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Utilization of Comminuted MoS_2 Fine Particles for Hydrodesulfidation of Diesel-Fuel

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Residual sulfur fraction in diesel-fuel is currently interpreted as a factor of air-pollution in urban area. With a view to improving the hydrodesulfidation (HDS) process for the diesel-fuel, we examined the HDS activity of comminuted MoS_2 fine particles through the reaction of dibenzothiophenes (DBTs), which are the representative sulfur compounds, using a batch-autoclave. The comminuted MoS_2 catalyzed the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) more than that of DBT in the reaction, but on the other hand 4,6-DMDBT was refractory over conventional HDS catalyst, CoMo/γ-Al_2O_3, as compared to DBT. Kinetic analysis on the Langmuir-Hinshlwood rate equation showed that 4,6-DMDBT was easily adsorbed on the catalyst as compared to DBT. These results indicate that the enhanced hydrogenation activity of the comminuted MoS_2 reduced hindrance for formation of a reactive intermediate for C-S bond scission following the adsorption by the methyl groups of 4,6-DMDBT. In activating MoS_2, dry comminution was more effective than wet comminution. The former comminuted MoS_2 was coarser powder with poorly crystalline structure, as compared to the latter.

Key word: comminution, molybdenum sulfide, catalyst, hydrodesulfidation

1. INTRODUCTION

In near future, residual sulfur content in diesel-fuel must be limited to significant low value compared with present regulation (500ppm) in order to prevent air-pollution in urban area. Because the future strict regulation on the residual sulfur content seriously makes cost to upgrade diesel-fuel increase, research on hydrodesulfidation (HDS) of diesel-fuel was recently activated. Most of the researches are based on the conventional HDS process, in which trickle bed hydrotreater packed with CoMo or NiMo/γ-Al_2O_3 extrudate is used and the improvement of the support or metallic component had been reported. [1]-[2]

It is well-known that dibenzothiophenes (DBTs) are refractory over the conventional HDS catalyst [3]. As the sulfur extrusion from alkyl-DBTs was dominated by the aromatic ring hydrogenation of the reactant, the future HDS catalyst satisfying the strict regulation on the residual sulfur content must necessitate enhanced hydrogenation activity. We have shown enhanced hydrogenation activity of mechanical comminuted MoS_2 fine powder in previous paper [4]. In this paper, we examined catalysis of the comminuted MoS_2 in the reaction of DBTs to improve the HDS process.

2. EXPERIMENT

2.1 Comminution of MoS_2

Commercially available MoS_2 powder was comminuted in a media-agitation mill with zirconia vessel under two different conditions. One was conducted with n-C_{10} vehicle for 50h, and the other under Ar of 0.1MPa to prevent the MoS_2 from oxidizing for 10h. The former comminuted MoS_2 was termed " WET ", and the latter " DRY ". In the latter comminution, a little quantity of butanol was added to prevent the fine particles from agglomerating.

Particle size distribution of the comminuted MoS_2 was measured by a centrifugal sedimentation photo-extinction method (Shimadzu SA-CP3). The particle morphology was observed with scanning electron microscope (SEM, Hitachi S-800). The crystalline structure was analyzed with X-ray diffraction (Phillips PW-1800).

2.2 Activity measurement

HDS activity of the comminuted MoS_2 was examined through the reaction of DBTs in a batch-autoclave. Feedstock for the above reaction was composed of dibenzothiophene (DBT) ,4,6-dimethyldibenzothiophene (4,6-DMDBT) as a reactant and dodecane vehicle. The reactions were carried out at 260~300℃ for 1h. The initial charge to the autoclave was 4g of feedstock, 3MPa of H_2 and 0.03~0.16g of the comminuted MoS_2. In order to elucidate the product selectivity of the comminuted MoS_2, the conventional HDS catalyst, CoMo/Al_2O_3, was employed for the reaction after the sulfidation in a stream of 10%H_2S/H_2 gas mixture at 400℃ for 2h. The employed conventional catalyst was termed " CoMo ".

The feedstock and liquid product were analyzed with GCFID (HP6890) and GCMS (HP5970) using a HP Ultra-1 capillary column.

2.3 Kinetic analysis

Langmuir-Hinshelwood kinetics for the reaction of DBTs with the comminuted MoS_2 was analyzed in order to examine the HDS mechanisms. Eq. (1) represents the Langmuir-Hinshelwood kinetics modified for the reaction.

$$r=[k\cdot K\cdot(C_{DBTs}/Cat.)]/[1+K\cdot(C_{DBTs}/Cat.)]^2 \qquad (1)$$

where r is the rate of the reaction; k is the rate constant of the reaction; K is the adsorption equilibrium constant of DBTs; C_{DBTs} is the initial amount of DBTs and Cat. is the amount of the comminuted MoS_2 employed. The rate of the reaction was calculated by multiplying a ratio of decrease in DBTs by the initial amount of DBTs .

By plotting an inverse of $[(C_{DBTs}/Cat.)/r]^{0.5}$ against (C_{DBTs}/Cat.), k and K were observed from the slope and intercept.

3. RESULT AND DISCUSSION

3.1 Properties of the comminuted MoS_2

Fig.1 shows the particle size distributions of comminuted MoS_2 under different conditions. The particle size distribution curve for WET shifted to the low value in comparison with DRY. This result corresponded to the SEM image of the comminuted MoS_2. Evidently, WET was finer powders than DRY.

In X-ray diffraction patterns of the comminuted MoS_2, Fig.2, the peaks representing MoS_2 was broader for coarser DRY than for finer WET, indicating that DRY had a poorly crystalline MoS_2 structure as compared with WET.

3.2 HDS activity and product selectivity

It has been reported that HDS of DBTs was progressive through two reaction paths reported, as shown in Fig.3 [3]. One was termed " direct sulfur extrusion ", at which DBTs is converted into biphenyls (BPs). The other was termed " hydrogenation sulfur extrusion ", at which DBTs is converted into cyclohexylbenzenes (CHBs) or bicyclohexyl (BCHs) following the aromatic ring hydrogenation. In the present reaction, hydrogenated derivatives of DBTs, THDBTs, HHDBTs, and PHDBTs remained.

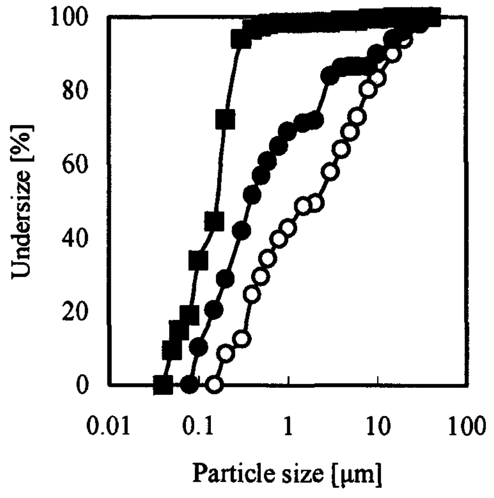

Fig.1 Particle size diameter of the comminuted MoS_2, ○; As received, ■; WET, ●; DRY

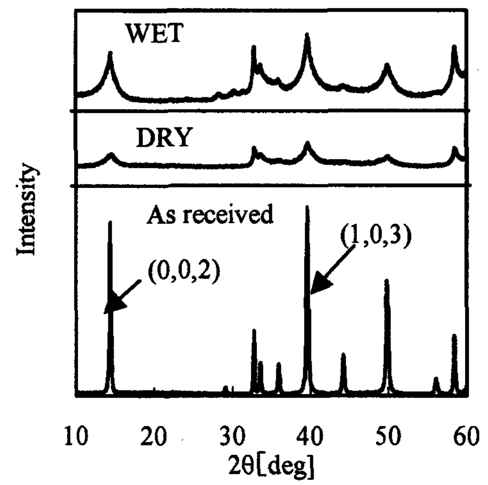

Fig.2 XRD patterns of the comminuted MoS_2

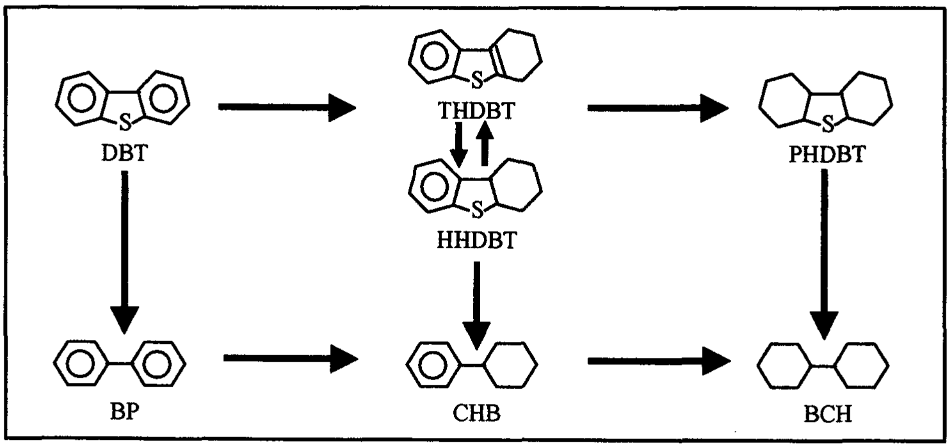

Fig.3 Reaction pathway in HDS of DBT

Fig.4 shows HDS product yield in the reaction of DBT. Primary, the effective comminuting procedure in activating MoS_2 was examined through the reactions with WET and DRY.

Total HDS product yield (○) was higher for DRY than for WET. It is evident that the dry comminution was more effective in activating MoS_2 for the HDS of DBTs than the wet comminution. DRY was coarser powder with more poorly crystalline structure than WET as described above. These results indicated that the distortion of crystalline structure was dominant in activating MoS_2 by comminution.

Enhancement of the total HDS product yield with increased catalyst/DBT ratio, not only for DRY but also WET, resulted from increase in the yield of CHB+BCH (▲). BP yield (●) for both DRY and WET was kept constant at all the catalyst/DBT ratios. It was appreciated that the comminuted MoS_2 catalyzed the hydrogenation sulfur extrusion in the HDS of DBTs.

The selectivity of the comminuted MoS_2 was elucidated through the reaction with DRY and CoMo.

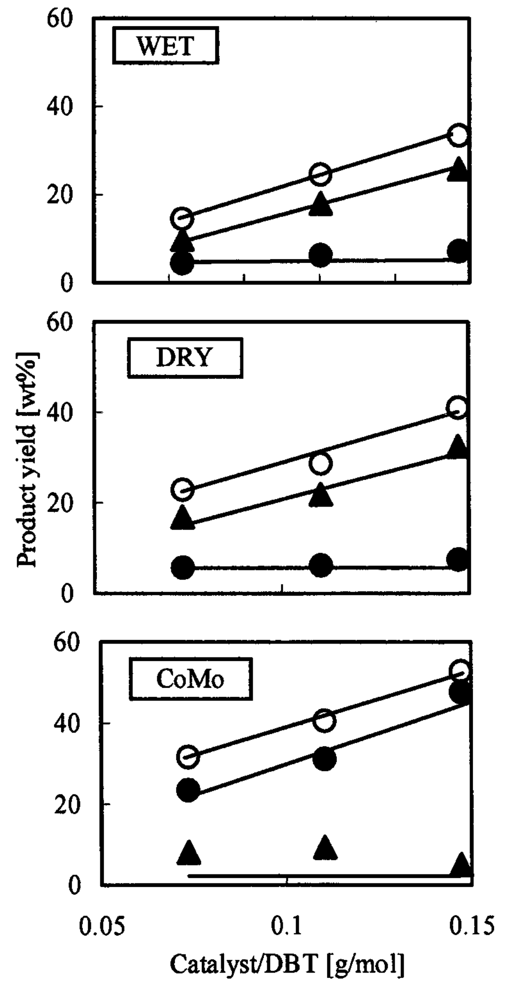

Fig.4 HDS product yields in reaction of DBT with WET, DRY, or CoMo at 300℃ for 1h in batch-autoclave charged H_2,of 3MPa ○; Total HDS products, ●; BP, ▲; CHB+BCH

Appreciable differences in the HDS product yield between these two catalysts were observed in Fig.4. For CoMo, the increased catalyst/DBT ratio resulted in an increase of BP yield, while CHB+BCH yield was kept constant at every catalyst/DBT ratio. These were inverse results as compared to the reaction with DRY. Evidently, the conventional HDS catalyst enhanced the direct sulfur extrusion in the reaction of DBTs.

Fig. 5 shows the percentages of HDS in the reaction of DBT/4,6-DMDBT mix feedstock with DRY and CoMo. For CoMo, the HDS percentage for 4,6-DMDBT was plotted below that for DBT at every catalyst/DBTs ratio. This represented 4,6-DMDBT being refractory over the conventional HDS catalyst. The refractory 4,6-DMDBT prevents the reduction of residual sulfur content in diesel-fuel from enhancing under current HDS process. Inversely, the HDS percentage was higher for 4,6-DMDBT than for DBT in the reaction with DRY. These results indicated that the comminuted MoS_2 was effective in making the residual sulfur content decrease.

3.3 Reaction kinetics

Kinetic analysis on the Langmuir-Hinshlwood rate equation helps to sufficiently understand the mechanisms on catalytic reaction. The reaction mechanism of DBTs over the comminuted MoS_2 was examined on the kinetic analysis. The reaction kinetics was analyzed on the percentage of residual DBTs in the present reaction.

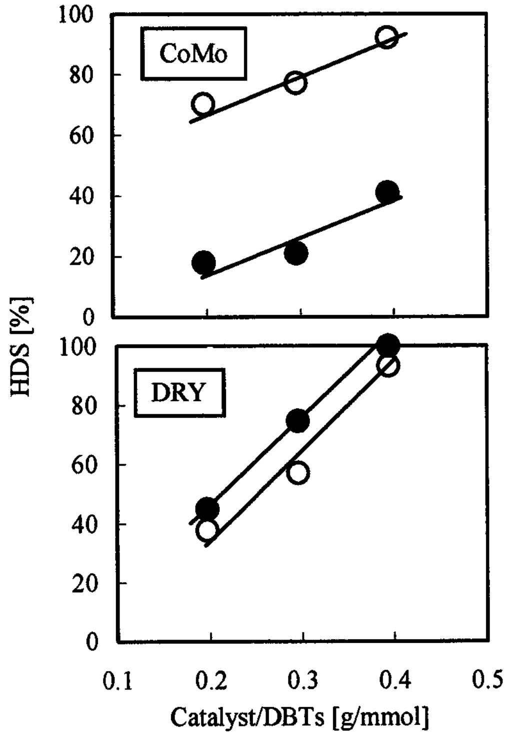

Fig.5 Comparison of percentage in HDS of DBT and 4,6-DMDBT between DRY and CoMo at 300℃ for 1h in batch-autoclave charged H_2 of 3MPa ○; DBT, ●; 4,6-DMDBT

Fig 6-(a) makes a comparison between DBT and 4,6-DMDBT for the rate constant, *k*, in the reaction with DRY, and Fig. 6-(b) for the adsorption equilibrium constant, *K*. Both of the *k* and *K* were plotted against the reciprocal absolute temperature in the every figure and were higher for 4,6-DMDBT than for DBT. The heat of adsorption, -*H*, corresponded to the order of the *K*, 4,6-DMDBT(31.3kJ/mol) > DBT(23.7kJ/mol). The order of the -*H* agreed with a report on the kinetic study for the conventional HDS catalyst [5]. It is evident that 4,6-DMDBT was easily adsorbed on the catalyst surface as compared to DBT. These results indicate that the reason why 4,6-DMDBT was refractory over CoMo compared to DBT is a hindrance for formation of a reactive intermediate for C-S bond scission following the adsorption The activation energy, *E*, was higher for DBT(59.0kJ/mol) than for 4,6-DMDBT(44.6kJ/mol). This was an inverse result to the kinetic report above referred. Since the sulfur extrusion from 4,6-DMDBT was progressive over the comminuted MoS_2, the hydrogenation of the aromatic ring resulted in the reduction of the hindrance. It is reasonable that the methyl groups of 4,6-DMDBT prevented the reactant from contacting the C-S bond scission site on CoMo. These results gave a reaction mechanism on 4,6-DMDBT shown in Fig.7. Fig.7 shows that the reactant was horizontally adsorbed on the catalyst surface, then it stood up and vertically contacted with the C-S bond scission site. The present mechanism was consistent with that in literature [5].

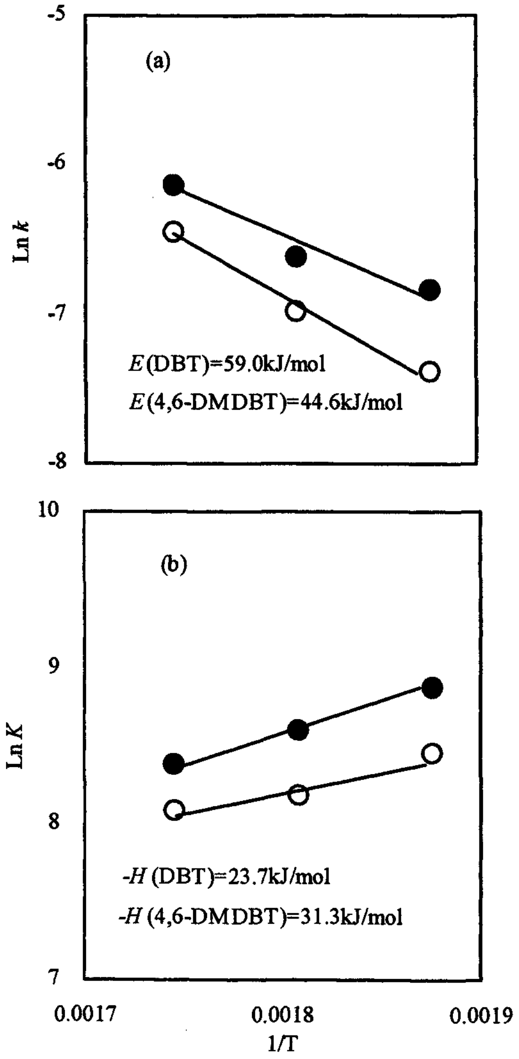

Fig.6 Comparison of the reaction rate constant and the adsorption equilibrium constant on Langmuir-Hinshelwood kinetics
(a) Arrhenius plot, (b) Van't Hoff plot
○; DBT, ●; 4,6-DMDBT

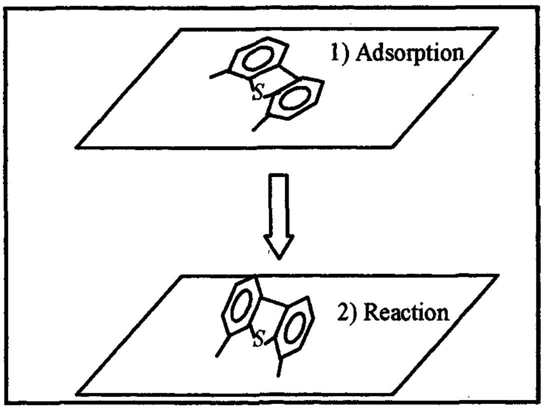

Fig.7 Reaction mechanism of 4,6-DMDBT On catalyst surface

4. CONCLUSION

HDS activity of the comminuted MoS_2 was examined through the reaction of DBTs using batch-autoclave. Although 4,6-DMDBT was refractory over the conventional HDS catalyst, CoMo/ γ -Al_2O_3, as compared to DBT, the comminuted MoS_2 catalyzed more to 4,6-DMDBT than to DBT. In HDS of 4,6-DMDBT, the hydrogenation sulfur extrusion, which represents desulfidation following the aromatic ring hydrogenation, was dominant. The kinetic analysis on the Langmuir- Hinshelwood rate equation showed that 4,6-DMDBT was easily adsorbed on the catalyst as compared to DBT, indicating that formation of a reactive intermediate for C-S bond scission following the adsorption was hindered in the reaction of 4,6-DMDBT over the conventional HDS catalyst. Since the hindrance was reduced in the reaction with the comminuted MoS_2, it is reasonable that the methyl-group of 4,6-DMDBT prevented the reactant from contacting with the C-S bond scission site.

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