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Hydrotreating Behavior of Ni-Mo/SiO$_2$-Al$_2$O$_3$ for the Upgrading of Heavy Oil From Coal Liquefaction

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Abstract   *Ni-Mo/SiO$_2$-Al$_2$O$_3$ with different Si/Al molar ratios were synthesized, characterized, and evaluated for upgrading of heavy oil derived from the direct coal liquefaction process. The results indicated that the Si/Al ratio has a significant influence on the dispersion of MoS$_2$ and the hydrodenitrogenation activity. The larger Si/Al ratio causes the Ni-Mo/SiO$_2$-Al$_2$O$_3$ to form the larger MoS$_2$ crystallite. In the upgrading of coal-derived heavy oil, the hydrodenitrogenation and hydrodearomatization activities of Ni-Mo/SiO$_2$-Al$_2$O$_3$ (Si/Al: 5) reached 53 and 60%, respectively, which are significantly higher than that of Ni-Mo/Al$_2$O$_3$.*

Keywords   direct coal liquefaction, heavy oil, hydrodearomatization, hydrodenitrogenation

1.   Introduction

With fast increasing demand in liquid transportation fuels and limited petroleum resources, production of transportation fuels from direct coal liquefaction (DCL) technologies has been an important option to lessen the deficiency in petroleum supply. The challenge for product upgrading in DCL is to design a better catalyst, especially for feeds of high aromatic and nitrogen contents (Liu et al., 2010). Nitrogen compounds are certainly an inhibitor in hydrotreatment and cracking processes, and lead the catalysts used in the downstream secondary processing of these stocks to deactivate faster. The aromatic nature of DCL products is another challenge. Advanced refinery technologies, such as hydrodenitrogenation (HDN) and hydrodearomatization (HDA), must be implemented in order to fulfill the acceptable levels in petroleum refining.

   Some studies have been conducted to investigate the hydrotreatment of coal-derived products on various catalysts (Liaw et al., 1994; Sumbogo Murti et al., 2005). In order to improve the activity of hydrotreating catalysts, the modification of hydrotreating catalysts by using different support is more effective and cheaper since it has an immense effect on the catalytic activity. Generally, SiO$_2$-supported hydrotreating catalysts are known to

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be less active for hydrotreating reactions compared with conventional Al_2O_3-supported catalysts, but they have better textural properties and possess some acidity on the support. Therefore, it is felt that the combination of these two oxides as a support could have a synergistic impact on the hydrotreating and such properties make them potentially attractive particularly as a support of catalysts used for the hydrotreatment of heavy oil (Kunisada et al., 2005). Recently, the use of mesoporous solids based on silica and silica–alumina attracted increasing attention because of possible applications as acidic carriers with unique properties. In contrast to zeolites, their pores are larger, approaching several nanometers, which allow the entering and more facile diffusion of bulky molecules. At the same time, their acidic strength is weaker, thus avoiding the undesirable cracking and coking. Some applications of these materials in hydrodesulfurization/HDN have already been published (Daniela et al., 2009). However, no report is available on the hydrotreating of coal-derived liquid from pilot plant on the mesoporous SiO_2-Al_2O_3 supported catalysts.

In this investigation, Ni-Mo catalysts supported on mesoporous SiO_2-Al_2O_3 (Ni-Mo/SiO_2-Al_2O_3) with 15 wt% Mo and 5 wt% Ni were synthesized and evaluated for the upgrading of DCL heavy oil at simulated industrial conditions. Also, the results were compared with those of a Ni-Mo/Al_2O_3 catalyst.

2. Experimental

2.1. Samples

The Shengli coal-derived heavy oil (HO) used was generated from direct liquefaction of Shengli coal in a 0.1 ton/day continuous unit at China Coal Research Institute, Beijing. The DCL reactor was operated at 455°C and 19 MPa in the presence of Shenhua Fe-based catalyst. The HO used in this study was the narrow fraction of Shengli coal-derived liquid, in which the distillation temperature was in the range of 320–340°C. Al_2O_3 was provided by Fushun Petrochemical Co. (BET surface area of 185 m^2g^{-1}).

2.2. Catalyst Preparation

SiO_2-Al_2O_3 samples with various Si/Al ratios were prepared via the hydrothermal approach. Cetyltrimethylammonium bromide powder was dissolved in deionized H_2O and stabilized at 35–40°C. Then NaOH solution was added. The mixture was stirred vigorously for 5 min. The required amounts of tetraethyl orthosilicate and aluminum citrate were added to the above solution and the gel was continuously stirred for 1 h at 35°C. The molar composition of the gel was SiO_2:(0.4–0.04)Al:0.6 NaOH:0.4CTAB:95H_2O. Then the synthesized gel was transferred to a Teflon-lined autoclave and heated under static conditions at 110°C for 72 h. The solid product was then cooled down to room temperature, filtered, and washed thoroughly with deionized H_2O and dried at ambient temperature. After that, the samples were calcined at 550°C under the flowing air for 5 h. The calcined samples are designated as SA-m, where m denotes the Si/Al ratio.

The loading of Ni-Mo was carried out by incipient wetness impregnation of the SiO_2-Al_2O_3 or Al_2O_3 support using mixed solutions of ammonium heptamolybdate and nickel citrate. The impregnated sample was dried and calcined at 500°C for 3 h. These calcined precursors were then sulfided at 400°C with a CS_2/H_2 gas (10/90%, 60 ml/min) for 2 h followed by outgassing at the same temperature in the stream of H_2 for 1 h. The sample was then cooled to room temperature and passivated in the stream of N_2 for 6 h. The prepared Ni-Mo catalyst contains 5 wt% Ni and 15 wt% Mo.

2.3. Catalyst Characterization

Brunauer-Emmett-Teller (BET) surface area of the sulfided catalyst was determined by nitrogen adsorption at $-196°C$ using an ASAP2000 volumetric adsorption analyzer (Micrometrics, Norcross, GA). All the samples were degassed at $150°C$ for 12 h before the measurement.

X-ray diffraction patterns (XRD) of sulfided catalysts were obtained on a Rigaku computer-controlled D/max $2500×$ using Cu-Kα as the radiation source.

2.4. Catalyst Performance Test

The hydrogenation experiments of HO were carried out batch-wise in a 30-ml tubing reactor shaken vertically, which simulates typical online hydrotreating conditions for heavy liquids in DCL with an initial H_2 pressure of 5 MPa and a temperature of $400°C$. An amount of 3.0 g of HO was charged into the reactor together with 0.15 g of sulfided catalyst. After loading the sample, the reactor was sealed and flushed three times with hydrogen followed by turning the system to the desired initial pressure of 5 MPa H_2. The reactor, agitated vertically at 120 rpm, was submerged into a eutectic salt bath, which had been heated to the desired temperature and maintained for 60 min. After the reaction, the reactor was quenched to ambient temperature in a water bath before the overhead pressure in the reactor was released slowly. The liquid and catalyst in the reactor were removed and separated by centrifuge.

2.5. Products Analyses

Nitrogen analysis was performed using an Elementar Vario EL III. The liquid samples in elemental analysis were sealed in the capsule. Air in the capsule was forced out of the capsule via a gas stream of oxygen. The mean blank values of several samples were subtracted for evaluation.

Aromatic distribution analysis was carried out on a Shimadzu LC-2000 high performance liquid chromatography with an UV detector ($\lambda = 254$ nm). A Sepax NH_2 (30 cm length, 0.8 cm i.d.) separation column was operated isothermally at $25°C$. Hexane was used as the mobile phase with a flow rate of 1.2 ml/min. The identification of aromatic components (biaromatic and triaromatic) was carried out by the retention time of selected representative components of the mono-, di-, and triaromatic groups (toluene, naphthalene, anthracene, and phenanthrene).

3. Results and Discussion

3.1. Catalyst Characteristics

3.1.1. BET Surface Area, Pore Volume, and Pore Size Distribution. The BET surface area, pore volume, and mean pore radius of the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts are shown in Table 1. The surface area and pore volume of the SiO$_2$-Al$_2$O$_3$ supports were in the range 44.5–71.8 m^2/g and 0.138–0.126 cm^3/g, respectively. Ni-Mo/SA-100 had the smallest surface (about 44.5 m^2/g) compared to Ni-Mo/SA-5 and Ni-Mo/SA-50 samples, which is caused by the difference of the pore size of the samples.

The N$_2$ adsorption-desorption isotherms of the sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts are shown in Figure 1. All the sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts exhibited the typical

Table 1
Textural properties of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts

Catalyst	Surface area, m^2/g	Pore volume, cm^3/g	Mean pore radius, nm
Ni-Mo/SA-5	66.5	0.132	7.9
Ni-Mo/SA-50	71.8	0.138	7.7
Ni-Mo/SA-100	44.5	0.126	11.3

type IV isotherms, which exhibit the condensation and evaporation step characteristic of the mesoporous materials. The pore diameter distribution curves of the samples are shown in Figure 2. It clearly shows that the sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts exhibit bimodal distributions of the pore size with a specific range (3–12 and 12–100 nm, respectively).

3.1.2. XRD. Figure 3 shows the XRD patterns of the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts. The broad hump (at 2 Theta: 18–30°) of amorphous silica is clearly noticeable for all of the samples. The XRD patterns of the sulfided Ni-Mo/SA-5 and Ni-Mo/SA-50 catalysts displayed very weak XRD peaks of the hexagonal phase of MoS$_2$. But for Ni-Mo/SA-100, the MoS$_2$ phases can be confirmed and the intensity of MoS$_2$ is significantly higher than that of Ni-Mo/SA-5 and Ni-Mo/SA-50 catalysts. These results indicate that the addition of Al promotes the dispersion of MoS$_2$. Also, Massoth et al. (1994) and Rana et al. (2003) found that the dispersion of molybdenum decreased with the increase of SiO$_2$ content in the support.
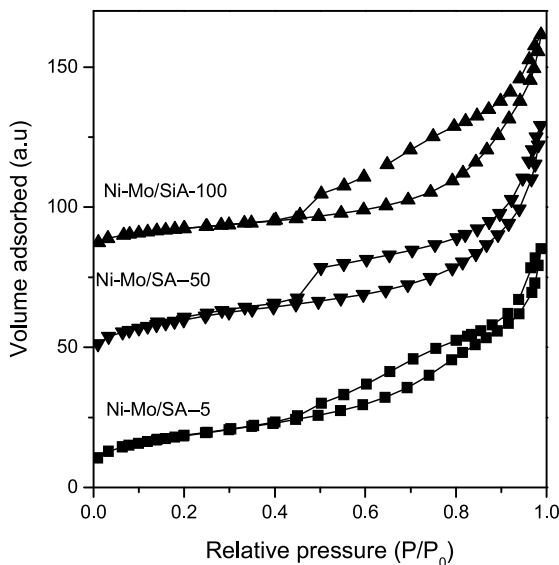

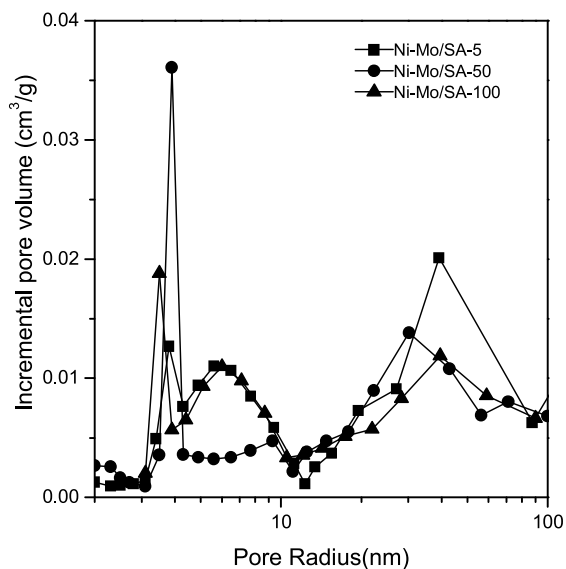**Figure 1.** The nitrogen-adsorption/desorption isotherms of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.

Figure 2. The pore size distributions of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.

3.2. Activities Evaluation

3.2.1.   HDN. Figure 4 shows the HDN activities of the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts. It can be seen that the HDN conversions of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalyst were 53, 51, and 45%, respectively. This indicates that the HDN activity of Ni-Mo/SiO$_2$-Al$_2$O$_3$ decreased with the increase of the Si/Al ratio. The Si/Al ratio in the range of 5 to 50 has no significant effect on the HDN activity towards the hydrogenation
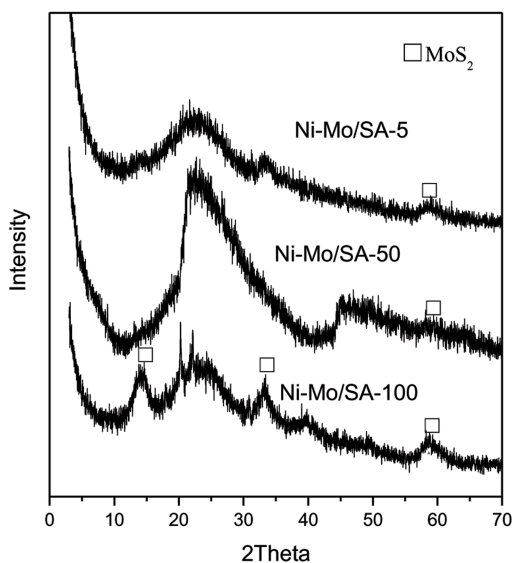

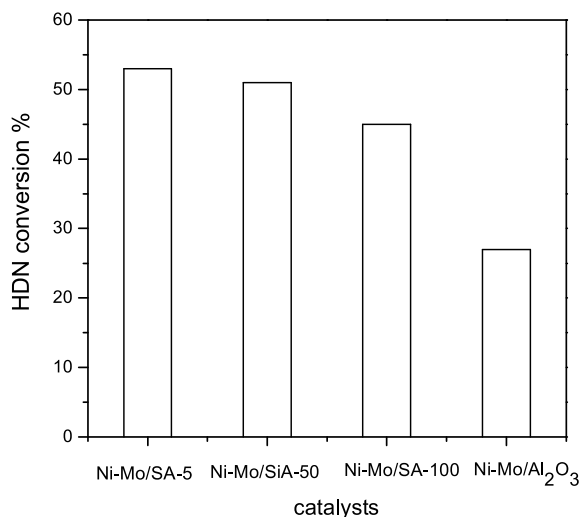**Figure 3.** X-ray diffraction patterns of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.

Figure 4. HDN conversion of HO over sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.

of coal-derived heavy oil. Also, it can be seen that the HDN activity of Ni-Mo/SA-5 is two times that of Ni-Mo/Al$_2$O$_3$.

3.2.2. HDA. Figure 5 shows the aromatic hydrocarbons distributions of the feedstock (HO) and its hydrogenation products on the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.
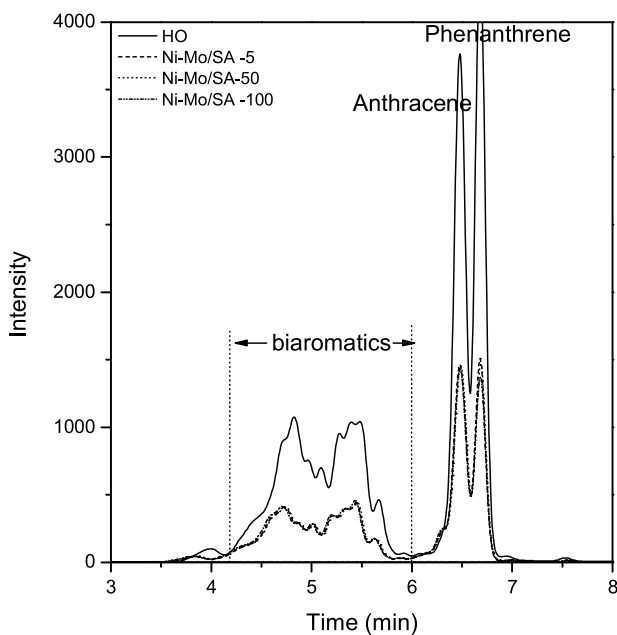

Figure 5. Aromatic distributions of the feedstock (HO) and its hydrogenation products on different Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts.

Table 2
HDA activities of the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts

	HDA	HDA (bi), %	HDA (tri), %	HDA (anthracene), %	HDA (phenanthrene), %
Ni-Mo/SiO$_2$-Al$_2$O$_3$	60	60	61	56	68
NiMo/Al$_2$O$_3$	50	51	50	49	55

The percentile decrease of aromatic content was determined and defined as HDA activity and calculated by the difference of the peak area of aromatic hydrocarbons before and after the hydrotreatment. It shows that HO mainly contained biaromatics (naphthalene and its derivatives) and triaromatics (anthracene and phenanthrene). After hydrogenation, the amounts of aromatics significantly decreased on all of the catalysts. Table 2 shows the HDA activities of the three sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts. It shows that the HDA activities of sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts were the same (about 60%). This result indicates that the Si/Al ratio has no effect on the HDA activity. Also, it can be seen that hydrogenation of HO on the sulfided Ni-Mo/SiO$_2$-Al$_2$O$_3$ results in a 56 and 68% decrease of anthracene and phenanthrene, respectively. The HDA activity increased for about 10% compared to that of Ni-Mo/Al$_2$O$_3$. The results above clearly show that the support indeed influences the activities and the support effect is different for different functionalities.

4.   Conclusions

Ni-Mo/SiO$_2$-Al$_2$O$_3$ catalysts with different Si/Al ratios have been prepared, characterized by N$_2$ adsorption-desorption and XRD, and evaluated for the hydrotreatment of coal-derived heavy oil. The XRD results show that the Si/Al ratio has a significant influence on the dispersion of MoS$_2$. The larger Si/Al ratio causes the Ni-Mo/SiO$_2$-Al$_2$O$_3$ to form the larger MoS$_2$ crystallite. Ni-Mo/SiO$_2$-Al$_2$O$_3$ has higher HDN and HDA activities for upgrading the coal-derived heavy oil compared to that of Ni-Mo/Al$_2$O$_3$.

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