Research Article

Hydrodesulfurization of Diesel Oils by MoS_2 Catalyst Prepared by *in situ* Decomposition of Ammonium Thiomolybdate

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Received October 26, 2007; Accepted January 2, 2008

Abstract

An unsupported MoS_2 catalyst was prepared by *in situ* decomposition of ammonium thiomolybdate (ATM) in the presence of water. The catalyst was characterized by XRD, scanning electron microscopy (SEM) and specific surface area measurements (BET, BJH). Its catalytic activity was evaluated for the hydrodesulfurization (HDS) of diesel oils (straight run gas oil, SRGO and light cycle oil, LCO). Selected refractory sulfur compounds: benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in oils were investigated. The high catalytic activity resulted from the large surface area of the catalyst due to water addition. Reactivity order of the sulfur compounds were determined. The results showed that the reactivity order in SRGO which contains nitrogen content is different from that in LCO. This reveals that matrix effect of the oil has some influences on the reactivity of the sulfur compounds.

Key Words: Ammonium thiomolybdate; Diesel oils; Hydrodesulfurization

Introduction

Stringent environment regulations are exerting pressure to reduce the maximum allowance sulfur content in diesel. Many countries have issued regulations to reduce the sulfur content of gasoline to 15 ppmw (Song, 2000). The current hydrotreating technology is difficult to reduce some refractory sulfur compounds, these are alkyl dibenzothiophenes and alklyl substituents on 4- and/or 6- positions (Ma et al., 1996).

Transition metal sulfides are the optimal catalysts to carry out the hydrogenation and hydrogenolysis, particularly, molybdenum and tungsten sulfides (Chianelli, 1984). In 2001, ExxonMobil, Akzo Nobel and Nippon Ketjen introduced a new unsupported catalyst called NEBULA. It is a Mo-W-Ni trimetallic catalyst with three times better than any other hydrotreating catalysts available (Soled et al., 2001).

Unsupported transition metal sulfide catalysts have been prepared by different methods, including comaceration (Hagenbach et al., 1973), homogeneous sulfide precipitation (Candia et al., 1982). These methods require an activation step using a H_2/H_2S mixture. This resulted in different activity of the catalyst due to heating conditions and reacting atmosphere (Zdrazil, 1988). Ammonium thiomolybdate is a well-known precursor for MoS_2 catalyst via thermal decomposition (Kalathod and Weller, 1985). By *in situ* activation method, the thiosalt precursor was decomposed directly in an autoclave in the presence of a hydrocarbon solvent to yield MoS_2 with high surface area (Alonso et al., 2000; Alonso et al., 2002). Comparative study of MoS_2 catalysts prepared by *ex situ/in situ* activation of ammonium and tetraalklylammonium thiomolybdates was reported (Pecoraro et al., 1985; Alvarez et al., 2004). In our previous work, high surface area MoS_2 and bimetallic catalysts were synthesized *in situ* from ammonium thiomolybdate or tetrabutylammonium thiomolybdate in the presence of decalin and water. They showed improved activity for the hydrodesulfurization (HDS) of refractory model sulfur compounds: dibenzothiophenes (DBT) and 4, 6-dimethylbenzothiophenes (4,6-DMDBT) (Trakarnpruk and Seentrakoon, 2007).

The use of a model system simplifies the quantification of the sulfur compounds. The hydrocarbon and nitrogen matrix of the model feed, which also plays an important role in HDS, was very different from the real feeds encountered under industrial hydrotreating conditions. Therefore, the model compound studies could not fully capture the interaction between different types of hydrocarbons and compounds present in a real feed. The study of real feed should provide more appropriate information.

Therefore, in this work, the MoS_2 catalyst prepared by *in situ* decomposition of ammonium thiomolybdate precursor in the presence of water was used for the HDS of real diesel feeds. The studied diesel oils are straight run gas oil (SRGO), directly obtained from atmospheric distillation of crude oil and light cycle oil (LCO), produced in the fluid catalytic cracking unit (FCC). Percentage conversion of selected refractory sulfur compounds (benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene) in both oils were also determined.

Experimental Procedures

Chemicals and apparatus

Ammonium thiomolybdate (ATM),benzothiophene and dibenzothiophene were purchased from Fluka, and 4,6-dimethyldibenzothiophene from Aldrich. All of the other reagents were reagent grade and used as received. Straight run gas oil (sulfur 6100 ppm) and light cycle oil (sulfur 310 ppm) were donated from Thai Oil Plc., Thailand.

The surface area was measured in a Quantachrome Autosorb-1 nitrogen adsorptometer by nitrogen adsorption at -196°C using the BET method. The samples were outgassed in vacuum at 250°C before adsorption of nitrogen. The pore size distribution was obtained from the desorprtion isotherm following the Barrett-Joyner-Hallenda (BJH) method.

The X-ray diffraction patterns were obtained on a Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer with Cu $K\alpha$ radiation operating at 43 kV and 30 mA. The diffractograms were analyzed using standard JCPDS files.

Scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray mapping were performed using JEOL JSM-5800LV for the morphology and elemental analysis.

Quantitative analyses of the selected sulfur compounds were performed by Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25µm film thickness) CP-5 capillary column and by GC-MS using Varian, Star 3400CX and mass spectrometry Varian, Saturn 4D. The GC response factor for each compound was determined using pure compounds. The GC separation was performed under the following conditions: helium as carrier gas, column temperature programmed from 40 (1 min) to 320°C (1 min) at a rate of 5°C/min, injector in split mode at temperature of 270°C (split ratio of 1:2). The detector is set at 300°C. The internal standard for GC is 2-bromoethyl benzene.

Total sulfur in oil feeds before and after the hydrodesulfurization was determined by SISONS energy-dispersive X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method). Aromatic contents of the feeds were determined by GC-MS method. The amount of nitrogen was determined using ASTM D2896.

Properties of oil feeds

Properties of oil feeds (light cycle oil, LCO and straight run gas oil, SRGO) used in this work are compared as shown in Table 1. The results show that SRGO contains higher sulfur content and aromatics than LCO. Its nitrogen content is 80 ppm. Sulfur is present in different organic structures: mercaptans, aliphatic sulfides, cyclic sulfides, and thiophenic compounds. In this work, only some refractory sulfur compounds are monitored (BT, DBT and 4, 6-DMDBT). Their contents cover about 30% of the total sulfur in oils.

Table 1 Properties of real oil feeds

Property	Light cycle oil (LCO)	Straight run gas oil (SRGO)
Total sulfur (ppm)	310	6100
Total nitrogen (ppm)	-	80
Aromatics (%wt)		
monoaromatic	5.0	25.0
diaromatic	-	3.8
polyaromatic	-	0.4

In situ generation of MoS_2

In a Parr Model 4842 high-pressure batch reactor (300 mL) shown in Fig. 1, the catalyst precursor, ATM (0.52 g, 2.0 mmol), decalin (50 mL) and water (4 mL) and were loaded, then the reactor was pressurized with hydrogen to 30 atm. Temperature was increased to 350 °C. The stirring speed was kept at 600 rpm for 1 h. The as-formed catalyst was filtered and dried at 120°C.

Catalytic activity

The HDS reactions were performed in the same reactor as above. The reactor was loaded with ATM (0.52 g, 2.0 mmol), water (0-4 mL) and oil (SRGO or LCO, 50 mL). The reactor was purged three times with hydrogen gas and then pressurized to 30 atm. Temperature was increased to 350°C. The stirring speed was kept at 600 rpm. At this stirring speed, reaction rates were free of external mass transfer limitations. After 90 min, the catalysts were separated from the reaction mixture by filtration, washed with isopropanol and dried. The quantities of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in oil before and after reactions were measured using GC-FID. Total sulfur in oil was analyzed by XRF.

In other experiments, effect of matrix (nitrogen compoundscontained in oil) was investigated. Various amount of pyridine (a model nitrogen compound, 20 and 40 ppm) was also added to SRGO. The reaction was performed using the same reaction conditions as mentioned above.

The catalyst before and after the HDS reaction was characterized by XRD, BET, EA and SEM.

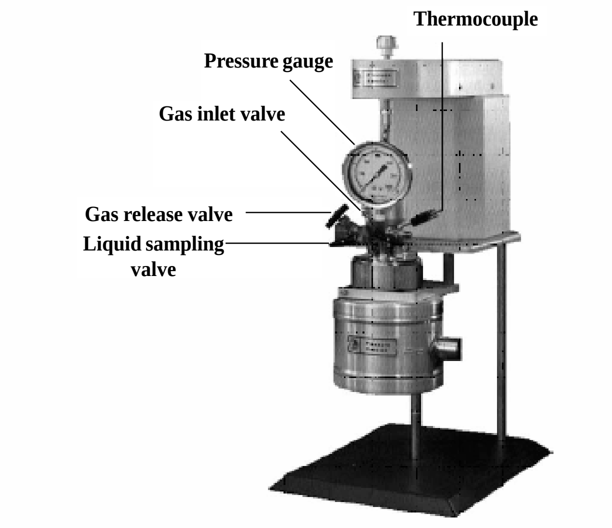

Figure 1 High pressure batch reactor used for the *in situ* decomposition of ammonium thiomolybdate and for hydrodesulfurization.

Results and Discussion

Catalyst characterization

The MoS_2 catalysts were prepared by *in situ* decomposition of ATM precursor in decalin with addition of water, as shown in equation 1.

$$(NH_4)_2MoS_4 \rightarrow 2NH_3 + H_2S + MoS_2 + S \qquad \text{(eq.1)}$$

The occurrence of MoS_2 was confirmed by the XRD technique, the XRD pattern shows MoS_2 phase (JCPDS-ICDD 3701492, 2θ (Å) = 14 (002), 33 (100), 40 (103) and 58 (110) (Song et al., 2000). The XRD pattern of the catalyst after the HDS reaction shows less crystallinity.

Specific surface areas, total pore volume of the *in-situ* prepared MoS_2 are determined using BET. The catalyst prepared in the presence of water shows high surface area of 544 m^2/g and pore volume of 1.16 cm^3/g. It was proposed that water helps dispersion of the precursor droplets in decalin under agitation (Trakarnpruk and Seentrakoon, 2007). Specific surface area, total pore volume as well as elemental analysis (EDX) of the MoS_2 catalyst before and after HDS reactions are reported in Table 2. The surface area and pore volume of the catalyst after HDS reaction decreased considerably to 332 m^2/g and 0.63 cm^3/g, respectively. This might be attributed to sintering of MoS_2 crystallites. From EDX analysis, it shows the slight decrease of S/Mo ratio from 1.7 to 1.6. On the other hand, C/Mo ratio was increased from 5.9 to 7.1, the carbon detected in the catalyst before the HDS comes from decomposition of decalin which was used as solvent. This reveals contribution of decalin in the preparation of MoS_2 catalyst by *in-situ* decomposition of ATM. The carbon increased in the catalyst after the HDS is derived from oil.

The adsorption-desorption curve of catalyst (shown in Figure 2) corresponds to type IV isotherm with desorption curves characteristic of mesoporous materials. The desorption Barrett-Joyner-Hallenda (BJH) pore size distribution (shown in Figure 3) demonstrates the pore size distribution of 3-7 nm with mean pore size of 4.7 nm.

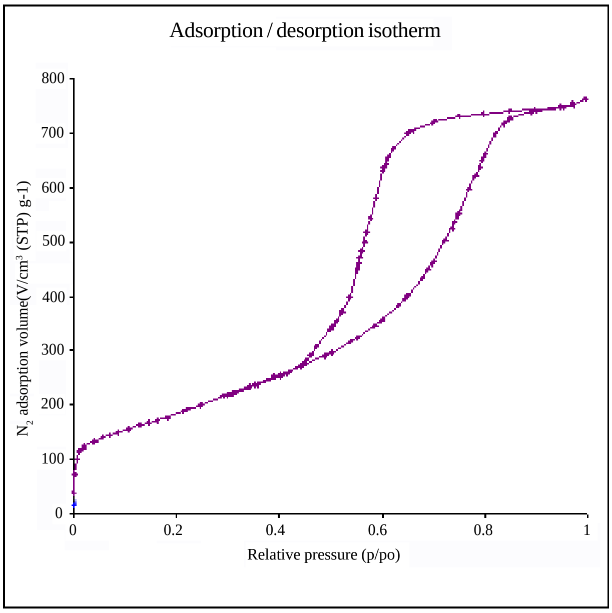

Figure 2 Adsorption-desorption isotherm of the MoS_2 catalyst.

Scanning electron microscopy (SEM) of the MoS_2 catalyst (Figure 4) reveals a highly porous and rough surface. The water addition increases dispersion of MoS_2 generated from ATM precursor since it is insoluble in oil. The surface of the catalyst after the reaction is less porous.

Table 2 Specific surface area, total pore volume and elemental analysis of the catalyst before and after HDS reaction

	Specific Surface area (m^2/g)	Total Pore volume (cm^3/g)	S/Mo (EDX)	C/Mo (EDX)
Before HDS	544	1.16	1.7	5.9
After HDS	332	0.63	1.6	7.1

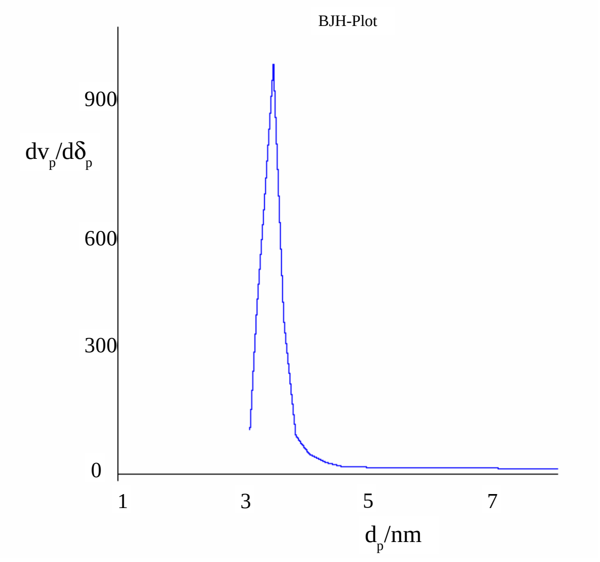

Figure 3 BJH pore size distributions of the MoS_2 catalyst.

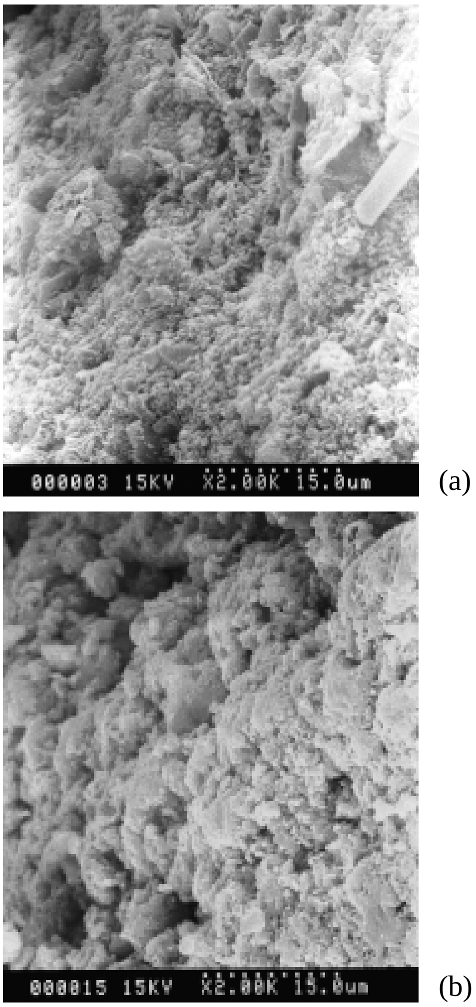

Figure 4 SEM micrographs of the MoS_2 catalyst (a) before HDS (b) after HDS

Catalytic activity

The HDS of oil feeds was investigated using MoS_2 catalyst prepared *in situ*. It should be mentioned that this reaction conditions are not optimized. The relative activity order of several sulfur compounds is studied, the results shown in Table 3. Percentage conversion of total sulfur is calculated from difference between original and remaining amount of sulfur which were determined by XRF. Percentage conversion of each sulfur compound was determined by GC analysis.

For LCO, the reactivity order of the sulfur compounds is: BT > DBT > 4,6-DMDBT. This trend is previously mentioned in the literature (Laredo and Cortes, 2003). The poor reactivity of 4,6-DMDBT is attributed to the steric hindrance of the methyl groups, which makes the sulfur atom inaccessible to the active sites of the catalysts (Kabe et al., 1999).

For SRGO, the reactivity order of sulfur compounds is: BT > 4,6-DMDBT > DBT. This is similar to the result reported on the reactivities of various sulfur compounds in diesel fuel (Song and Saini, 1995). The SRGO used in this work contains nitrogen and high amount of aromatics. The matrix effect of these components might be responsible for this reactivity order. However, the inhibition of organic nitrogen compound on the HDS was reported, and its effect is pronounced for the HDS of 4,6-DMDBT (Sano et al., 2004; Yang et al., 2005). To prove this, pyridine (a model nitrogen compound) was added into SRGO before HDS was performed. It was found that under the reaction conditions used in this work, percentage conversion of DBT in SRGO was decreased with the increasing of added pyridine (Table 4). Therefore, the results obtained in this work which reveals the higher activity of 4,6-DMDBT than DBT cannot be accounted from the coexistence of nitrogen in the SRGO. It might be resulted from the higher amount of aromatics. The study on this effect should be continued.

Table 3 % Conversion of sulfur compounds in SRGO and LCO

		%Conversion			
Feed	Water (mL)	Total Sulfur	BT	DBT	4,6-DMDBT
SRGO	0	35	65	25	25
	2	62	67	41	55
	4	70	70	50	60
LCO	0	36	68	25	28
	2	65	68	45	43
	4	70	70	55	50

Conditions: oil 50 mL, ATM 0.52 g, 350°C, 30 atm H_2, 90 min.
BT (benzothiophene), DBT (dibenzothiophene), 4,6-DMDBT (4,6-dimethyl-dibenzothiophene)

Table 4 % Conversion of DBT in SRGO in the presence of pyridine

Pyridine (ppm)	DBT (%conversion)
0	50
20	24
40	16

Conditions: SRGO 50 mL, ATM 0.52 g, 350°C, 4 mL water, 30 atm H_2, 90 min.

Conclusions

The MoS_2 catalyst prepared *in situ* from the decomposition of ammonium thiomolybdate (ATM) in the presence of water has high surface area, it is efficient for hydrodesulfurization of gas oils. 70% Conversion of total sulfur can be obtained in both oils at the reaction conditions of temperature 350°C, hydrogen pressure 30 atm in 90 min. reaction time. The reactivity orders of the sulfur compounds in straight run gas oil (SRGO) and in light cycle oil (LCO) are in different trend, which might be due to coexistence of higher amount of aromatics in SRGO.

Acknowledgements

The authors appreciate support from Graduate School, Chulalongkorn University and oil feedstocks from Thai Oil Plc., Thailand.

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