Morphology, Dispersion and Catalytic Functions of Supported Molybdenum Sulfide Catalysts for Hydrotreating Petroleum Fractions

Hiromichi SHIMADA *

National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 1, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8561, JAPAN

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The relationships between the morphologies and dispersion of supported Mo sulfide catalysts and their catalytic functions evaluated by model test reactions are reviewed. The catalyst support had large effects on the morphologies through the electronic interaction and geometrical relationship between the catalyst and the support surface. High hydrogenation activities were obtained for Al2O3 supported catalysts due to high dispersion, whereas high hydrogenolysis activities were obtained for TiO2-supported catalysts due to the electronic interaction. Relatively large single-layered MoS2 structures were formed on the (110) γ-Al2O3 surface, whereas microclusters and multilayered MoS2 structures were more favorably formed on the (111) and (100) γ-Al2O3 surfaces. Multi-layered MoS2 structures had the edge-bonding orientation on anatase-TiO2 with an epitaxial relationship by sulfidation in H2S/N2. Single-layered MoS2 catalysts exhibited relatively hydrogenation-oriented function, whereas multi-layered MoS2 catalysts had relatively hydrogenolysis-oriented function. Steric hindrance affected the catalytic functions, particularly in hydrogenation that required η6 adsorption of aromatic rings. Long-term uses in hydrotreating caused growth of the MoS2 structures in the lateral direction, which decreased the number of active sites. Simultaneously, the aging caused deep sulfiding of the catalysts, which weakened the interaction with the support and increased the intrinsic activities of the catalysts.

Keywords
Hydrodesulfurization, Hydrogenation, Hydrocracking, Catalyst characterization, Catalyst deactivation

1. Introduction

Molybdenum sulfide catalysts have long been used for hydrotreating petroleum fractions. In most industrial uses, the catalysts contain nickel or cobalt as a promoter and are supported on porous materials such as alumina. Such promoters significantly enhance the catalytic activities of molybdenum sulfide catalysts, so the structures of the promoted catalysts, namely Ni-Mo (W) or Co-Mo binary sulfides supported on alumina, have been intensely studied for both scientific and practical interests. By 1980, at least three structural models1)–3) had been proposed as the active catalytic sites of the binary sulfide systems. In all the models, coordinatively unsaturated sites (CUS) of molybdenum (or tungsten) disulfide with a layered structure act as the active center for hydrosulfurization (HDS) or hydrogenation (HYD), although the function of the nickel or cobalt differs between the three models. Subsequently, the “Co(Ni)MoS” phase4)–5) has been widely accepted as the active catalytic center of the binary sulfide catalysts.

In the Co(Ni)MoS phase, Co or Ni atoms are located at the edges of the MoS2 sheets. The sulfur atoms bonded to the Co or Ni are more easily dissociated than those bonded to Mo and thus form highly active catalytic sites. In fact, the function of the Co or Ni atoms is not a catalyst promoter but as an active catalytic center. The common conclusions of the old structural models and the CoMoS model indicate that the dispersion and morphology of MoS2 structures on the catalyst supports are important factors to improve the catalytic performances of binary sulfide catalysts.

Our group has been studying the catalytic performances and structures of molybdenum sulfide-based catalysts, aiming at the development of high performance hydrotreating catalysts for heavy hydrocarbon feedstocks. During the course of the study, we found that the catalyst support species significantly affected the catalytic functions of the molybdenum sulfide catalysts. Therefore, we speculated that the morphology and dispersion of the molybdenum sulfide were controlled by the electronic interactions and geometric relationships between the catalysts and supports. The present review introduces a series of our studies on the relationship between the catalytic functions and the

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* E-mail: h-shimada@aist.go.jp

moldiphenyleneimine and dispersion of molybdenum sulfide catalysts, in particular the support effects.

Section 2 provides a brief introduction of the common experimental procedures, Section 3 discusses the structure-activity relationships of molybdenum sulfide catalysts supported on four types of metal oxide supports and Section 4 discusses the catalytic functions of γ-Al₂O₃ supported catalysts that are most commonly used in petroleum refining. The changes in the catalytic functions and dispersion of MoS₂ catalysts with Mo loading are discussed. In addition, Section 4 discusses the relationship between the morphologies of MoS₂ crystalites and geometrical structures of the γ-Al₂O₃ support surface. Section 5 applies the analytical method of the interface between catalysts and supports to TiO₂ supported catalysts that have recently shown high performances in industrial hydrotreating reactions. Section 5 also introduces the development of high-performance hydrocracking catalysts with TiO₂ doping based on our findings. Section 6 describes the changes in the morphology and dispersion of the MoS₂ crystallites of Co-Mo/Al₂O₃ catalysts during a commercial HDS run of vacuum gas oil (VGO) and accelerated aging tests. Finally, Section 7 provides a summary with reference to recent studies using scanning tunneling microscopy (STM).

2. Experiments

Typical experimental procedures used in our group are described here. Please refer to the original papers for the detailed experimental procedures and conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HCK of DPM</th>
<th>HYD of 1-MN</th>
<th>HDS of DBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Al₂O₃</td>
<td>2.9</td>
<td>2.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Mo/TiO₂</td>
<td>28.1</td>
<td>27.3</td>
<td>20.3</td>
</tr>
<tr>
<td>Mo/SiO₂</td>
<td>6.5</td>
<td>5.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Mo/MgO</td>
<td>0.0</td>
<td>0.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>

a) Each catalyst contained 10 wt% Mo as MoO₃.
b) Total conversion.
c) Yields of benzene and toluene.
d) Yields of 1- and 5-methyltetralins.
e) Yields of biphenyl and cyclohexylbenzene.
f) Ratio of cyclohexylbenzene to biphenyl.
g) Commercially available γ-Al₂O₃ with surface area (SA) of 170 m²/g and pore volume (PV) of 0.47 cm³/g.
h) Laboratory-prepared TiO₂ with SA of 66 m²/g and PV of 0.17 cm³/g.
i) Commercially available SiO₂ with SA of 266 m²/g and PV of 0.89 cm³/g.
j) Commercially available MgO with SA of 51 m²/g and PV of 0.16 cm³/g.

2.1. Catalyst Preparation

Unless otherwise noted, molybdenum sulfide supported catalysts were prepared by a conventional impregnation method using an aqueous solution of ammonium heptamolybdate, followed by drying at 383-523 K for 1 h, and calcining at 773-823 K for 1 h. The catalyst was then presulfided in a flow of 5-10 % H₂S/H₂ at 673 K for 1 h.

2.2. Evaluation of Catalyst Functions

Three catalyst evaluations were performed using model test reactions. To evaluate HYD function, the yields of 1- and 5-methyltetralin (MT) were measured in the reaction of 1-methylnaphthalene (1-MN). To evaluate hydrocracking (HCK) or hydrogenolysis function, the yields of benzene and toluene were measured in the reaction of diphenylmethane (DPM). To evaluate HDS function, the yields of biphenyl and cyclohexylbenzene were measured in the reaction of dibenzothiophene (DBT). All reactions were carried out in 50-mL batch-type autoclaves under high initial hydrogen pressure, typically 6.9 MPa. The reaction temperature ranged from 573 to 673 K depending on the activities of the catalyst, and similar to industrial hydrotreating temperatures.

2.3. Catalyst Characterization

The major techniques used for catalyst characterization were X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure spectroscopy (XAFS) and transmission electron microscopy (TEM). The XAFS and TEM analytical methods are described elsewhere.

3. Catalysts Supported on Four Types of Metal Oxides

Table 1 shows the results of catalytic activity tests of molybdenum sulfide catalysts supported on four types of metal oxides. The catalytic activities for each
reaction decreased in the order shown below.  
HC: TiO2 > SiO2 > Al2O3 > MgO  
HY: Al2O3 > TiO2 > MgO > SiO2  
HDS: TiO2 > SiO2 > Al2O3 > MgO  

The most striking difference was observed for HCK activity. The cracking of DPM to benzene and toluene was easily catalyzed over strong Brønsted acid sites such as those on HY zeolites, which yielded various products formed over molybdenum sul-

cides. In fact, the order of the catalysts for HYD of aromatic rings occurs via π bonding and requires at least two different active cata-

ytic sites, such as CUS and stable sulfur ions [1]. These findings indicated that the molybdenum sul-

side catalysts had two different catalytic functions, one for catalysis of HCK or HDS and the other for catalysis of active sites as those for hydro-

tonic sites, such as CUS and sta-

blization and requires at least two different active cata-

lytic sites, such as CUS and stable sulfur ions [12]. These findings indicated that the molybdenum sulfide catalysts had two different catalytic functions, one for catalysis of HCK or HDS and the other for catalysis of active sites as those for hydro-

lysis, namely coor-

dination unsaturated sites (CUS) of molybdenum sul-

fides. In fact, the order of the catalysts for HDS was the same as that for HCK.  

In contrast, the order of the catalysts for HYD of 1-MN was different from those for HCK and HDS. HYD of aromatic rings occurs via π bonding and requires at least two different active cata-

lytic sites, such as CUS and stable sulfur ions [1]. These findings indicated that the molybdenum sulfide catalysts had two different catalytic functions, one for catalysis of HCK or HDS and the other for catalysis of HYD and that the function depended on the support species. TiO2 support was the most active for HCK, whereas MgO was the least. Al2O3 was the most active for HYD, whereas SiO2 was the least. Note that the results of the catalytic activity tests in Table 1 cannot be applied directly to the support effects, because the physical properties, such as surface areas, of the supports were not the same as shown in the footnotes of Table 1.

Table 2 (10, 13) shows the characterization results of the supported molybdenum catalysts before and after sulfidation. Raman spectroscopic analysis of the sulfided catalysts indicated the formation of MoS2 micro-

crystals and detected few differences in the structures of the catalysts. XPS also showed similar spectra that were characteristic of MoS2, although the peak energies ranged from 228.4 to 229.0 eV. In contrast, Raman spectroscopic analysis of the oxide catalysts demonstrated evident differences between supported catalysts. The molybdate species were two-dimensionally dispered on the TiO2 and Al2O3 supports and relatively easily reduced, whereas molybdate species on the MgO support formed monomeric molybdate (MoO42–) with tetrahedral coordination that was relatively difficult to reduce. In contrast, three-dimensionally developed MoO3-like structure was formed on the SiO2 support. The EXAFS and XANES results supported the above findings and further indicated differences in the structure between the TiO2 and Al2O3 supported molybdate species at low loading. Octahedral molybdate was formed on TiO2 at 2 wt% loading, whereas tetrahedral molybdate was preferentially formed on Al2O3 at 2 wt% loading. The morphology and dispersion of molybde-

num sulfide catalysts on each support probably depended on the structure of the molybdate before sulfidation, although the sulfidation procedure reduced the differences in the structures. XPS analysis detected large differences in the peak energies of Mo3d spectra between the oxide catalysts, and suggested that the Mo-support interaction affected the electronegativity of the Mo cations on the support and that less electronegative Mo catalysts on MgO provided fewer active catalytic sites for HCK and HDS.

In summary, the formation of active catalytic sites of molybdenum sulfide catalysts depended on the Mo-support interaction. TiO2 and Al2O3 supports that...
formed two-dimensional dispersion of polymolybdate before sulfidation resulted in high HYD activity, whereas SiO₂ that formed three-dimensional MoO₃ structure resulted in low HYD activity. TiO₂ that formed electronegative Mo resulted in the highest HCK activity, whereas MgO that formed the least electronegative Mo resulted in the lowest HCK activity. These findings agree with a recent study in which MoS₂ on TiO₂ possessed strong metallic character and had high catalytic activities.

4. Catalysts Supported on Al₂O₃

4.1. Catalysts with Different Mo Loadings

Figures 1(a) and 1(b) show the HYD and HCK activities of Al₂O₃ supported molybdenum sulfide catalysts with different Mo loadings. For A-series of the catalysts, both HYD and HCK activities almost linearly increased with higher Mo loading up to 25 wt% as MoO₃. These results indicated that the number of active catalytic sites increased with Mo loading up to 25 wt% as MoO₃. Figure 1(c) shows the relative ratio of HCK/HYD activities obtained in the reaction of DPM. The HCK/HYD ratios were low for the A-series catalysts with Mo loading between 5 wt% and 15 wt%. The active sites of the catalysts with Mo loading between 5 wt% and 15 wt% as MoO₃ were relatively HYD-oriented, whereas the active sites of the catalysts with lower loading (<5 wt%) and higher loading (>15 wt%) were relatively HCK-oriented. The B-series catalysts prepared with a different method gave lower HYD (Fig. 1(a)) but higher HCK (Fig. 1(b)) activities compared with the corresponding A-series catalysts. The HCK-oriented character of B-series catalysts was clearly shown by the high HCK/HYD ratios (Fig. 1(c)).

Table 3 summarizes the TEM observations of MoS₂ microcrystals in the catalysts. The A-series catalysts with loading lower than 10 wt% had very few MoS₂ layers, which indicates that most of the MoS₂ catalysts formed very small clusters. The catalysts with intermediate loading of 10-15 wt% had single-layer MoS₂ structures with lengths between 3 nm and 4 nm. Catalysts with higher loading than 15 wt% had multi-layer MoS₂ structures with lengths over 8 nm. The MoS₂ structures observed in the B-series catalysts were more highly stacked.

Assuming that the active catalytic sites are limited to the edge of MoS₂, the linearly increasing catalytic activities with higher Mo loading shown in Fig. 1 suggest that the lateral dimensions of the MoS₂ layers remained constant irrespective of the Mo loading. However, Table 1 showed that the lateral dimensions of the MoS₂ structures increased with higher Mo loading. These results suggest that the intrinsic activities of the edge sites of MoS₂ structures increased with higher Mo loading. This aspect will be discussed again in Section 5. These findings of the catalytic character of the active sites (Fig. 1 and Table 3) have lead us to propose the model of the active sites for HYD and HCK as shown in Fig. 2. More details of this model will be discussed in the following section.

4.2. Catalysts on γ-Al₂O₃ with Different Surface Orientation Ratios

Figure 3 shows the TEM photographs of two types of γ-Al₂O₃, plate-like (PL) Al₂O₃ and spherical (SP) Al₂O₃, with different surface orientation ratios. As shown in Fig. 3(a), the lattice distances parallel to the periphery of the PL Al₂O₃ were 0.45 nm, which is similar to that of (111) γ-Al₂O₃. This observation in-
indicates that the side surfaces of the PL Al₂O₃ were \{111\} planes and that the top and bottom surfaces were \{110\} planes as shown in Fig. 4(a). Considering the average crystal dimensions obtained using Scherrer’s equations and the XRD pattern, about 80% of the surface area of the PL \(\gamma\)-Al₂O₃ was present as \{110\} planes. Similarly, the outside surfaces of the SP Al₂O₃ were indexed as shown in Fig. 4(b), assuming a rhombohedral structure. The surface area of the SP Al₂O₃ consisted of mainly \{111\} and \{100\} planes. Industrially manufactured \(\gamma\)-Al₂O₃ supports, with main surface orientation of \{110\} planes, has a similar surface character to that of the PL Al₂O₃.

Table 3  TEM Observation of MoS₂ Microstructure on \(\gamma\)-Al₂O₃ Support

<table>
<thead>
<tr>
<th>MoO₃ loading (X wt%)</th>
<th>Series A</th>
<th>Series B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X&lt;10</td>
<td>10(\leq X)(\leq 15)</td>
</tr>
<tr>
<td>Size of MoS₂ layer</td>
<td>invisible</td>
<td>3-4 nm</td>
</tr>
<tr>
<td>Number of MoS₂ layers</td>
<td>monolayer</td>
<td>2-4 layers</td>
</tr>
</tbody>
</table>

*1) BET surface was 117 m²/g.
*2) BET surface was 64 m²/g.

Fig. 3  TEM Photographs of (a) Plate-like (PL)*1) and (b) Spherical (SP)*2) \(\gamma\)-Al₂O₃ Powders

Fig. 4  Catalytic Features of the Active Sites of MoS₂ Structures Supported on \(\gamma\)-Al₂O₃

Figure 5 shows the schematic of the morphologies of MoS₂ structures on each plane of \(\gamma\)-Al₂O₃ deduced from the TEM images of the supported catalysts. The top and bottom \{110\} planes of the PL Al₂O₃ supported relatively large single-layer MoS₂ structures. In contrast, the top and bottom \{111\} and \{100\} planes of the SP Al₂O₃ supported small stacked-layered MoS₂ structures. Formation of edge-bonded MoS₂ clusters on \{100\}\(\gamma\)-Al₂O₃ single crystal surfaces was reported, but the present TEM investigation did not detect edge-bonded clusters on the SP Al₂O₃. Note that most molybdenum sulfides on the SP Al₂O₃ were not observed, because the cluster sizes were too small to be detected by the present TEM analysis.

Table 4 shows the HYD and HDS activities of the PL Al₂O₃ and SP Al₂O₃ supported MoS₂ catalysts. Both HYD and HDS activities of the SP Al₂O₃ supported catalysts were superior to those of the PL Al₂O₃ supported catalysts. The activity ratios of the two catalysts (\(k_{SP}/k_{PL}\) in Table 4) for HDS (2.2) were higher than that for HYD (1.5). These findings indicated that the PL Al₂O₃ supported catalyst was relatively HYD-oriented, whereas the SP supported catalyst was relatively HDS-oriented. Detailed analyses of the product distribution in HDS reactions indicated that direct S-extrusion (DDS selectivity in Table 4), yielding biphenyl, was predominant on both catalysts. The DDS selectivity on the SP supported catalyst (0.88) was relatively higher than that on the PL supported catalyst.
(0.85). Consequently, the results shown in Table 4 indicate that single-layered MoS2 structures were more 
HYD-oriented than multi-layered MoS2 structures. These catalytic characteristics of the active sites of 
MoS2 structures were incorporated in Fig. 5. This structure is consistent with the discussion in the previous 
Section 4.1, and the model shown in Fig. 2, provided that the catalytic function required for direct 
S-extrusion is similar to that for HCK of DPM.

Table 4 Catalytic Activity of PL-Al2O3 and SP-Al2O3 Supported
MoS2 Catalysts\(^a\)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>HYD (k^a)</th>
<th>HDS (k^a)</th>
<th>DDS selectivity(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2/PL-Al2O3</td>
<td>0.66</td>
<td>0.028</td>
<td>0.85</td>
</tr>
<tr>
<td>MoS2/SP-Al2O3</td>
<td>0.97</td>
<td>0.062</td>
<td>0.88</td>
</tr>
<tr>
<td>(k_{SP}/k_{PL})</td>
<td>1.5</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

\(a\): Reaction rate (mol sec\(^{-1}\) Mo\(^{-1}\)).
\(b\): Relative ratio of HDS reaction path via direct S-extrusion (DDS).
Remaining conversion was via hydrogenation of aromatic rings.

(0.85). Consequently, the results shown in Table 4 indicate that single-layered MoS2 structures were more 
HYD-oriented than multi-layered MoS2 structures. These catalytic characteristics of the active sites of 
MoS2 structures were incorporated in Fig. 5. This structure is consistent with the discussion in the previous 
Section 4.1, and the model shown in Fig. 2, provided that the catalytic function required for direct 
S-extrusion is similar to that for HCK of DPM.

The catalyst was prepared by the equilibrium adsorption method 
using an aqueous solution of ammonium heptamolybdate, followed 
by sulfiding in a flow of 10% H\(_2\)S/N\(_2\) at 673 K. Mo loading as 
MoO\(_3\) was 6.9 wt%.

5. Catalysts Supported on Anatase-type TiO\(_2\)

Figure 6\(^9\) shows a TEM image of anatase-type TiO\(_2\) 
supported molybdenum sulfide catalyst which evidently 
shows that MoS\(_2\) layers were “standing on” the TiO\(_2\) 
surface. Detailed analysis of the interface geometry 
between MoS\(_2\) and anatase\(^9\) showed the MoS\(_2\) crystals 
maintained epitaxial relationships with the anatase surface, for instance, (002) MoS\(_2\) \(\perp\) (001) Anatase in Fig. 6. 
Table 5\(^9\) shows the effects of the preparation conditions 
on the dispersion and sizes of the MoS\(_2\) structures. 
The edge-bonded MoS\(_2\) clusters were formed by sulfidation 
of the catalysts in a flow of H\(_2\)S/N\(_2\), irrespective 
of the preceding calcination atmosphere. The edge- 
bonded MoS\(_2\) structures changed orientation to basal- 
bonded structures on sulfidation at temperatures higher 
than 673 K. As shown in Table 5, the edge-bonded 
MoS\(_2\) structures aggregated to a higher degree than the 
basal-bonded MoS\(_2\) structures at the corresponding tem-

temperature.

Figure 7 shows the HYD activities of the molybdenum sulfide catalysts listed in Table 5. Catalytic activity decreased with higher sulfidation temperature for the catalysts sulfided in H$_2$S/N$_2$. In contrast, the catalytic activity increased with higher sulfidation temperature for the catalysts sulfided in H$_2$S/H$_2$. The highest catalytic activity was obtained for the catalyst sulfided in H$_2$S/N$_2$ at the lowest temperature, 573 K. Figure 8 shows the dispersion of the molybdenum sulfide catalysts estimated by NO uptake by the edges of MoS$_2$. The dispersion decreased with higher sulfidation temperature irrespective of the sulfidation atmosphere. The trend observed in Fig. 7 was consistent with the results in Fig. 8 for the catalysts sulfided in H$_2$S/N$_2$, because sulfidation at high temperature caused aggregation of the MoS$_2$ structures in the lateral direction as shown in Table 5. However, catalysts sulfided in H$_2$S/H$_2$ at higher temperature exhibited higher catalytic activity than those sulfided at a lower temperature despite the large lateral dimensions (Table 5) and the smaller number of active catalytic sites (Fig. 7). This finding indicated that the intrinsic activity of the molybdenum sulfide catalyst sulfided at higher temperature is superior to that sulfided at lower temperature probably due to the weaker electronic interaction with the support. Considering that the electronic interaction between each layer of MoS$_2$ is negligibly weak, the intrinsic activity of the single-layer MoS$_2$ catalyst basal-bonded to the support is relatively lower than that of the

### Table 5 Characteristics of MoS$_2$/TiO$_2$ Catalysts Calcined and Sulfided under Various Conditions Revealed by TEM Observation

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Air H$_2$S/H$_2$</td>
<td></td>
<td>573</td>
<td>Few MoS$_2$ clusters were observed.</td>
<td></td>
<td></td>
<td></td>
<td>basal bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>673</td>
<td>Few MoS$_2$ clusters were observed.</td>
<td></td>
<td></td>
<td></td>
<td>basal bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>773</td>
<td>12 (edge)</td>
<td>5.7 (edge)</td>
<td>3-20 (edge)</td>
<td>9.3 (edge)</td>
<td>edge + basal</td>
</tr>
<tr>
<td>H$_2$S/N$_2$</td>
<td></td>
<td>573</td>
<td>Few MoS$_2$ clusters were observed.</td>
<td></td>
<td></td>
<td></td>
<td>basal bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>673</td>
<td>12 (edge)</td>
<td>8.0 (basal)</td>
<td>1-5 (basal)</td>
<td>2.0 (basal)</td>
<td>edge + basal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>773</td>
<td>20 (basal)</td>
<td>3.5 (edge)</td>
<td>3-9 (edge)</td>
<td>6.3 (edge)</td>
<td>edge + basal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>873</td>
<td>60 (basal)</td>
<td>24.9 (basal)</td>
<td>1-9 (basal)</td>
<td>3.0 (basal)</td>
<td>edge + basal</td>
</tr>
<tr>
<td>N$_2$ H$_2$S/H$_2$</td>
<td></td>
<td>573</td>
<td>Few MoS$_2$ clusters were observed.</td>
<td></td>
<td></td>
<td></td>
<td>basal bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>673</td>
<td>Few MoS$_2$ clusters were observed.</td>
<td></td>
<td></td>
<td></td>
<td>basal bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>873</td>
<td>40</td>
<td>15.5</td>
<td>1-10</td>
<td>3.2</td>
<td>edge bonding</td>
</tr>
<tr>
<td>H$_2$S/N$_2$</td>
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<td>3</td>
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<td>4.8</td>
<td>edge bonding</td>
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<td>673</td>
<td>10 (edge)</td>
<td>6.2 (edge)</td>
<td>5-20 (edge)</td>
<td>10.4 (edge)</td>
<td>edge + basal</td>
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<td>873</td>
<td>100</td>
<td>9.7 (basal)</td>
<td>1-5 (basal)</td>
<td>2.1 (basal)</td>
<td>edge + basal</td>
</tr>
</tbody>
</table>

The “average length and average number of MoS$_2$ layers” were obtained by averaging all the MoS$_2$ layers observed in three images with a magnification of 1,000,000 (15 cm × 20 cm).

The reaction rate constant was obtained using the conversion data in the hydrogenation of 1-MN on the assumption of pseudo-first-order kinetics.

Fig. 7 Hydrogenation Activity of Molybdenum Sulfide Catalysts Supported on TiO$_2$ Calcined and Sulfided under Different Calcination Atmospheres, Different Sulfidation Atmospheres and Sulfidation Temperatures.
second or higher layer of the catalyst and that of the edge-bonded catalyst. As shown in Fig. 1 in Section 4., the catalytic activities of Al₂O₃ supported molybdenum sulfide catalysts increased almost linearly with higher Mo loading despite the increase in the lateral dimensions of the MoS₂ structures. This increased activity is probably due to the low intrinsic activities of the small or invisible MoS₂ layers that have strong electronic interactions with the catalyst support.

Based on our findings for TiO₂ supported molybdenum sulfide catalysts, we designed and developed a HCK catalyst for heavy petroleum20). To minimize coking on the catalyst and to accommodate large molecules including residues, ultra-stable Y (USY) zeolites with high Si/Al and large mesoporosity were chosen as the active catalytic center for HCK. The USY zeolites were treated with an aqueous solution of titanium sulfate to further reduce the Brønsted acid sites and to further increase the mesoporosity. Subsequently, these molybdenum sulfide catalysts with HYD function were loaded on USY zeolites to reduce coking and over-cracking. As described in Section 3., the surface of SiO₂-rich USY zeolites was supposed to have poor dispersion of molybdenum sulfide catalysts with low HYD activity. The TiO₂ particles formed during the calcination of titanium sulfate treated-USY zeolites were expected to function as a suitable support for the molybdenum sulfide catalysts. Figure 9²⁰ shows the schematic of the structure of the prepared Mo-Ti/USY catalysts. TEM observation of the catalyst after sulfidation confirmed that highly dispersed MoS₂ structures were deposited on TiO₂ particles with diameters less than 10 nm.

Figure 10²⁰ compares the catalytic performances of Mo-Ti/USY catalysts with those of Mo/USY catalysts without titanium sulfate treatment for the HCK of residual oil. The atmospheric residue (AR) conversion over the Mo-Ti/USY catalysts increased with higher number of acid sites indicated as Al/Si in Fig. 10, but not for the Mo/USY catalysts. Subsequently, the catalytic performances of Ni-Mo sulfide catalysts prepared using Mo-Ti-USY and Al₂O₃ support were tested in a bench-scale plant as shown in Fig. 11²¹. AR and VGO conversion increased at the beginning of the reaction for both catalysts, due to the gradual desorption of basic compounds that were adsorbed on the HCK active sites at lower temperatures, because the AR feed was started at 523 K²². The Ni-Mo/(Mo-Ti/USY + Al₂O₃) catalyst evidently showed higher AR conversion and higher yield of middle distillate at temperatures between 663 K and 683 K than the Ni-Mo/(USY + Al₂O₃) catalyst. Finally, the stability of the catalytic activities of the Ni-Mo/(Mo-Ti/USY + Al₂O₃) catalyst was confirmed over 2500 h using a large-scale bench plant system with a catalyst volume of 150 cm³ for HCK²³.

6. Catalysts Used in Commercial Run and Accelerated Aging

Figure 12²⁴ exhibits the morphological changes of the MoS₂ structures of Co-Mo/Al₂O₃ catalysts during a long-term reaction in a commercial plant. Both average lateral size \(L_{av}\) and stacking number \(N_{av}\) of the MoS₂ crystallites increased with higher catalyst loading consistent with the trends described in Table 2. During the one-year reaction, the crystallite size increased, whereas the stacking number did not change.
As a result, the aspect ratio, defined as $N_{\text{ave}}$ divided by $L_{\text{ave}}$, decreased from about 0.8 for the fresh catalysts to below 0.6 for the aged catalysts as shown in Fig. 13. As already described in this paper, small MoS$_2$ clusters could not be detected by TEM. Therefore, many molybdenum sulfide species were invisible for the catalysts with low Mo loading. Figure 12 suggested that these invisible MoS$_2$ clusters were aggregated or bonded to the edge of the visible MoS$_2$ layers.

Table 6 shows the changes in the morphologies of MoS$_2$ crystallites observed by TEM during the accelerated aging tests of a Co-Mo/Al$_2$O$_3$ catalyst using feedstocks of VGO and VGO + AR. Extended aging (500 h) caused increases in $L_{\text{ave}}$ and decreases in $N_{\text{ave}}$, resulting in lower aspect ratios. The decrease in $N_{\text{ave}}$ shows that invisible clusters aggregated and were detected as a single MoS$_2$ layer by TEM observation during long-term and high-temperature aging. The large $\Sigma$ values observed for the long aged catalysts supported the idea that invisible MoS$_2$ clusters aggregated to the edge of the MoS$_2$ layers and became visible. The final $\Sigma$ values for the fresh catalysts were consistent with those in Figs. 12 and 13. The final temperature of 693 K in the accelerated deactivation tests for 500 h was higher than that of the commercial run, so the aspect ratios of the aged catalysts in Table 6 were lower than those in Fig. 13.

For the catalysts aged in blank tests (aging in H$_2$S/H$_2$), both $L_{\text{ave}}$ and $N_{\text{ave}}$ increased during extended aging. The aspect ratios of the catalysts aged in blank tests were higher than those of the other catalysts. The growth of MoS$_2$ crystallites preferentially progressed in the normal directions to the layers during H$_2$S/H$_2$ sulfidation in contrast to that during hydrotreatment of petroleum fractions. In fact, the catalyst used in a commercial run had a lower aspect ratio than catalysts aged in H$_2$S/H$_2$ despite the large $\Sigma$ value.

Figure 14 shows the EXAFS analysis results of the aged catalysts. Both $N$(S) and $N$(Mo) of the catalysts aged for 500 h were higher than those aged for 30 h. The increases in $N$(S) indicated that the sulfidation of molybdenum species further progressed after 30 h.
The increases in $N$ (Mo) were probably due to the increase in the order of MoS$_2$ structures in parallel with higher sulfidation.

Figure 15$^{25}$ shows the relationship between the catalytic activities and the amounts of carbonaceous deposits on the aged catalysts in Table 6. The trend observed in Fig. 15 indicated that the major cause of the catalyst deactivation was carbonaceous deposition, although deactivation by pore plugging was hard to discriminate from direct active site poisoning. Deactivation by the growth of MoS$_2$ crystallites or by changes in the CoMoS structures was not clearly observed in Fig. 15, including the catalyst used in a commercial run. Our previous study of the catalysts used in hydrotreating coal-derived liquids found serious structural changes in Ni–W catalysts$^{26}$. We proposed that the aggregation
of WS$_2$ layers in the lateral direction was a major cause for deactivation of Ni–W/SiO$_2$–Al$_2$O$_3$ catalysts during HDS of VGO. The “CoMoS” structure was probably more stable than the “NiWS” structure. Further, the high concentrations of polar compounds contained in coal-derived liquids likely accelerated the segregation of “NiWS” into Ni$_3$S$_2$ and WS$_2$, and accelerated the aggregation of the WS$_2$ structure.

7. Summary and Discussion

The present review has shown that many factors determine the morphologies and dispersion of molybdenum sulfide catalysts and can affect the catalytic functions, such as activity and selectivity. Support species have large effects on the morphologies through electronic interaction and geometrical relationship between the catalysts and the support surface. Although the support effects are reduced with higher sulfidation, the interaction remains after completion of presulfiding or even after use in a commercial run, because Mo–O bonding cannot be completely replaced by Mo–S bonding as shown in Fig. 14. Sulfidation conditions also affect the morphologies, consistent with a recent theoretical study that shows the sulfidation agent can influence the morphologies and dispersion of molybdenum sulfide catalysts.

The morphologies of the molybdenum sulfide catalysts influence the catalytic functions. We proposed a model of active catalytic sites as shown in Fig. 16. The stacked MoS$_2$ layers provide a larger number of edge sites for CUS than a large single-layered structure, but the bottom layer may not act as active catalytic sites due to steric hindrance (Fig. 16(c)). Past studies on unsupported catalysts indicated that although all edge sites might function for HDS, only the top and bottom layers (rim sites in Fig. 16(d)) could provide active sites for HYD because of steric hindrance. Adsorption of $\pi$ bonding cannot occur on the edge sites except at the top and bottom layers. As discussed earlier in this paper, HYD requires two different adsorp-

$k$(HYD) [h$^{-1}$]: Hydrogenation rate constants over the catalysts obtained using the conversion data in the hydrogenation of 1-MN on the assumption of pseudo-first-order kinetics.

Fig. 15 Relationship between Hydrogenation Activities and Amounts of Carbon Deposit of the Aged Catalysts

Fig. 16 Morphology, Orientation, and Active Catalytic Sites of MoS$_2$ Clusters on Supports

(a) Edge-bonded MoS$_2$ cluster, (b) Single-layered MoS$_2$ cluster basal-bonded to the support (Co-Mo-S(I) type), (c) Multi-layered MoS$_2$ cluster basal-bonded to the support (Co-Mo-S(II) type), (d) Unsupported MoS$_2$ cluster.
tion sites, one on the edge or corner sites and the other on the basal plane of MoS$_2$). In a recent study using STM and MoS$_2$ nanoclusters on gold, 4,6-DMDBT could adsorb on the “brim sites” of MoS$_2$ sheets in a flat configuration, so two sites, one for HYD and the other for sulfur extrusion, were needed for the HDS of S-containing molecules that required preceding HYD of aromatic rings. These discussions concur with our conclusion that single-layer MoS$_2$ catalysts were HYD-oriented. DBT is adsorbed on the edge sites of CoMoS or MoS$_2$ sheet, but only the corner sites of the sheets (Fig. 16(d)) could catalyze the HDS of DBT due to steric hindrance. For the HDS of large molecules including DBT even without substituents, steric hindrance may be a more important fact that limits HDS reaction than suggested in Fig. 16.

Single-layer MoS$_2$ catalysts might be efficient for high HYD from the viewpoint of steric hindrance, but the electronic interaction with the support probably reduces the intrinsic catalytic activities. The present review shows that higher intrinsic activities can be obtained for deeply sulfided multi-stacked MoS$_2$ structures than for single-layered or invisible microclusters of MoS$_2$, because the second layer that is not bonded to the support has no electronic interaction with the support. This suggestion agrees with the discussion of one for HYD and the other for sulfur extrusion, were needed for the HDS of S-containing molecules that required preceding HYD of aromatic rings. These discussions concur with our conclusion that single-layer MoS$_2$ catalysts were HYD-oriented. DBT is adsorbed on the edge sites of CoMoS or MoS$_2$ sheet, but only the corner sites of the sheets (Fig. 16(d)) could catalyze the HDS of DBT due to steric hindrance. For the HDS of large molecules including DBT even without substituents, steric hindrance may be a more important fact that limits HDS reaction than suggested in Fig. 16.

Single-layer MoS$_2$ catalysts might be efficient for high HYD from the viewpoint of steric hindrance, but the electronic interaction with the support probably reduces the intrinsic catalytic activities. The present review shows that higher intrinsic activities can be obtained for deeply sulfided multi-stacked MoS$_2$ structures than for single-layered or invisible microclusters of MoS$_2$, because the second layer that is not bonded to the support has no electronic interaction with the support. This suggestion agrees with the discussion of two types of CoMoS phases that claimed CoMoS(II) with weak electronic interaction with the support has superior catalytic activities to CoMoS(I) with strong interaction. The behavior and role of Co or Ni that occupies the edge of MoS$_2$ during the growth of CoMoS structures require further investigation.

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References
要  旨

石油精製用モリブデン硫化物触媒の形状、分散と触媒機能

島田 広道

産業技術総合研究所、305-8561 茨城県つくば市東1-1-1産総研中央第1

本稿では、各種担体に担持した Mo 硫化物触媒、使用済 Co-Mo/Al2O3 触媒の触媒機能をモデルテスト反応によって評価し、触媒の形状、分散との関係について提案した。硫化物活性については Al2O3 担体が、脱硫活性および硫化分解活性については TiO2 担体が優れた活性を示した。Al2O3 担体では、比較的な大きな単層 MoS2 が形成しやすい結晶面と複層以上の MoS2 が形成しやすい結晶面があった。また、TiO2 担体上では硫化条件によって MoS2 が担体上に垂直配置することが分かった。複層以上の MoS2 触媒は、相対的に硫化分解や脱硫反応に優れる一方、単層 MoS2 触媒は硫化分解に優れていた。触媒活性点の機能には反応分子の立体障害が影響し、特に pπ 吸着が必要な硫化反応では立体障害の影響が大きく考察された。実反応使用済触媒では、MoS2 構造が面内方向に成長して活性点は減少するが、硫化の進行に伴い担体との相互作用が弱まって活性点あたりの活性は向上した。