

Hydro-treatment of middle lubricating base oil on sulfided promoted molybdenum catalysts



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ABSTRACT

Nickel- molybdenum and cobalt -nickel- molybdenum catalysts were prepared via impregnation technique, with loadings of 7wt. % Ni; 15 wt.% Mo and 2 wt.% Co, followed by drying at 120 °C, calcination at 450 °C and then sulfidation was performed at 400 °C. The prepared catalysts characterized by X-ray diffraction, temperature-programmed reduction and N₂ adsorption –desorption techniques. The catalysts investigated towards hydro-treatment of lubricating base oil. Temperature-programmed reduction results revealed that Ni-Mo has lower support interaction than Co-Ni-Mo/kaolinite catalysts. Catalytic evaluation results displayed that the sulfur and total aromatic contents in the reaction products using Co-Ni-Mo were lower than that on Ni-Mo/kaolinite catalysts at 275 °C. The sulfur in the product decreased from 2400 to 900 ppm (sulfur removal reached 62.5 %) and consequently, the aromatic contents decreased from 13 to 6 wt% on using Co-Ni-Mo catalyst. The produced hydro = treated lubricating base oil can be used as technical white oil according to Egyptian pharmacopeia's tests.

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1. Introduction

Catalytic hydro-treating process is one of the important processes for decreasing sulfur and aromatic contents in petroleum fractions and hence the improvement of catalysts has become vital to maintain profitability. Transition metal (Mo, W) sulfides supported on γ -Al₂O₃ promoted by other transition metals (Ni, Co) are widely used as hydro-treating catalysts [1–3].

One of the important factors that affect the efficiency of a Ni (Co)-Mo catalyst is the interaction between the active phases and the support. Metal-support interactions (MSI) influence not only the dispersion of the active components, but also their reducibility and sulfide-ability (4, 5). The development of new supports for hydro-treatment catalysts have been very active urged by the stringent regulations concerning the restricted level of sulfur admitted in fuels. Many supports were used for preparing sulfided catalyst that have lower MSI, higher specific surface area and larger pore diameters as amorphous-silica-alumina (ASA) [4], carbon [5,6], carbon nano-tubes (CNT) [7], carbon coated alumina [8] and or MgO–Al₂O₃ composite oxides [9]. Modifications of hydro-treatment catalysts by incorporation of acid supports have also performed. Acid supports like meso-porous MCM-41, SBA-15 [10,11] possess uniform meso-pores, high surface area and have potential catalytic application for reactions including hydro-desulfurization of petroleum fractions. These supports allow the adsorption of sulphur

species, and promote hydrogenation via protonation followed by hydride transfer.

Kaolinite, Al₂Si₂O₅(OH)₄, is a naturally occurring mineral composed of layers of a tetrahedral sheet of SiO₂ bound to an octahedral sheet of Al₂O₃ [12] which is held together by hydrogen bonds and van der Waals interaction. The kaolinite particles are plate-like and the aspect ratio (particle diameter/particle thickness) is about 5–15. Kaolinite applied in many areas, including an adsorbent for phosphate species [13], as well as a catalyst support nano-species like TiO₂ [14] that used for photo-catalytic degradation of methyl orange. The catalytic activity of these materials can be ascribed to their relatively high Lewis and Brønsted acidities as well as their large pore size. Utilizing clay catalysts is advantageous because they are readily available, cost effective, and versatile.

This work concerns on preparing Ni-Mo catalyst using local kaolinite clay material as support. The effect of adding Co species with small amount (2 wt%) on the metal-support interaction and consequently on the catalytic activity of the sulfided catalysts were also investigated towards hydro-treatment process of middle lubricating base oil.

2. Experimental

2.1. Preparation of support

Kaolinite clay material supplied from El-Tih district with Si/Al molar ratio = 1.6, was activated using hydrochloric acid with concentration of 2% under reflux condition for duration of 6 h. After that the acidified

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sample washed with distilled water until chlorine free, dried, grounded and then sieved to mesh size 100–150 to be used as a support for preparing di- and tri- functional catalysts.

2.2. Preparation of Ni-Mo/Kaolinite and Co-Ni-Mo/ Kaolinite catalysts

Bimetallic Ni-Mo/kaolinite catalyst was prepared via two successive incipient impregnation method with an aqueous solution containing the desired amounts of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ to get a concentration of 15 wt% of MoO_3 and 7 wt% of NiO, respectively. The impregnation carried out in two stages to avoid the precipitation of catalyst metal from the saturated solution. The solution heated carefully to ensure that $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was completely dissolved before impregnation. The sample was dried at 120 °C overnight and then calcined in presence of purified air flow at 450 °C with a heating rate of 5 °C/min for 5 h. The molar ratio of Ni/Mo is 1:3 which has demonstrated as the optimal ratio for the HDS catalysts [15,16]. Trimetallic Co-Ni-Mo/kaolinite catalysts was also prepared with the same procedure on using appropriate amount of an aqueous solution of Co $(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$. The prepared Co-Ni-Mo/kaolinite catalyst contains 15 wt. % of MoO_3 , 7 wt. % NiO and 2 wt.% CoO.

2.3. Catalyst characterization

2.3.1. X-ray diffraction (XRD)

XRD studies were performed using a Rigaku X-ray diffractometer with a nickel filtered Cu Ka radiation filtered by a graphic monochromator at a voltage of 40 kV and a current of 80 mA for identifying the presence of crystalline phases in supported catalysts. The recording was carried out for 2θ angles from 4° to 80° at a scanning speed of 1°/min.

2.3.2. Total acidity

The amount of surface acidic groups on the studied materials were estimated by Boehm titration [17]. A 0.5 gram of the sample was mixed in 25 ml of 0.02 N NaOH solution and stirred at room temperature for 24 h. The mixture was filtered out and 5 ml of this filtrate was titrated against 0.02 N HCl. The amount of HCl consumed was used to calculate the quantity of total acidic groups.

2.3.3. Differential Scanning Calorimetry Analysis (DSC)

DSC was carried out using the Differential Thermal Analyzer, Perkin Elmer apparatus, to study the phases formed upon thermal treatment and the enthalpy of prepared catalysts.

2.3.4. Temperature programmed reduction (TPR)

TPR profiles of the calcined catalysts were recorded using a Micromeritics TPD-TPR 2900 system. 0.1 g sample was placed in the TPR reactor and was heated to a temperature of 130 °C at a rate of 10 °C/min and then was held at this temperature for 30 min under helium flow of 50 cm³/min for removing moisture. Then, it was cooled to 40 °C and hydrogen flow was started at a rate 50 cm³/min (using 9.5% v/v H₂ in Ar). The temperature was raised at a rate of 10 °C/min from 40 °C to 600 °C and held at this temperature for 60 min.

2.3.5. N₂ physical adsorption

The surface area of the support and the catalysts were measured at 77 K in a Micromeritics 2000 ASAP analyzer by N₂ adsorption-desorption method. Around 0.2-gram sample was degassed at 200 °C for 1 h in 0.55 mmHg vacuum to remove the moisture from the pores of the material. Pore diameter and pore size distribution were calculated using BJH method.

2.4. Hydro-treating processes

The hydro-treating activity “in terms of hydrodesulphurization (HDS) and hydrogenation processes (HDG)” of the prepared Ni-Mo

and Co-Ni-Mo catalysts supported on kaolinite material was studied in a stainless steel continuous-flow reactor operated under hydrogen pressure using the middle lubricating base oil as feedstock. The prepared oxide catalysts (Ni-Mo and Co-Ni-Mo/kaolinite) were subjected to sulfidation on using a 5% CS₂ in clean gas oil. Firstly, the oil flow rate was kept at 30 ml/h to wet the catalyst at 100 °C for 3.5 h. Then the flow was set to 5 ml/h and temperature was raised to 200 °C with the introduction of hydrogen to commence the first stage sulfidation. After that (24 h), the temperature of the catalyst bed rose to 320 °C and maintained at this temperature for 24 h to complete the sulfidation process. The catalytic activity measurement was carried out at reaction temperatures ranged 225–300 °C, LHSV = 0.6 h⁻¹, gas-to-oil ratio = 500 Nm³/m³ and under hydrogen pressure 80 atm. The product samples collected at an interval of 12 h. The samples stripped by purging with nitrogen for 2 h to get rid of the residual H₂S. The total sulfur contents of the reaction products were measured using Antek 9000 NS analyser involving fluorescence (ASTM 5453-06 method) technique. Aromatic distribution (Mono-, Di-, polycyclic compounds) was deduced from Ultra-violet spectrometry using the Burdett method [18].

3. Results and Discussions

3.1. Catalysts Characterization

3.1.1. XRD characterization

X-ray diffraction pattern of the support and the studied catalysts are depicted in Fig. (1a-f). The XRD pattern of the raw material detected the main diffraction lines at d-spacing 7.14 and 3.33 Å that are characteristic to kaolinite material (ASTM 14-164). After acid activation, the pattern still displays reflections of the support except the appearance of some new peaks that may be accompanied the cleaning of the clay surface from the organic matter and the soluble salts. For the Ni-Mo/kaolinite catalyst, the pattern (Fig. 1-c) reveals a notable decreasing of the ordering, indicated by the decrease in intensity and broadening of the basal reflections of kaolinite material, evidence of a new crystalline phase emerging. The diffractogram displays peaks at d-spacing of 3.81 Å, 3.46 Å and 3.26 Å which are related to MoO₃ phase. The lower intensity of the MoO₃ peaks suggests that the dispersion is high and the active phase interacts with the –OH groups of kaolinite that results in this dispersion. New features appear at d-spacing of 3.35 and 3.28 Å, which is assigned to and diffraction lines of NiMoO₄ formed upon the interaction of nickel and molybdenum species on kaolinite surface (ASTM-45-0142). Peaks associated with NiO are not detected signifying

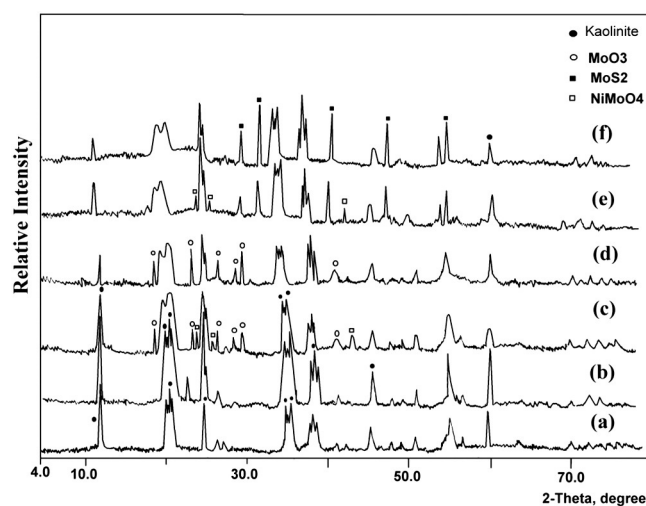


Fig. 1. X-ray Diffraction Patterns for: (a) Raw Kaolinite (b) Active Kaolinite. (c) Ni-Mo/kaolinite catalyst (d) Co-Ni-Mo/kaolinite catalyst. (e) Sulfided Ni-Mo/kaolinite catalyst (f) Sulfided Co-Ni-Mo/kaolinite catalyst.

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