3/1) was investigated at temperature of 245 ^{0}C with H_2/CO = 2:1, GHSV of 2000 cc/g cat/h and a total pressure of 15 bar for 130 h time on stream. No appreciable deactivation was observed for the catalyst at the above operating condition after 130 h run. The spent catalyst was characterized to understand the structural changes that might have occurred during FT synthesis, amount & nature of coke formation. Analysis revealed that mixture of magnetite, iron carbide and iron are the final phases of Fe based FT catalyst. Ultimately, a most promising catalyst is developed along with suitable operating domain for production of fuel from synthesis gas generated from coal, pet coke and biomass.

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CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS