Research article

Insights into individual and combined effects of phosphorus and EDTA on performance of NiMo/MesoAl$_2$O$_3$ catalyst for hydrotreating of heavy gas oil

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ABSTRACT

The individual and combined effects of phosphorus, EDTA and support modification on hydrotreating of bitumen derived heavy gas oil were studied. The EDTA/Ni molar ratio was varied from 0.5 to 2 for optimization and studying the effect of EDTA on activity of mesoporous alumina supported NiMo catalyst. The phosphorus was impregnated using two different methods: modified co-impregnation (MCI) and sequential impregnation (SI), and their effect on physico-chemical properties was studied. The catalysts were characterized using N$_2$-physisorption, CO-chemisorption, pyridine-FTIR, H$_2$-TPR, NH$_3$-TPD, X-ray diffraction, High resolution-TEM and XANES. HRTEM and XANES techniques were predominantly used to determine the structural changes, and to visualize and measure active metal dispersion. All catalysts were tested for hydrotreating reactions in a continuous trickle-bed reactor at industrial conditions. The activities were measured in terms of hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA). The studies on NiMo/γ-Al$_2$O$_3$ were also performed for comparison purpose. The increase in HDS and HDN activities was observed for NiMo/MesoAl$_2$O$_3$ catalyst and this is assigned to high metal dispersion due to large surface area and pore volume of synthesized mesoporous alumina. The addition of EDTA in NiMo/MesoAl$_2$O$_3$ catalyst resulted in increasing the MoS$_2$ slab length and stacking degree, which resulted in decrease in dispersion, and HDN and HDS activities. However, the catalyst NiMoP/MesoAl$_2$O$_3$(MCI) containing only 2.5 wt.% P prepared by modified co-impregnation method showed the best HDS (97 wt.%) and HDN (77 wt.%) activity among all other studied catalysts. This increase in activity is attributed to the effect of mesoporous alumina and influence of P on reducibility, acidic strength, structural changes and desired molybdenum dispersion.

1. Introduction

The increasing demand of energy leads to the extraction of crude oil from unconventional sources such as oil sands and shale oil. The oil sands bitumen derived heavy gas oil contains higher amount of sulfur (~4%) and nitrogen (~0.4%), which needs to be lowered before it can be processed in existing refinery settings. Consequently, the highly efficient hydrotreating process is required. Hydrotreating is a catalytic process operating at high temperatures (350–400 °C) and moderate pressures (8–9 MPa) in the presence of hydrogen for removing impurities such as sulfur and nitrogen from gas oil.

The catalyst consists of active metals and support material. Mo or W, promoted with Ni or Co are most commonly used as active metals and γ-Al$_2$O$_3$ is widely used as support material. The support material not only helps in the dispersion of active metals but also favors the

modification of the electronic properties of the active phase, which could drastically improve the catalytic activity [1]. Therefore, with the aim to increase the catalytic activity, various researchers have worked on changing or modifying the support materials. Different materials such as carbon, metal oxides (TiO$_2$, ZrO$_2$), silica, modified silica (Al-SBA-15, Zr-SBA-15), zeolites, amorphous alumino-silicates, mixed oxides (TiO$_2$-ZrO$_2$) and ordered mesoporous materials such as MCM-41, SBA-15, have been tested as support materials for NiMo/CoMo hydrotreating catalysts [2–7]. It was observed that these materials showed difference in hydrotreating activity, which confirmed the role played by support materials in active metal dispersion and metal support interactions. In our previous work we have synthesized mesoporous alumina and found it to be the most promising support for hydrotreating catalyst [8].

Additional ways adopted to increase the catalytic activity include (i) the use of chelating ligands such as citric acid, glycol, nitriloacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA), 1,2-cyclohexanediamine-tetraaceticacid (CyDTA), and (ii) the use of additives

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such as phosphorus and boron [9,10]. The chelating ligands are those molecules, which consists of two or more atoms having the tendency to donate electron with which they can bind a metal cation and form a metal-chelating ligand complex. The chelating ligands such as EDTA has shown beneficial effect on hydrotreating activity by (a) delaying the nickel sulfidation to the temperatures where molybdenum oxide already started to sulfide and hence favoring the formation of active NiMoS phases, and (b) formation of Type II NiMoS phases by decreasing the metal support interactions [7,9]. The interaction of EDTA with support and active metals and its influence on increasing the hydrotreating activity was discussed in details in our previous work [9].

The additives such as phosphorus and boron has been known for improvement in hydrotreating activity and phosphorus is often called as second promoter [11]. Phosphorus adsorbs strongly on the surface OH groups of alumina, thereby reducing the number of basic OH available for molybdenum oxo-species. This results in lowering the interaction of active metals with support, and favors complete sulfidation/reduction of active metals, resulting in the formation of catalytically active Type II NiMoS phase [11,12]. (Type I NiMoS phase are single layered partially sulfided Ni-MoS$_2$ slabs, and Type II NiMoS phases are two or more layered fully sulfided Ni-MoS$_2$ slabs). The increase in stacking degree (no. of layers per slab) of MoS$_2$ slabs favors the hydrogenation reactions. This implies that the phosphorus addition enhances hydrodenitrogenation (HDN) reactions more as compared to hydrodesulfurization (HDS) reactions because the former mainly follows the hydrogenation pathway. Likewise, Eijsbouts et al. [13], has reported that phosphorus has more positive effect on HDN activity. Phosphorus also reduces the formation of non-reactive nickel aluminate, thereby providing more nickel to the active sites [14]. The influence of phosphorus on hydrotreating activity majorly depends on phosphorus concentration and method of preparation [15]. It was reported that catalyst prepared using sequential impregnation procedure showed higher activity as compared to the one prepared using co-impregnation. Contrary to this, Maity et al. [14], showed that catalyst prepared using co-impregnation method has shown higher hydrotreating activity for gas oil. They also reported that the increase in activity was observed with increasing the phosphorus concentration and it reaches maximum at 1 wt.% loading. Further increase in concentration decreases the active metal dispersion and hence decreases the activity due to formation of agglomerates of crystalline MoO$_3$. Phosphorus also has positive effect on hydrogenolysis reactions, which require acidic property. Eijsbouts et al. [13], proposed that phosphorus leads to the formation of acidic AlPO$_4$ sites, which enhances the HDN reactions. It can be concluded that phosphorus addition induces the structural and morphological changes of active sites. However, its effect on catalytic activity strongly depends on method of preparation, amount of loading, type of support material and feed [11].

Further to capitalize together the beneficial influence of chelating ligands and additives on hydrotreating activity, catalysts containing both chelating ligands and additives would be of great interest. Rinaldi et al. [16], has studied the effect of boron and citric acid on the hydrodesulfurization (HDS) of thiophene over CoMo/γ-Al$_2$O$_3$ catalyst. Mo K-edge EXAFS studies revealed the formation of citric acid-Co and citric acid-Mo complexes. They observed the increase in HDS activity with addition of citric acid and boron to CoMo catalyst. Escobar et al. [17], has studied the effect of ethylene glycol on phosphorous doped NiMo/γ-Al$_2$O$_3$ catalyst. They have tested different ethyleneglycol/Ni ratio (1, 2.5 and 7) and observed increase in activity for HDS of DBT and straight run gas oil (SRGO). In another study, phosphorus and glycol was added in CoMo/γ-Al$_2$O$_3$ catalyst, and the activity was determined in terms of HDS of 4,6-DMDBT and SRGO [18]. Based on the physico-chemical characterization the increase in activity was attributed to the change in co-ordination of Mo and Co species in presence of glycol. However, based on the available open literature, the combined effects of EDTA and phosphorus on the activity of synthesized mesoporous alumina supported NiMo catalysts have not been explored. Therefore, with

the aim to improve the catalytic activity to enhance the sulfur and nitrogen removal from oil sands bitumen derived heavy gas oil, the objective of this work was defined.

In this work, the mesoporous alumina with high surface area was synthesized based on the procedure developed in our recent work, and the combined effect of EDTA, phosphorus and mesoporous alumina on the activity of NiMo catalyst for hydrotreating of heavy gas oil was studied. To elucidate the role of EDTA and phosphorous on activity, the individual effects of EDTA and mesoporous alumina, and phosphorus and mesoporous alumina on the hydrotreating activity of heavy gas oil was studied. The corresponding γ-Al$_2$O$_3$ based NiMo catalysts were also synthesized and tested for hydrotreating of heavy gas oil for comparison. The phosphorus was impregnated using new method and the effect of method of phosphorus impregnation on activity was also studied. All synthesized catalysts were characterized by N$_2$ physisorption (BET), CO chemisorption, X-ray diffraction, XANES, H$_2$-TPR, NH$_3$-TPD, HRTEM and FTIR. All catalysts were tested in continuous fixed bed reactor at industrial conditions. The observed differences in catalytic activity were well explained using characterization techniques. Results show that the catalyst NiMoP/MesoAl$_2$O$_3$/(MCI) prepared by modified co-impregnation method showed best activity among all catalyst under study in this work.

2. Experimental

2.1. Materials

Ammonium dihydrogen phosphate, anhydrous ethanol and 67 wt.% nitric acid were obtained from Fisher Scientific, Saskatoon, Canada. The tri-block copolymer Pluronic P-123 (EO$_{20}$PO$_{70}$EO$_{20}$), aluminum isopropoxide (>98%), ammonium heptamolybdate (99.98%), Ethylene diamine tetraaceticacid (EDTA) (>99%), and nickel nitrate (99.99%) were obtained from Sigma-Aldrich, Edmonton, Canada. γ-Al$_2$O$_3$ was obtained from Alfa Aesar, Ward Hill, USA.

2.2. Support preparation

The mesoporous alumina was synthesized using method described in our previous work [8]. 12.24 g of aluminum isopropoxide was added to 40 ml of anhydrous ethanol in a container and stirred for 30 min at 40 °C. This material was then added drop wise to a solution of 6 g P123, 80 ml anhydrous ethanol, 6.5 ml HNO$_3$ and 2.5 ml distilled water. The resulting solution was stirred for 2 h at 40 °C and kept for hydrothermal treatment at 65 °C for 4.5 days. The material was then dried and calcined at 600 °C for 6 h with ramp rate of 0.5 °C/min. The material was named as MesoAl$_2$O$_3$.

2.3. Catalyst preparation

The catalysts containing phosphorus (P) were prepared by two methods, (i) sequential impregnation (SI) and (ii) modified co-impregnation (MCI). In SI method, 2.5 wt.% P was wet impregnated on mesoporous alumina using ammonium dihydrogen phosphate as precursor. The material was dried overnight at 110 °C and then calcined at 550 °C for 5 h with ramp rate of 1.0 °C/min. 13 wt.% molybdenum using ammonium heptamolybdate as precursor was then wet impregnated on the resulting material, followed by drying and calcination. The material was named as MoP/MesoAl$_2$O$_3$ (SI). On this material, 2.5 wt.% of nickel using nickel nitrate as precursor was wet impregnated, dried at 110 °C for 5 h and calcined at 550 °C for 5 h to obtain the catalyst NiMoP/MesoAl$_2$O$_3$(SI).

In MCI method, 2.5 wt.% P was wet impregnated on mesoporous alumina using ammonium dihydrogen phosphate as precursor. The material was dried overnight at 110 °C and then 13 wt.% molybdenum was wet impregnated and the material was again dried for 10 h at 110 °C. The resulting material was then calcined at 550 °C for 5 h with ramp rate of 1.0 °C/min. This material was named as MoP/MesoAl$_2$O$_3$ (MCI).