



Full Length Article

Hydrocracking of FT-wax to fuels over non-noble metal catalysts



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ABSTRACT

Hydrocracking is an important reaction in petrochemical industries to synthesize the high value low molecular weight hydrocarbons from low valued feedstock and also from waxes which are produced from Fischer-Tropsch synthesis. Ni was impregnated over the NaOH treated Zeolite ZSM-5, Beta, H-Y and Mordenite. The catalysts were characterized by XRD, N₂-sorption, SEM and TEM, etc. Under the optimized conditions of temperature (300 °C), pressure (10 barg), reaction time (1 h) and catalyst weight (300 mg), with eicosane as feed, conversion, liquid products and gaseous products selectivities were 97.6%, 84.1% and 15.9% respectively. It was found that Sasol FT-wax and FT-wax from KIST pilot plant showed gaseous products 10.6 and 12.8% respectively and the product distribution for both the feeds were in the range of C₅–C₃₀. Eicosane conversion improved after desilicating zeolite and conversion improved further over Ni impregnated desilicated zeolite. The activity of catalyst depends on the acidic strength of zeolite framework irrespective of their acid site density. Bi-functional catalyst with non-noble metal performed well under the studied conditions.

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1. Introduction

International oil price fluctuates depending on the supply, which cannot be satisfied according to the increasing demands. Most of the oil reserves are concentrated only on a few places on the earth may be contributing to the imbalance of supply [1]. This natural resource being a non-renewable source said to show a peak maximum production called as peak oil and later oil production tend to decline [2]. Earlier projections predict that we are at a peak of oil production but considering the new oil reservoirs discovered new technologies utilizing low-value crude and tar sands, etc., the recent projections shows that peak oil may be observed 2–3 decades later [3]. However, humankind have already overexploited these non-renewable resource to the maximum extent, which can be seen as increase in the CO₂ level in the atmosphere, which makes few cascading process on the earth, like, increase in the global temperature, resulting in melting of polar ice caps, increase in sea levels, climate change, etc. [4,5]. Reversing these effects may take a long time but further increase in the global temperature can be checked by controlling the CO₂ and other greenhouse gas emissions [6]. One among the major source of greenhouse gasses is associated petroleum gas (APG). APG is found in the crude oil in dissolved form or on top of the oil bed, in the case of onshore oil fields, there are lots of options to utilize the gas instead of

flaring. But in the case of offshore oil fields, it can be only used to a certain extent to re-inject to the oil field to enhance oil recovery. This can be utilized as a feedstock for converting these gases to fuel by Fischer-Tropsch synthesis on the offshore conditions on a ship specially built for the purpose. This type of process is familiarly known as Gas to Liquid Floating Production Storage and Offloading (GTL-FPSO) [7–9].

Fischer-Tropsch synthesis (FTS) has a history of around 90 years, but considerable development was achieved in the process in the recent 63 years by various research groups which are extensively covered in the review [10,11]. FTS is catching attention and concern in the world due to various reasons like energy security, economics, strategic reasons and environmental issues [9,12]. Even though the FTS is studied from a long time, still new catalysts are reported with marginal improvements to achieve desired product distribution and also to remove the excess heat evolved in the reaction to make the process viable, economical and also competitive with the fossil fuel [12].

There are two major types of FT process based on the operating temperature, they are, Low-Temperature-Fischer-Tropsch Synthesis (LTFTS) and High-Temperature-Fischer-Tropsch Synthesis (HTFTS). Based on these processes two different catalysts are widely studied (Co-based catalyst for LTFTS and Fe-based for HTFTS). Each system has its own advantage and disadvantage, but due to higher productivity of Co-based catalyst under low temperature, is preferred to Fe-based catalyst for GTL-FPSO process due to reactor design and activity. Due to limitations for the

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available space on the ship in the maritime environment, production of high-density wax material instead of liquid range hydrocarbons are preferred. By which overall productivity of the GTL-FPSO can be increased and also produced wax can be converted to various products depending on the requirement.

Catalysts systems studied for hydrocracking reaction are many, to name a few, Pt/SBA-15, sulphided Ni + Mo/HY, sulphided Ni + Mo/SiO₂-Al₂O₃, Pt-W/SiO₂-Al₂O₃, Pd/SiO₂-Al₂O₃, Ni/Siralox, Mo/Sirolax, Sulphided NiMo/Al₂O₃, CoMo/Al₂O₃ extrudates, Pt/ZSM-5, Pd/ZSM-5, Pt/HY, WNiPd/CeY-Al₂O₃, Mesoporous NiMo/Al₂O₃, Mesoporous NiMo/SiO₂, Pt/SAPO-11, Pt/amorphous SiO₂-Al₂O₃, Ni-Mo/γAl₂O₃, physical mixture of MgAPO-11 and Pt/MCM-41, Pt/WO₃/ZrO₂, MoO₃-CrO₂/SiO₂, steamed ZSM-5/Mordenite composites, desilicated and steamed HY have been studied widely using different feeds like hexane (C6), heptane (C7), octane (C8), nonane (C9), decane (C10), hexadecane (C16), eicosane (C20), Octacosane (28) and also Sasol H1 FT wax [13–32]. Mechanism of the reaction is said to be a dual site with both acid site and active metal function are necessary [22]. In this article, we present our study on the Ni impregnated on hierarchical pore zeolites catalyst for hydrocracking. Eicosane is used as a model compound for FT wax and under optimized conditions catalytic performance for FT wax from KIST pilot plant and Sasol H1 FT wax were tested and observed yields for FT wax and FT wax from the pilot plant were similar to Eicosane.

2. Experimental

Zeolite ZSM-5 and Beta (BEA) were purchased from Zeolyst, Mordenite (MOR) and Faujasite (FAU) from Alfa-Aeser. Sodium hydroxide (NaOH) and Nickel Nitrate hexahydrate (Ni(NO₃)₂·6H₂O) were from Samchun chemicals. Eicosane was purchased from sigma Aldrich, FT wax H1 from Sasol and LTFTS FT wax from in-house pilot plant were used in the study.

2.1. Catalyst preparation

Desilication of zeolite was carried out by the optimized method reported earlier [33]. In a typical procedure, Na form of zeolites were treated with 0.2 M NaOH at 70 °C for 1 h to remove silicon from the frame-work which results in the formation of mesopores through the zeolites. NaOH treated zeolites were washed with deionized water and dried in an oven at 100 °C. After drying, the catalysts were treated with 1 M ammonium nitrate solution with stirring at 90 °C for 8 h, followed by filtration and drying, this was repeated three times to ensure complete removal of sodium from the desilicated catalysts and calcined at 500 °C for 8 h. These desilicated catalysts were represented as Me-zeolites (zeolites = respective zeolite names). Ni (1 wt% metal basis) was loaded on the desilicated zeolites by wet impregnation method. In a typical procedure required amount of nickel nitrate was dissolved in a beaker containing water (about 10 ml). To this solution, 1 g of zeolite was added and resulting slurry was stirred at 80 °C until the water was evaporated followed by complete drying at 100 °C for 4 h. Dried catalysts were calcined at 500 °C for 8 h (5 °C per minute to reach the temperature). Before reaction, the catalyst was reduced at 450 °C for 12 h under the flow of pure hydrogen.

2.2. Catalyst characterization

X-ray diffraction studies of the catalysts were performed in Xpert pro instrument. Diffraction data was collected in the 2 theta range of 5–60° with the step of 0.02° using monochromatic Cu Kα radiation. Nitrogen sorption was performed in Moonsorb-I (KIST, Korea fabricated by BEL - Japan). In a typical procedure, about 100 mg of catalyst was taken in the sample bulb and pre-

treatment was carried out at 300 °C under reduced pressure for 4 h. Sorption measurement was carried out at 77 K from the relative pressure of 0.05–0.95 with an increment of 0.05. BET surface area was calculated in the range of 0.1–0.25 and total pore volume was calculated at the relative pressure of 0.95. Temperature programmed desorption of ammonia was carried out in Micromeritics instrument. In a typical procedure, 100 mg of the catalyst was taken in a 'U' tube and placed in a furnace and was pretreated at 400 °C for 1 h with He flow. The temperature was decreased to 100 °C and NH₃ was adsorbed by passing a stream of 10% NH₃ in He through the catalyst bed for 1 h, physisorbed NH₃ was then purged by dry He for another 1 h. The desorption of NH₃ was carried out with the He flow (30 ml min⁻¹) by increasing the temperature to 550 °C at the rate of 10 °C min⁻¹. TPR (Temperature Programmed reduction) was carried out in the same instrument, pretreatment of samples were carried out at 200 °C for 1 h under He flow. Reduction was carried out with 10% H₂ in Ar (30 ml min⁻¹), with ramp rate of 10 °C/min up to 900 °C. CO Chemisorption was carried out in the same instrument for exsitu reduced catalysts. Pretreatment of the catalysts were carried out at 400 °C for 1 h under hydrogen. CO chemisorption was studied by pulse technique, pulse of 10% CO in He were passed until no change in the area of CO was observed in 3 consecutive pulses. Pyridine adsorbed IR-Spectra of catalysts were studied to understand the type of acid sites on the catalyst. Experiments were carried out in the Thermo Scientific Nicolet iS50 FT-IR with praying mantis accessory which is designed to pass vapours onto the packed catalysts bed while heating the catalyst bed and spectra were collected with the Diffuse Reflectance Infrared Fourier Transform Spectroscopic (DRIFTS) technique. In a typical procedure catalyst powders were packed into the sample cup and activated at 300 °C for 1 h and cooled to 25 °C and pyridine vapours were passed. After 30 min of pyridine flow, complete setup was purged with He flow of 50 ml/min at 150 °C temperature for 4 h to completely remove the physisorbed pyridine. And the DRIFTS spectra were collected in absorbance mode with the resolution of 4 cm⁻¹ with the average of 64 scans. Difference spectra of before and after pyridine adsorption are reported here. In the difference spectrum, area under the peak corresponding to Bronsted acid sites (B) (~1540 cm⁻¹) and Lewis acid sites (L) (~1450 cm⁻¹) were integrated and B/L ratio is calculated by the following relation. $\frac{B}{L} = \frac{A_{py-B}}{A_{py-L}} \left(\frac{\epsilon_{py-L}}{\epsilon_{py-B}} \right)$ where A_{py-B} and A_{py-L} are the integrated absorbance of Bronsted sites and Lewis sites respectively and ϵ_{py-L} , ϵ_{py-B} are the molar extinction co-efficients of Lewis and Bronsted sites respectively and the value for $\left(\frac{\epsilon_{py-L}}{\epsilon_{py-B}} \right)$ is taken as 1.5 [34]. From the calculated B/L ratio and total acidity, Bronsted acid sites and Lewis acid sites were calculated by simultaneously solving B + L = total acidity; and B/L = ratio (Solving method is given in SI). Scanning electron micrographs were acquired in the FEI-Inspect F-50 instrument equipped with field emission gun as an electron source. For collecting the micrographs small amount of samples were smeared on the adhesive carbon tape, sputtered with Pt for 1 min and micrographs were saved with different magnifications under the pressure of 10⁻¹–10⁻⁸ torr < 300 kV of energy. Characteristic X-ray of the Ni was collected to map Ni distribution over the catalyst. The sample for Transmission electron microscopy (TEM) was prepared by dispersing the catalyst in ethanol followed by sonication for 5 min, 2 drops of resulting suspension was placed on the Cu grid designed for TEM application. Transmission electron micrograph of a catalyst was acquired in Technai F20 instrument.

2.3. Catalytic activity

Catalytic activity tests were carried out in a stainless steel batch reactor under pressure (Parr reactor). In a typical procedure, the

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