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Selective poly-aromatics saturation and ring opening during hydroprocessing of light cycle oil over sulfided Ni-Mo/SiO_2-Al_2O_3 catalyst

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ABSTRACT

Hydroprocessing of light cycle oil was carried out in a fixed bed reactor. Sulfided hydroprocessing catalyst, Ni-Mo/SiO_2-Al_2O_3 was used, and poly-aromatic hydrocarbons in the obtained products were reduced to 5 wt%, from 64 wt% in the feed, at 380 °C and 60 bar. The GC–MS analysis confirmed that 3-ring poly-aromatic compounds converted to alkyl substituted tetralin compounds. Aromatics yield increased by nearly 4–6 times (50 wt%) in the hydroprocessed products, which could be suitable for gasoline pool due to improved octane number. Mono-aromatic hydrocarbons concentration obtained was 35–55% at all the operating conditions in the hydroprocessed products. Higher concentration of mono-aromatics leads to the improved octane number of the fuel. Properties like viscosity, cetane index, °API, and density of hydroprocessed LCO products, lead us to conclude that the obtained products are suitable for diesel as well. Under severe reaction conditions (380 °C, 70 bar), °API and cetane index values increased whereas viscosity and the density value of the products decreased. The results indicate that the catalyst shows very stable performance with time regarding meeting the required specifications for diesel.

1. Introduction

Increased energy consumption and strict environmental specifications throughout the world for transportation fuels is pushing the researchers to either improve the existing processes or to develop alternate energy sources [1,2]. Presently, diesel fuels used in the vehicle have limitations [3] on sulfur (< 10 ppm), poly-aromatic hydrocarbons (< 11 wt%) and a minimum cetane number (> 51).

The demand for middle distillates (diesel and jet fuel) has been increasing day by day; however, heavy FCC fraction contains high amounts of aromatics compounds (50–80%), and high sulfur content ($> 3\%$), present in the form of dibenzothiophene and substituted alkyl compounds [4]. These molecules have different reactivity during hydroprocessing. Depending on their complexity, they alter the path of reactions and block the active sites, which further leads to reduced catalytic activity and rapid deactivation of the catalyst [5].

The heavy oil upgrading process involves sulfur and nitrogen content decrease and poly-aromatics compounds reduction to enhance cetane number by ring opening of naphthenes [6]. In these processes, the use of bi-functional catalysts is essential. The high cost and easy susceptibility to sulfur compounds limits the use of noble metal catalysts, and hence to the use of bi-metallic sulfided catalysts over different supports is preferred. The supports must have high surface area and large sized pores, to allow the bulk molecules to access the active sites present inside the pores easily. Additionally, the catalyst must have closer proximity to the metal and, acid sites provided by the support, to provide the synergy effect [7]. SiO_2 and γ-Al_2O_3 have commonly used supports in this type of process due to their low cost and high thermal and hydrothermal stability [8]. Nevertheless, the acidity of support might play an important role in the distributions of obtained products. Moreover, the SiO_2-Al_2O_3 mixture contains Brönsted acid sites [9] which might be favorable for hydrocracking reactions, thereby improving the product quality. Frequently, NiMo sulfide phase is employed for hydrocracking process, due to its hydrogenation and hydrodesulfurization activity [10].

The high demand for middle distillates is fulfilled by straight run gas oil (SRGO) obtained from atmospheric distillation unit (ADU). FCC units in refineries produce a large amount of light cycle oil (LCO) along with SRGO, which used as diesel blending component. Light cycle oil obtained from FCC unit has high sulfur, nitrogen, and poly-aromatic content and low cetane number, so the direct addition to diesel pool makes difficult to match the fuel specifications. Researchers have

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studied the hydroprocessing of light cycle oil under a wide range of operating conditions. The results show that higher temperature, pressure and lower space velocity is needed to obtain improved product quality fuel. Higher hydrogen consumptions are also required to obtain improved diesel fuel final properties. Researchers have also studied the hydroprocessing of SRGO–LCO blends over commercial Co-Mo/γ-Al_2O_3 catalyst and similar conclusions were drawn [8,11].

In light of this, present work intends to evaluate the activity and selectivity during hydroprocessing of light cycle oil (LCO) feedstock over sulfided NiMo/ SiO_2-Al_2O_3 catalyst to look into its suitability as a diesel blending component.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by using incipient wetness impregnation method, described by Betancourt et al. [4]. The catalyst prepared using nickel salt (Sigma-Aldrich) and molybdenum (Sigma-Aldrich) salts. The commercial extrudates of mesoporous SiO_2-Al_2O_3(Sasol) were used as support. An appropriate amount of $(NH_4)_6Mo_7O_{24}.4H_2O$ was used in aqueous solution. The obtained solid was dried at 120 °C for 24 h. Further, $Ni(NO_3)_2.6H_2O$ salt in aqueous medium impregnated with the Mo-loaded catalyst. The Ni promoter was prepared via the sequential impregnation step. The final catalyst dried at 120 °C for 24 h, and calcined at 500 °C for 6 h.

2.2. Experimental set-up and product analysis

Before the experimental study, 3 ml of NiMo/SiO_2-Al_2O_3 catalyst was loaded into the fixed bed reactor and sulfided via the in-situ method. A mixture of gas-oil and dimethyl disulfide (DMDS, 2.5 wt%) used as sulfidation feed. The catalytic activity measurement was performed in a continuous down flow high-pressure fixed bed unit using Light Cycle Oil (LCO) as a feedstock, supplied by Guwahati refinery in India.

The experimental set-up used in this study is shown in Supporting information Fig. S1. The catalyst bed diluted with silicon carbide (SiC: catalyst in 1:1(v/v) ratio). The stainless steel tubular reactor operated in an isothermal model, and the electric furnace was used as a heater to provide heat to the furnace. The temperature in the reactor was monitored and maintained by using two thermocouples and a temperature controller. A high-pressure syringe pump was used to monitor the feed (light cycle oil) flow into the reactor. During operation, a Brooks mass flow controller (range 0–500 ml min^{-1}), was used to control hydrogen gas flow. A high-pressure gas-liquid separator was used to separate the gaseous and liquid products. The catalyst activity was evaluated over a period of 6 h for each run and the reactor products were collected at regular intervals.

Hydroprocessed liquid hydrocarbons products were analyzed using Agilent GCxGC analyzer (model 7890B 2D-GC), employing FID and MS detection system; the first column was non-polar DB-5 ms column (30 m × 0.25 mm × 0.25 µm), with a second PAC polar column (5m × 0.25 mm × 0.15 µm), a capillary flow modulator and ZOEX software. On the other hand, a Varian CP-3800 Gas Chromatographer, with a vf-5 ms column (30 m × 0.25 mm × 0.25 µm) capillary column and FID detection system, was used to obtain product simulated distillation analysis. The total sulfur analysis obtained over Oxford Instruments, model Lb X3500 SCL. ASTM D-4294 method was used for the sulfur analysis. The instrument was calibrated for various ranges of sulfur concentrations. Nitrogen analysis of the feed and hydroprocessed products were performed on Elementar MICRO cube analyzer equipped with a thermal conductivity detector**.** Accuracy for sulfur analysis is ± 2.5%, and that for nitrogen analysis is ± 1%.

The ASTM test methods used for the characterization of feed and hydroprocessed products are given in Supporting information Table S1. The cetane index, viscosity density values were calculated by ASTM D-4737, ASTM D-7042, and ASTM D-7042 methods, respectively. SimDist analysis results were reported according to ASTM D-2887 method.

2.3. Characterization

N_2 adsorption/desorption isotherms were measured with a Belsorb-Max (BEL JAPAN) instrument at liquid N_2 temperature. For pre-treatment, 40–50 mg of catalyst was taken in a quartz tube and evacuated for 3 h at 250 °C using a vacuum. Specific surface areas calculated by the BET method, pore volume (Vp) determined by nitrogen adsorption, and pore size distributions from the adsorption isotherms by the Barrett-Joyner-Halenda (BJH) method from the desorption isotherm. Micrometrics 2900 with a thermal conductivity detector was used to measure the amount and strength of the acid sites by ammonia adsorption-desorption technique. 0.20 g sample was saturated with NH_3 at 120 °C, after that flushed with helium to remove the physically adsorbed NH_3. The NH_3 desorption was carried out at a heating rate of 10 °C/min in helium gas flow. X-ray diffraction (XRD) patterns were recorded using a PROTO XRD benchtop powder diffraction X-ray Diffractometer with monochromatic radiation Cu Kα ($\lambda = 1.5418$ Å). The operating voltage of 34.6 kV used during the analysis, and a current of 14.3 mA, in the step scanning mode in the range $10^\circ < 2\theta < 80^\circ$ with a continuous scan rate of 2.0 °C/min. SEM (scanning electron microscopy) images were obtained on a field emission scanning electron microscope, FEI Quanta 200F. Transmission electron microscopy (TEM) images of synthesized mesoporous materials were recorded on a JEOL electron microscope, model JEM 2100, operated at 200 kV.

3. Result and discussion

3.1. Catalyst behavior

3.1.1. BET, BJH and acidity analysis

Physicochemical properties of fresh and used catalysts (NiMo/SiO_2-Al_2O_3) are presented in Table 1. Fig. 1(inset) shows pore size distribution in the mesoporous range. A characteristic isotherm obtained can be classified as type IV in the IUPAC classification, which is characteristic of mesoporous materials as shown in Fig. 1. Large mesopores allow an easy movement of bulk molecules through pores. Moreover, the sharp inflection in sorption isotherm indicates capillary condensation inside uniform and large pores. The used catalyst showed a small loss in porous properties after hydroprocessing reactions. The textural results indicate that, at the end of the experimental run, the catalyst has a very slight reduction in pore volume and surface area in spite of severe operational conditions (temperature, pressure) used during all the experiments. Additionally, the strong adsorption of inhibitor organic compounds on the active sites of the catalyst is evidence of the deposition of a carbon layer in the surface of the material, which resulted in the reduction of pore volume and surface area from 187 to 146 m^2/g after the reaction. Pore diameter and pore volume of fresh catalyst was 10.4 nm and 0.48 ml/g and reduced to 7.9 nm and 0.33 ml/g respectively after 200 h of the continuous experimental run. TPD of NH_3 results shows that the catalyst has moderate and weakly acidic sites with total acidity of 0.77 $mmol.g_{cat}{}^{-1}$.

Table 1
Physicochemical properties of fresh and used catalysts.

Sample code	S_{BET} (m^2/g)	D_p (nm)	V_p (cm^3/g)
SiO_2-Al_2O_3	236	10.6	0.50
NiMo/SiO_2-Al_2O_3	187	10.4	0.48
NiMo/SiO_2-$Al_2O_3^{(used)}$	146	7.9	0.33