



Hydrotreating of coker light gas oil on Ti-modified HMS supports using Ni/HPMo catalysts

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ABSTRACT

In the present investigation, Ti-HMS materials with variable Si/Ti molar ratios of 20, 40, and 80 were synthesized and employed as supports for Ni-promoted 12-molybdophosphoric acid (NiPMo) catalysts. The effect of the Ti ions and the immobilization of 12-molybdophosphoric acids on mesoporous materials were studied. Supports and catalysts were thoroughly characterized by using XRD, N₂ adsorption analysis, FT-IR, Raman, TPR, DRIFT, SEM and TEM techniques. Results from XRD and IR measurements confirm the hexagonally ordered mesoporous structure and incorporation of Ti into the HMS support, respectively. It was found that incorporation of Ti and presence of HPA into the HMS structure increased the reducibility of the catalysts. Hydrotreating experiments were conducted using coker light gas oil under industrial conditions of temperature, pressure, LHSV, and gas to oil ratio of 330–370 °C, 8.8 MPa, 1 h⁻¹, and 600 mL/mL, respectively. It was found that NiPMo catalysts prepared from heteropolyacids showed better performance in HDS and HDN of coker light gas oil (CLGO) than the NiMo catalysts prepared by conventional method using ammonium hepta molybdate (AHM) as Mo source.

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1. Introduction

Hydrotreating is an important process in crude oil refining, which ensures the production of clean fuels by the removal of various contaminants (sulfur, nitrogen and oxygen-containing compounds, as well as aromatics) commonly found in different oil fractions. In recent years, the production of heavy oil increased and the quality of crude oil is becoming more and more inferior [1,2]. Coker light gas oil (CLGO) also contains a large amount of heteroatoms such as sulfur, nitrogen, etc. Therefore, hydrotreating is important for upgrading the undesirable feedstocks to valuable products [3–5].

By the end of this decade, the sulfur level as in the case of diesel fuels is expected to be lowered to 10 ppm in a large part of the world. To fulfill these new stringent legislative requirements, ultra-deep hydrodesulfurization (HDS) should be performed instead of a conventional HDS, in which sulfur content is mostly reduced up to 300–500 ppm over Ni(Co)Mo/alumina catalysts [6]. The demand for lower sulfur content in fuels requires the synthesis of more active HDS catalysts [7]. Many studies have shown that one of the major factors affecting the activity of an HDS catalyst is the interaction between the active components of the catalyst and the support.

Among the different approaches towards increasing the efficiency of hydrotreating catalysts, using new catalyst supports [8] and changing the nature of the active phase are very crucial [9–11]. Another common industrial practice is the introduction of additives like P, F, B and chelating agents to the catalytic active formulation. Kwak et al. [12] observed that the behavior of P helps to increase the active sites by enhancing metal dispersion and increases Bronsted acidity in CoMo/γ-Al₂O₃ catalysts. Using different catalytic precursors is another way towards catalyst modification. Mo (W) oxides are commonly used as precursors in the preparation of HDS catalysts. Keggin-type heteropolyacids (HPAs) are also well-known catalysts applied in acid catalysis and catalytic oxidation [13,14]. However, there are few reports available on the application of heteropolyacids in hydrotreating reactions. The structural stability as a function of temperature and reaction atmosphere and their structural transformation during the catalyst activation are important aspects for understanding the working catalyst system. However, the main disadvantage of heteropolyacids is their very low surface area. Finding a suitable support that can attach itself firmly and disperse the HPA is of great practical interest because catalytic activity is related to the high surface area and also to the thermal stability of the supported heteropolyanion.

Different carriers have been used to support HPA and their thermal stability has been shown to depend on the type of support and the loading of HPA. It was found that when HPAs are deposited on alumina, their characteristic heteropolyanion structure is destroyed and their catalytic activities become similar to that

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of the conventional Mo and W catalysts [15]. Different materials such as silica [16], carbon [17], titania [18], zirconia [19], and mixed oxides [20] have proven to be excellent carriers for supporting heteropoly compounds with a preserved Keggin structure up to higher temperature of calcination (400–500 °C) compared with that of bulk ones. Shafi et al. [21] showed that silica-supported $H_3PW_{12}O_{40}$ (HPW) is an efficient precursor that yields active catalyst for HDS of dibenzothiophene comparable to commercial $CoMo/\gamma-Al_2O_3$ catalysts under industrial conditions.

In 1992, the discovery of mesoporous silicate molecular sieves by Mobil scientists [22] stimulated deep interest in the synthesis of mesoporous materials and the use of these materials as carriers for heteropoly compounds. The most widely studied mesoporous silica was MCM-41, which has a hexagonal ordered structure with pore diameter ranging from 1.5 to 10 nm. The hexagonal nature of the mesoporous materials and their thermal and hydrothermal stability are increased when transition metals are anchored into the framework of mesoporous silicate. Substitution of foreign ion (Al^{+3} , Ti^{+4} , Zr^{+4}) into the silicate framework is an efficient route in order to enhance acidity and stability of the mesoporous silica. Some authors have reported that Al, Ti, or Zr-containing SBA-15 provided a better dispersion of Ni (Co) and Mo (W) species as compared to the pure SBA-15 and alumina-supported catalysts [23–30].

The surface grafting of mesoporous materials with strong acidic groups such as that of HPA on the surface of Zr-MCM-41 solids increased the Bronsted acidity by 4–8 times, relative to that of the bare support [31]. These catalysts showed good catalytic activity and high isomerization selectivity in the *n*-heptane hydro-isomerization reaction. Zepeda et al. [32] concluded that Ti-incorporation into the HMS framework resulted in good support substrate for the preparation of highly active Ti-containing catalysts. Ti-containing CoMo catalysts were effective in promoting the isomerization pathway in the HDS of 4,6-DMDBT and the hydrogenation pathway in the HDS of DBT due to their high acidity compared to Ti-free samples [33].

In this work, double modification of HMS silica was made by combining surface grafting with $H_3PMo_{12}O_{40}$ (HPMo) and frame modification with Ti^{+4} ions. Firstly, a series of Ti-containing HMS samples were prepared using Ti-butoxide as Ti precursor, Pluronic P123 polymer as a structure directing agent (SDA) and TEOS as a silica source. Secondly, to enhance the number of surface Bronsted acid sites, surface modification of Ti-HMS was done using a suitable amount of $H_3PMo_{12}O_{40}$ based on previous investigations [34–36]. To our knowledge, no published work has been found whereby hydrotreating catalysts obtained from HPA precursors were screened using real feedstock. Thus, the aim of this work was to study the effect of Ti on HMS-supported HPA catalysts, which are better oxidic precursors than the conventional Mo salts. For comparison, $NiMo/\gamma-Al_2O_3$ and $NiMo/HMS$ catalysts were prepared through conventional methods using AHM as the Mo source.

2. Experimental

2.1. Synthesis of HMS and Ti-HMS support

The HMS material was synthesized using the neutral $S^\circ I^\circ$ templating route, proposed by Tanev and co-workers [37,38]. The Ti-HMS material was prepared using the procedure described by Gotier and Tuel [39] using dodecylamine as the surfactant, TEOS as the silica source and titanium butoxide as Ti source. The reaction mixture was slightly modified using mesitylene as the swelling agent. The Ti-HMS (*x*) materials were synthesized, where *x* indicates the Si/Ti molar ratios of 20, 40 and 80.

In a typical preparation of Ti-HMS, an initial solution was made by dissolving 13.39 g dodecylamine in a mixture of 173.57 mL H_2O

and 99 mL ethanol. To this solution, mesitylene (20.19 mL) was added with vigorous stirring for 15 min. The second solution was made by adding 60 mL of TEOS in the required amount of titanium butoxide mixed with 10 mL of 2-propanol, and added slowly to the first solution. After the addition of the last portion of the first solution, mechanical stirring was maintained for 20 h at ambient temperature. The obtained white solid was recovered by filtration, washed with distilled water and dried at room temperature, followed by drying at 100 °C for 24 h. The organic template was then removed by calcination at 550 °C for 6 h.

2.2. Synthesis of $NiPMo/Ti$ -HMS catalysts

In a typical preparation method, a calculated amount of $H_3PMo_{12}O_{40}$ was dissolved in methanol, at ratio of 10 mL methanol per gram of support. The Ti-HMS mesoporous material was then added to the $H_3PMo_{12}O_{40}$ -methanol solution. This suspension was transferred into a rotating evaporator placed in a water bath at a temperature of 40 °C. After the methanol was completely evaporated, the dried solid, showing slightly yellow coloration was dried at 80 °C for 24 h and calcined at 350 °C for 2 h. Methanol was chosen as the solvent for depositing Keggin HPA on the Ti-HMS support so as to avoid the presence of different structures on the silica surface as found when water solution was used at lower HPA loadings [40].

The promoter was incorporated in a second step by the impregnation of methanol solution of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, following the procedure previously described. The samples were designated as $HPMo/Ti-HMS(x)$ for unpromoted catalysts and $NiPMo/Ti-HMS(x)$ for promoted catalysts. The nominal composition of the catalysts was 2.5 wt.% Ni and 13 wt.% Mo.

The reference catalyst was also prepared by successive impregnations of aqueous solutions of ammonium heptamolybdate (AHM) and nickel nitrate using Ti-free HMS and $\gamma-Al_2O_3$ as supports. These samples were designated $NiMo/HMS$ and $NiMo/\gamma-Al_2O_3$. The nominal composition of these catalysts was also 2.5 wt.% Ni and 13 wt.% Mo.

2.3. Characterization

2.3.1. ICP-MS

The elemental compositions of calcined $NiMo/HMS$ and $NiPMo/Ti-HMS$ catalysts with different Si/Ti ratios were measured by ICP-MS and are given in Table 1, along with the targeted compositions. It indicates that the compositions of most of the catalysts closely match the targeted values.

2.3.2. Measurement of N_2 adsorption-desorption isotherms

The BET surface area, pore volume and pore size distribution of the samples were measured with a Micromeritics ASAP 2000 instrument using low temperature N_2 adsorption-desorption isotherms. Before measuring, the sample was degassed in vacuum at 200 °C. The surface area was computed from these isotherms using the multi-point Brunauer-Emmett-Teller (BET) method based on the adsorption data in the partial pressure P/P_0 range from 0.01 to 0.2. The value of 0.1620 nm² was taken for the cross-section of the physically adsorbed N_2 molecule. The mesopore volume was determined from the N_2 adsorbed at a $P/P_0 = 0.4$. The total pore volume was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$, assuming that adsorption on the external surface was negligible compared with adsorption in pores. The pore diameter and pore volume were determined using the (BJH) method. In all cases, correlation coefficients above 0.999 were obtained.

2.3.3. X-ray diffraction (XRD) analysis

The low-angle X-ray diffraction patterns of the samples were measured using a Bruker D8 Advance Powder diffractometer with

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