

Catalytic Nature of MoS₂ Fine Particles Prepared by Mechanical Milling for Hydrotreatment of Petroleum Fuel Oil

Masato Kouzu*, Kunio Uchida, Yasunori Kuriki, and Fumikazu Ikazaki

*National Institute of Advanced Industrial Science and Technology, 1-1-1, Higashi, Tsukuba, Japan
 Fax: 81-29-861-4763, e-mail: m-kouzu@aist.go.jp

Fine particles of molybdenum-sulfide (Mo-FP) were prepared by mechanical milling in order to study modifying catalyst for the hydrodesulfurization (HDS) of diesel fuel. Mo-FP was more active than the conventional HDS catalyst, alumina-supported cobalt-molybdenum sulfide (CoMo/Al), in converting 4,6-dimethyldibenzothiophene (4,6-DMDBT) as a model compound for the ultra-deep HDS of diesel fuel. This was due to its enhanced activity in catalyzing the hydrogenative HDS route, in which the aromatic ring was hydrogenated before scission of the C-S bond. This was in contrast with the CoMo/Al. However, the Mo-FP was unable to reduce the residual sulfur content lower than the CoMo/Al in the HDS reaction of real gas-oil feedstock using a down-flow tubular reactor. This was due to serious catalytic deterioration by the nitric inhibitor, carbazole, contained in the real feedstock. In order to study the reduction in the catalytic deterioration, some inorganic powders or carbons were used as the additive in the model reaction in the presence of carbazole.

Key words: Mechanical milling, Molybdenum-sulfide, Catalyst, Hydrodesulfurization, Diesel fuel

1. INTRODUCTION

The major purpose of hydrotreatment of petroleum fuel oil is to remove the sulfur species (hydrodesulfurization, HDS), and this results in a reduction in environmental damage and contributes to sustainable development. In the HDS of fuel oil, molybdenum sulfide (MoS₂) has been extensively used as the catalytic material. For MoS₂, whose crystalline structure is shown in Fig.1, the catalytic active site is classified into two types [1]. One is formed on the edge plane effective for scission of the C-S bond, and the other is the bottom or top of the edge effective for hydrogenation of the sulfur species. The latter active site is termed the "rim". Industrially, alumina-supported MoS₂ is used as the catalyst to enhance the dispersion. Further, MoS₂ on alumina is commonly promoted by cobalt or nickel to intensify the activity. The intensified activity accelerates the conversion of dibenzothiophene (DBT), which is one of the representative targets in diesel fuel, into biphenyl (BP), as shown in Fig.2. However, some alkyl-DBT, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), is difficult to be desulfurized over the industrial catalyst, which is a major obstacle in achieving ultra-deep HDS of diesel fuel (residual sulfur content: 10ppm) [2].

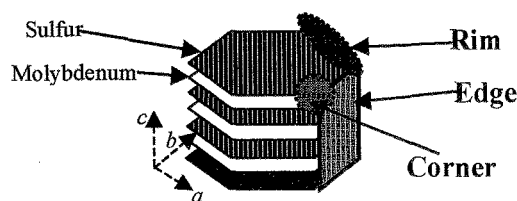


Fig.1 Crystalline structure of MoS₂

Because the slight amount of catalyzation with 4,6-DMDBT results from inhibited access between the active site and the reactant by its alkyl-groups, hydrogenation of the aromatic ring is effective in reducing the negative action of the alkyl-groups [3]. It had been reported that doping niobium is a profitable way to enhance the hydrogenation activity of alumina-supported nickel- molybdenum sulfide [4].

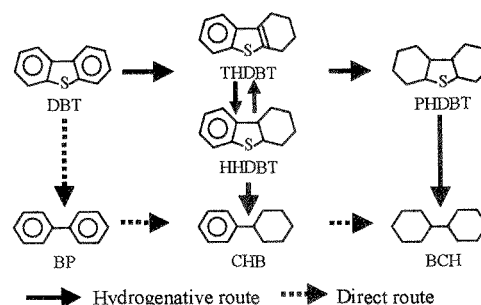


Fig.2 HDS reaction pathway for DBT

We found that fine MoS₂ particles prepared by mechanical milling provided considerably enhanced hydrogenation activity for 1-methylnaphthalene (1-MN) [5]. Due to the enhanced hydrogenation activity, fine MoS₂ particles were active in desulfurizing 4,6-DMDBT [6]. The mechanical milling turned bulk MoS₂ raw material into fine particles with a disordered crystalline structure. The disordered crystalline structure was caused by the synergistic effect of the large stresses and high temperatures generated in this process, which was concerned with increasing the active sites for hydrogenation [7]. Our previous results indicated that mechanical milling is a unique technique for improving

the catalysis, because it does not need the promoting metals. Further, we were able to tailor a catalyst pellets composed of fine MoS₂ particles prepared by mechanical milling to maintain higher activity [8]. In developing a discussion of our unique catalyst, it is necessary to examine the HDS activity in the actual reaction field, where the nitric constituents and the H₂S by-product act as the inhibitor [9-11].

In this study, the HDS reaction of real feedstock for diesel fuel was carried out over the MoS₂ pellets in a down-flow tubular reactor. HDS activity was evaluated for the MoS₂ pellet in comparison with the industrial catalyst. In addition, the reaction of the model feedstock was conducted using an autoclave in order to analyze the catalytic deterioration in the actual HDS reaction.

2. EXPERIMENT

2.1 Preparing the catalyst

As-received MoS₂ powder (6m²·g⁻¹) was ground for 20h using a media agitating mill with butanol as the milling additive in an argon atmosphere. The fine particles recovered after the milling (Mo-FP) were dried at 250 °C in a vacuum, followed by activity measurements and characterization of the particles.

The particles were characterized on the basis of their BET surface area, crystalline structure, and morphology. The BET surface area was measured using an N₂ adsorption unit (Quantachrome Autosorb-1-C). The crystalline structure was analyzed using the XRD pattern obtained from a Philips PW-1800. The morphology was observed with a scanning electron microscope (Hitachi S-800).

Before starting the HDS reaction of the real feedstock for diesel fuel, Mo-FP in powder form was turned into pellets using colloidal alumina-sol as the binder. The diameter of the pellets ranged from 0.5mm to 2.0mm. In the model reaction, Mo-FP was used in its original powder form.

On the other hand, the industrial HDS catalyst, alumina-supported cobalt-molybdenum sulfide (CoMo/Al), contained 3%Co-12%Mo in the original oxide precursor. This precursor had a diameter of 1mm and a length of 3mm. For the HDS reaction of the real feedstock, the original extrudate was cleaved horizontally into two or three pieces to form equivalent size to Mo-FP pellets. For the reaction of the model feedstock, the original extrudate was turned into a powder and passed through a 0.1mm sieve. Before the activity measurements, the catalyst precursor was sulfided at 400°C for 2h under an atmospheric gas flow comprising a 10%H₂S-H₂ mixture.

2.2 Activity measurements

A series of activity measurements were conducted to evaluate the HDS catalysis for Mo-FP.

The HDS reaction of the real feedstock for diesel fuel was carried out in a down-flow tubular reactor at 330-360°C with a liquid hourly space velocity (LHSV) of 1.5-3.0h⁻¹ under a hydrogen pressure of 5MPa at a hydrogen/oil volumetric ratio 250NL/L. These operating conditions approximate the industrial operation. The reactor was packed with 0.6ml of catalyst using silicon-carbide as the diluent to enhance

the oil's access to the catalyst in the narrow tube. After setting-up, the temperature was increased from ambient temperature to 330°C at a rate of 20°C/h in the flow of the real feedstock with 2% dimethyldisulfide (DMDS). The real feedstock, which was termed gas oil, contained 12,300ppm-sulfur and 120ppm-nitrogen. The sulfur content of the processed oil was measured using an APS-35 analyzer.

The model reaction was carried out using an autoclave with a volume of 50ml. The feedstock was composed of DBT (2%), 4,6-DMDBT (0.2%), 1-MN (5%), and decane as the vehicle. The operating conditions were as follows: 3MPa of initially-charged hydrogen, 5ml of model feedstock, 30-50mg of catalyst, at 320°C for 0.5-2.0h. The liquid product was subjected to GCFID (Agilent6890) and GCMS (Agilent 6890GC+5973MSD) for calculating the HDS yield.

3. RESULTS and DISCUSSION

3.1 Particle characterization

The mechanical milling increased the surface area of the bulk MoS₂ from 6m²·g⁻¹ to 98m²·g⁻¹. The surface area of the Mo-FP did not decrease in pellet form (95m²·g⁻¹). For CoMo/Al, the surface area was 200m²·g⁻¹ in the sulfided extrudate.

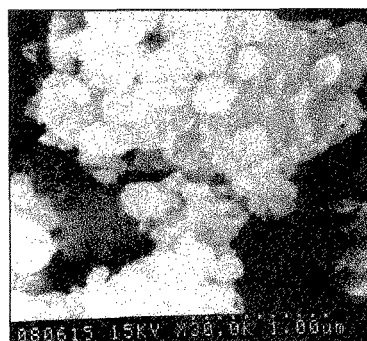


Fig.3 SEM image of Mo-FP

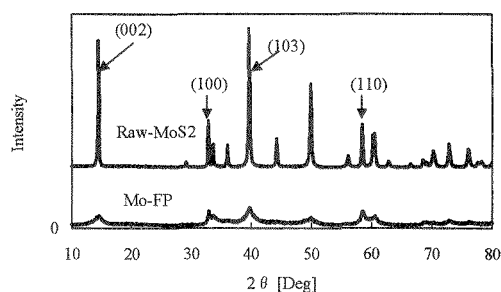


Fig.4 XRD pattern of Mo-FP

Fig.3 shows a SEM image of the Mo-FP observed at a magnification of 30,000. The agglomerate was formed of many fine flakes, whose length ranged from 50nm to 1000nm. It seemed that the mechanical milling exfoliated the MoS₂ bulk, and the vertically cleaving was responsible for the increase in the catalytic edge plane.

As shown in Fig. 4, the XRD patterns indicated that the mechanical milling made the crystalline structure of

the Mo-FP disordered. All the reflections representing MoS₂, for example: 14deg. (002), and 40deg. (103), were obviously broadened after the milling. This was similar to the micro-crystalline MoS₂ particles with enhanced hydrogenation activity prepared by sulfurization of ammonium tetra-thiomolybdate [12].

3.2 HDS activity

Table 1 shows the results of the preliminary test for evaluating HDS activity against Mo-FP, measured by the reaction of the model feedstock using an autoclave. As described above, Mo-FP was more active than CoMo/Al in the HDS of 4,6-DMDBT. On the basis of the unit surface, the rate constant calculated by 1st order kinetics was 14times larger for Mo-FP than for CoMo/Al. The kinetic ratio k_{HYD}/k_{DIR} was larger for Mo-FP than for CoMo/Al, which indicated that the catalytic selectivity was considerably weighted toward the hydrogenative route for Mo-FP. As Mo-FP catalyzed the hydrogenation of 1-MN more than CoMo/Al, the larger HDS rate constant for 4,6-DMDBT was possibly due to the enhanced hydrogenating activity.

Table 1 Kinetics of the model reaction measured at 320°C with 30mg of catalyst.

	Mo-FP	CoMo/Al
1-MN hydrogenation		
Overall k [h ⁻¹]	0.92	0.31
4,6-DMDBT HDS		
Overall k [h ⁻¹]	0.92	0.14
k_{HYD}/k_{DIR} [h ⁻¹]	100	11
DBT HDS		
Overall k [h ⁻¹]	0.67	0.77
k_{HYD}/k_{DIR} [h ⁻¹]	1.9	0.11

k_{HYD} : Rate constant for the hydrogenative reaction
 k_{DIR} : Rate constant for the direct reaction

Table 2 shows HDS activity in the reaction of real feedstock for diesel fuel, measured using a down-flow tubular reactor. Contrary to expectations based on the above preliminary test, the Mo-FP could not reduce the residual sulfur content more than CoMo/Al. Calculating the HDS rate constant per unit weight of catalyst at 330°C, Mo-FP (0.90 h⁻¹·g⁻¹) was less active than CoMo/Al (1.41 h⁻¹·g⁻¹). It was evident that Mo-FP was seriously deteriorated in the HDS reaction of the real feedstock. Commonly, carbonaceous materials originating from poly-aromatics in raw diesel oil do not seriously foul the catalyst under these HDS conditions. The serious catalytic deterioration was probably due to the inhibitors, nitrogen constituents, or H₂S by-product.

Table 2 Residual sulfur content in the HDS reaction of raw diesel oil, with LHSV of 1.5h⁻¹.

	Mo-FP	CoMo/Al
Sulfur content [ppm]		
330°C	273	194
340°C	66	64
350°C	27	28
360°C	15	7
(After 10days)	(47)	(7)

When the HDS operation was extended for 10days at 360°C, the accumulation of carbon deposit seemed to seriously deteriorate the Mo-FP. The sulfur content increased from 15ppm to 47ppm for the Mo-FP during the extended operation, whereas it was kept constant at around 7ppm for the CoMo/Al. The surface area of the Mo-FP decreased from 95m²·g⁻¹ to 28m²·g⁻¹ during the HDS operation, whereas there was no appreciable change in the crystalline structure on the basis of the XRD pattern. The surface area of the CoMo/Al did not decrease during the operation.

3.3 Analysis of catalytic degradation

In order to analysis the catalytic deterioration of the inhibitors, the model reaction was conducted in the presence of carbazole or DMDS. Carbazole is the representative nitric inhibitor contained in diesel fuel. DMDS was added in order to increase the H₂S content in the gas phase, because the model feedstock (3700ppm-S) was poor in sulfur compared to the real feedstock (12,100ppm-S).

Table 3 HDS activity in the presence of inhibitors, carbazole (130ppm-N in the liquid phase) and H₂S (1% in the gas phase), examined for the model reaction at 320°C for 2h with 30mg of catalyst.

a) Mo-FP			
Inhibitor	None	Carbazole	H ₂ S
4,6-DMDBT			
HDS product [%]	90.0	8.5	89.5
C ₂ -BP [%]	0.6	0.1	0.4
C ₂ -HYBP [%]	89.4	8.4	89.1
DBT			
HDS product [%]	92.6	33.5	90.8
BP [%]	25.9	22.3	14.4
HYBP [%]	66.7	11.2	76.4
b) CoMo/Al			
Inhibitor	None	Carbazole	H ₂ S
4,6-DMDBT			
HDS product [%]	32.5	9.9	25.1
C ₂ -BP [%]	2.7	0.8	0.9
C ₂ -HYBP [%]	29.8	9.1	24.2
DBT			
HDS product [%]	94.4	82.8	65.2
BP [%]	80.6	73.4	51.0
HYBP [%]	13.8	9.5	14.2

HYBP: Hydrogenated BP (CHB, BCH)

As shown in Fig.3, carbazole resulted in a considerable decrease in the HDS product for both the Mo-FP and the CoMo/Al. Between these catalysts, the decrease in the HDS product was more serious for Mo-FP than for the CoMo/Al. The serious decrease was due to the retardation of the hydrogenative HDS reaction that took priority over Mo-FP in the catalytic process, and which was validated by the data on the HDS of DBT. The major HDS product changed from HYBP (CHB and BCH) to BP in the presence of carbazole, as HYBP significantly decreased in comparison with BP.

The negative effect of H₂S was not as large as for carbazole. Interestingly, the HDS activity did not deteriorate at all for Mo-FP under the increased H₂S.

It was supposed that the nitric constituent was the determinative inhibitor in seriously deteriorating the HDS activity for Mo-FP.

As the hydrogenating site is characterized by an electron withdrawing, the nitrogen compound is strongly adsorbed on the hydrogenating site due to the basic Lewis nature [13]. The adsorbed nitrogen constituents stayed over the hydrogenating site, which inhibited the hydrogenative HDS, the major HDS reaction catalyzed for Mo-FP. It was supposed that controlling the adsorption of the inhibitor is effective in enhancing the nitrogen tolerance.

In order to look for a good adsorbent additive, a variety of materials were used in the model reaction in the presence of carbazole. The following materials were employed: magnesium oxide (solid base), activated clay (solid acid), γ -alumina (large surface polarity), active carbon (micro-porosity & low surface polarity), and carbon black (nano-particles). Table 4 shows the effects of the additive on the HDS activity. Among these additives, the carbons hardly enhanced HDS activity at all. On the other hand, all the inorganic additives increased the HDS activity, indicating that the chemistry of the additives was concerned with improving the adsorptive nature of the nitric inhibitor. However, further modification of the additive was necessary, because the improvement in the nitrogen tolerance was too low to achieve ultra-deep HDS. In fact, the improved HDS activity for Mo-FP was not as great as for the original activity with CoMo/Al. As none of the inorganic additives were as fine as the Mo-FP, it is supposed that the adsorptive potential was virtually swamped by the coarse powder. As the coarse powder is turned into nano-particles, it is thought to have resulted in further enhancement of the nitrogen tolerance of the Mo-FP, as shown in Fig. 6.

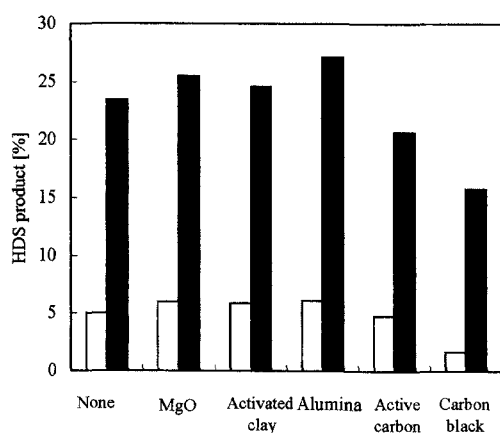


Fig.5 Effect of additives on the HDS activity in the presence of carbazole (130ppm-N), examined by the model reaction at 320°C for 2h over 50mg catalyst: □; 4,6-DMDBT, ■; DBT.

4. CONCLUSIONS

Fine particles of molybdenum-sulfide (Mo-FP) were prepared by mechanical milling in order to study modification of the catalyst for the hydrodesulfurization (HDS) of diesel fuel. Mo-FP was more active than the

conventional HDS catalyst, alumina-supported cobalt-molybdenum sulfide (CoMo/Al), in converting 4,6-dimethyldibenzothiophene (4,6-DMDBT) as a model compound for the ultra-deep HDS of diesel fuel. This was due to its enhanced activity in catalyzing the hydrogenative HDS reaction, in which the aromatic ring was hydrogenated before scission of the C-S bond. This catalytic selectivity was in contrast with CoMo/Al. However, in contrast, the Mo-FP could not reduce the residual sulfur content more than CoMo/Al in the HDS reaction of real feedstock for diesel fuel using a down-flow tubular reactor. This was due to serious catalytic deterioration by the nitric inhibitor, carbazole, contained in the real feedstock. The catalytic deterioration decreased with the inorganic additive responsible for positively controlling the adsorption of the inhibitor. However the positive effect of the additive was too low to achieve ultra-deep HDS since the additive was shaped as a coarse powder.

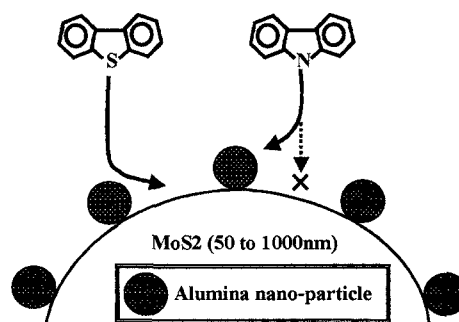


Fig. 6 Ideal representation of the fate of a nitric inhibitor in the presence of an adsorptive additive

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