[Review Paper]

Sulfidation State and Sulfur Behavior on Mo-based HDS Catalysts Supported on TiO₂ Using ³⁵S Tracer Methods

Atsushi ISHIHARA *

Dept. of Chemical Engineering, Graduate School of Engineering, Tokyo University of Agriculture and Technology,
2-24-16 Nakacho, Koganei, Tokyo 184-8588, JAPAN

(Received July 6, 2007)

A ³⁵S radioisotope pulse tracer method using ³⁵S-labeled H₂S was used to investigate the sulfidation state of Mo-based catalysts supported on TiO₂. Despite the coverage of Mo species on the TiO₂ support, sulfidation of the TiO₂ support still occurred at 300°C. The sulfided catalysts could be reduced under H₂ atmosphere. A ³⁵S radioisotope tracer method using ³⁵S-labeled dibenzothiophene ([³⁵S]DBT) was used to determine the sulfur mobility on the working sulfided Mo/TiO₂ catalysts. The amount of labile sulfur (*S*₀), which represents the amount of active sites, and the release rate constant of H₂S, which represents the mobility of the active site (*k*_{RE}), were estimated. Compared with Mo/Al₂O₃ catalyst, Mo/TiO₂ catalyst had slightly higher *S*₀ and about 2 times higher *k*_{RE}, which indicate that new mobile active sites were formed on sulfided Mo/TiO₂ catalyst. Comparison of the *k*_{RE} and *S*₀ of titania-based and alumina-based catalysts suggested that the active phase consisted of a 'TiMoS' phase exhibiting a promoting effect similar to the well-known 'CoMoS' phase (promotion of the MoS₂ active phase by Ti atoms). Hydrodesulfurization (HDS) of DBT was evaluated over Mo catalysts supported on titania synthesized by the pH swing method, which provides a TiO₂ carrier with a high specific surface area (134 m²·g⁻¹) and excellent mechanical properties. The activity increased linearly with Mo content up to ca. 16 wt% MoO₃ and then decreased for higher Mo loadings. The optimal Mo dispersion on this catalyst was 5.2 atom/nm², which is higher than the optimal Mo dispersion on 70 m²·g⁻¹ TiO₂ (4.2 atom/nm²). [³⁵S]DBT HDS catalyzed by CoMo/TiO₂ showed that *S*₀ increased in parallel with the catalytic activity up to a Co/Mo molar ratio of 0.4. Only a slight increase in *k*_{RE} was observed with Co addition, unlike CoMo/Al₂O₃ catalysts.

Keywords

Sulfidation state, Hydrodesulfurization, High surface titania, Molybdenum catalyst, Radioactive tracer method

1. Introduction

The sulfur content of transportation fuels has already been reduced to below 10 ppm, as required by recent environmental regulations. However, further developments are essential to satisfy stricter regulations in the near future, reduce the cost of fuel production, and provide ultra-deep desulfurized naphtha or kerosene for hydrogen production in fuel cell operation. Therefore, further improvement in hydrodesulfurization catalysts is needed, especially more active and selective catalyst formulations^{1)~7)}.

Much attention has been focused on the support, and titania^{8)~10)} or alumina-titania mixed oxides^{11)~14)} have shown promising results. Mo catalysts supported on titania are 4.4 times more active than those supported

on alumina for thiophene hydrodesulfurization⁸⁾. Also, the synergetic effect of a cobalt promoter in CoMo hydrodesulfurization (HDS) catalysts supported on alumina is greater than that in similar catalysts supported on titania⁸⁾. Therefore, the main beneficial effect of the TiO₂ support appears to be located on the Mo phases rather than on the Co promoter. However, titania supports generally have low specific surface area (~70 m²·g⁻¹) compared with alumina (~250 m²·g⁻¹), and poor thermal stability of the anatase phase at high temperatures¹⁵⁾. To overcome this problem, technologies to directly synthesize high specific surface area (SSA) TiO₂ have been proposed. Recently a titania support suitable for catalytic applications with a high surface area of ca. 134 m²·g⁻¹ and excellent mechanical properties was synthesized, which allows the direct use of titania support in industrial catalytic applications^{16),17)}.

Titania may promote the formation of polymolybdenum compounds with octahedral coordination molybdenum, leading to a higher dispersion of MoO₃ on

* E-mail: ishihara@chem.mie-u.ac.jp

* (Present) Dept. of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurima machiya-cho, Tsu 514-8507, JAPAN

Fig. 1 Pulse Tracer Apparatus for Sulfidation of Mo/TiO₂ Catalyst Using ³⁵S-labeled H₂S

the support and an increase in HDS catalytic activity^{18),19)}. Moreover, MoO₃ species on TiO₂ support can be converted much more easily into MoS₂ by sulfidation and reduction than MoO₃ species on Al₂O₃ support²⁰⁾. However, no explanation for the substantial difference in HDS activity between alumina- and titania-supported catalysts has been elucidated, since the increase in activity with TiO₂ support cannot be completely explained by the differences in dispersion or sulfidation of the active metallic species^{8),9)}. Compared with conventional supports such as Al₂O₃ and SiO₂, TiO₂ support can be easily reduced to Ti³⁺ by H₂ even at low temperature²¹⁾. Therefore, TiO₂ in HDS catalysts acts as both a conventional support and as an electronic promoter of the molybdenum sulfide phase. Recently, we demonstrated that ³⁵S radioisotope pulse tracer methods are very powerful tools for the investigation of catalytic characteristics.

This paper reviews the ³⁵S radioisotope pulse tracer methods to evaluate the behavior of sulfur on Mo/TiO₂ HDS catalysts^{22)~25)}. The ³⁵S radioisotope pulse tracer method using ³⁵S-labeled H₂S, which can accurately determine the sulfidation state of the catalyst²⁶⁾, was used to investigate the sulfidation and reduction state of Mo/TiO₂ catalyst. The ³⁵S radioisotope tracer method using ³⁵S-labeled dibenzothiophene (DBT), which can give information about the behavior of sulfur on the working catalyst^{27)~29)}, was used to elucidate the sulfur mobility on the sulfided Mo/TiO₂ catalyst under the reaction conditions. The sulfur mobility on Mo and CoMo catalysts^{30)~32)} supported on high surface area TiO₂ is also discussed.

2. Sulfidation of Mo/TiO₂ Catalyst Using ³⁵S-labeled H₂S^{22),23)}

The ³⁵S-radioisotope pulse sulfiding method was developed to investigate the sulfidation process. **Figure 1** shows the pulse tracer apparatus and the details are described elsewhere²⁶⁾. A pulse of 30 vol% [³⁵S]H₂S in hydrogen was introduced into the fixed-bed reactor with a gas sampler (2.46 ml) every 10 min using N₂ carrier gas (0.5 MPa, 40 ml·min⁻¹). The radioactivity of the unreacted [³⁵S]H₂S absorbed by a commercially available basic scintillation solvent was measured every 10 min by a liquid scintillation counter^{28),29)}. To investigate the sulfidation state under H₂ atmosphere after the sulfidation procedure, the catalyst was cooled in a N₂ carrier gas stream to the desired temperature and was pressurized to 0.5 MPa with H₂ carrier gas. The [³⁵S]H₂S released was better absorbed by carbsorb solvent and the radioactivity was measured every 15 min by a liquid scintillation counter.

Figure 2 shows the change in radioactivity of eluted [³⁵S]H₂S during the sulfidation of MT(6) catalyst (Mo/TiO₂, MoO₃ 6 wt%) and TiO₂ support³³⁾ at various temperatures. For the TiO₂ support, the radioactivity of unreacted [³⁵S]H₂S at each temperature increased with the number of introduced pulses and approached a constant value, equal to the radioactivity of the pulse introduced. Therefore, the sulfidation at each temperature was almost complete. For MT(6) catalyst, the radioactivity of unreacted [³⁵S]H₂S at 100 and 200°C approached a constant value, equal to the radioactivity of the pulse introduced, whereas [³⁵S]H₂S seemed to be accumulated on the catalyst slowly until the sulfidation process was complete at 300 and 400°C. The amount of sulfur incorporated into the catalyst could be calcu-

lated by subtracting the radioactivity of the released $[^{35}\text{S}]\text{H}_2\text{S}$ from the total radioactivity introduced²⁶⁾. The results are presented in **Table 1**. Using the geometrical model of crystalline TiO_2 (anatase), the area of each TiO_2 unit lattice of the TiO_2 support can be estimated. In crystalline TiO_2 (anatase), each Ti with associated oxygen atoms occupies $33.6 \times 10^{-3} \text{ nm}^3$, equivalent to an effective area of $10.4 \times 10^{-2} \text{ nm}^2$ ³⁴⁾. Therefore, if surface TiO_2 is converted to TiS_2 , the amount of surface sulfur is calculated to be 71.7 mg-S/g-cat . As shown in **Table 1**, the uptake of sulfur into TiO_2 support at 400°C was 73.0 mg-S/g-cat , indicating that the surface TiO_2 could be completely sulfided to the stoichiometric TiS_2 state at 400°C ³³⁾. In the case of MT(6) catalyst, the TiO_2 support will presumably not be sulfided until all surface Mo species are sulfided, since the TiO_2 support is almost covered by a monolayer of Mo species (see below). If all Mo species were present as MoS_2 , the total sulfur was calculated to be 29.1 mg-S/g-cat . As shown in **Table 1**, the uptake of sulfur into Mo/TiO₂ catalyst at 300°C was 38.9 mg-S/g-cat . Therefore, the surface Mo species was almost totally sulfided to MoS_2 and sulfidation of the sub-surface TiO_2 support also occurred at 300°C .

3. Reduction of Sulfided Mo/TiO₂ Catalyst^{22),23)}

Mo/TiO₂ catalyst sulfided with ^{35}S -labeled H_2S was reduced by H_2 carrier gas to investigate the reducibility

of the catalyst. **Figure 3** shows the change in radioactivity of released $[^{35}\text{S}]\text{H}_2\text{S}$ during the reduction of sulfided Mo/TiO₂ catalyst and TiO_2 support³³⁾ at various temperatures. Sulfided Mo/TiO₂ catalyst and TiO_2 support were maintained for 30 min at each temperature and the released $[^{35}\text{S}]\text{H}_2\text{S}$ was collected every 15 min. The amount of sulfur released at each temperature is shown in **Table 1**. For TiO_2 support, no released $[^{35}\text{S}]\text{H}_2\text{S}$ was detected at 200°C , which indicates that no reduction of TiS_2 occurred. Released $[^{35}\text{S}]\text{H}_2\text{S}$ was detected at over 300°C , and the amount was calculated to be 18.1 mg-S/g-cat up to 400°C , about one fourth of the amount of sulfur introduced into TiO_2 support, suggesting that the surface TiS_2 was reduced to $\text{TiS}_{1.5}$ and that Ti was present with an average oxidation state of Ti^{3+} under H_2 atmosphere at 400°C ³³⁾. Compared with TiO_2 support, the sulfided Mo/TiO₂ catalyst was reduced at a lower temperature of 200°C . This observation is quite important since the reduction temperature was shifted to lower temperature, suggesting that the MoS_2 phase and the support interacted during the reduction process.

Sulfidation of the TiO_2 support with H_2S will form TiS_2 , a narrow gap semiconductor, with an energy gap as low as 0.2 eV ^{35),36)}. Therefore, easily excited electrons may react with hydrogen to give Ti^{3+} through reduction of TiS_2 under hydrogen atmosphere and then sulfur vacancies may be formed on the TiO_2 . If the TiO_2 support is covered with a monolayer dispersion of

Fig. 2 Sulfidation of MT(6) Catalyst and TiO_2 Support with $[^{35}\text{S}]\text{H}_2\text{S}$ Pulse at Various Temperatures

Fig. 3 Reduction of Sulfided MT(6) Catalyst and TiO_2 Support in H_2 Atmosphere at Various Temperatures

Table 1 Amount of Sulfur ($\text{mg} \cdot \text{g-cat}^{-1}$) during the Sulfidation and Reduction Processes on MT Catalyst and TiO_2 Support

Catalysts	Sulfidation [$\text{mg} \cdot \text{g-cat}^{-1}$]					Reduction		
	100°C	200°C	300°C	400°C	Theo. ^{a)}	200°C	300°C	400°C
TiO_2	—	6.55	45.0	73.0	—	0	11.6	18.1
MT(6)	12.1	25.3	38.9	49.1	29.1	1.77	5.78	10.2
MA(6)	17.1	21.4	21.5	26.3	29.1	—	—	—

a) Theo. is the amount of sulfur required to convert all MoO_3 on the catalyst to MoS_2 .

Fig. 4 Apparatus for HDS of [³⁵S]DBT on Mo/TiO₂ Catalyst

MoO₃, the surface MoO₃ species can be almost totally sulfided into MoS₂ at 300°C, and sulfidation of sub-surface TiO₂ will also occur at 300°C. As shown in **Table 1**, less than 80% MoO₃ could be sulfided at 300°C on Mo/Al₂O₃ catalyst²⁶⁾. This finding suggests that the incorporation of TiO₂ decreased the temperature of the sulfidation of Mo species. MoO₃ species on TiO₂ support can be sulfided more easily into MoS₂ than those on Al₂O₃ support according to temperature programmed sulfiding (TPS) findings³⁷⁾. Compared with sulfided TiO₂ support, sulfided Mo/TiO₂ catalyst can be reduced more easily at the lower temperature of 200°C. Therefore, TiO₂ electronic promotion of Mo will change the reducibility of Mo species³⁸⁾. UV-vis diffuse reflectance spectroscopy (DRS) investigation showed that the Ti3d levels and titania conduction band of TiO₂ containing catalyst are located at much lower energies closer to those of the Mo4d orbitals³⁹⁾. Therefore, the supported Mo sulfide active phase also has semiconductor properties. In this case, the empty orbital of Mo in MoS₂ should lie very near the d orbital of Ti in TiS₂^{40,41)}. Under reaction conditions in the presence of a high hydrogen partial pressure, the partial reduction of TiS₂ surface layers seems to occur and electrons from formed Ti³⁺ species can easily be injected to the Mo3d conduction band. This is the requirement for MoS₂ promotion in HDS catalysts⁴¹⁾. In fact, low valence Mo species were found in an X-ray photoelectron spectroscopy (XPS) study of Mo/TiO₂⁴²⁾. These low valence Mo species may be formed through charge transfer from Ti³⁺ ions in the TiO₂ support. All these findings are also in good agreement with the proposed Bond Energy Model⁴³⁾, since the transfer of electrons from Ti to Mo will decrease the Mo-S bond energy resulting in a more active catalyst.

WHSV 28 h⁻¹, 5 MPa.

Fig. 5 Changes in the Radioactivities of Unreacted [³⁵S]DBT and Formed [³⁵S]H₂S with Reaction Time at 360°C over MT(70) Catalyst

4. Behavior of Sulfur on Sulfided Mo/TiO₂ Catalyst^{22),23)}

HDS of [³⁵S]DBT was performed to investigate the behavior of sulfur on MT(6) catalyst in the steady state using the pressurized apparatus illustrated in **Fig. 4**. **Figure 5** shows the typical operation procedure of ³⁵S tracer method. The HDS reaction of [³⁵S]DBT was carried out over sulfided MT(6) catalyst at 360°C. Initially, 1 wt% [³²S]DBT dissolved in decalin was pumped into the reactor until the conversion of DBT became constant. Then 1 wt% [³⁵S]DBT in decalin was substituted and the reaction was continued until the formation of [³⁵S]H₂S became constant. After [³⁵S]DBT was introduced, the radioactivity of unreacted

[^{35}S]DBT in the liquid product increased and approached a steady state immediately. However, the radioactivity of [^{35}S]H $_2$ S took about 75 min to achieve a steady state. To determine the behavior of sulfur more accurately, the [^{35}S]DBT solution was replaced with decalin. A portion of ^{35}S , represented by the shaded area A in **Fig. 5**, remained on the catalyst. If decalin and H $_2$ were used to purge the catalyst, less release of [^{35}S]H $_2$ S was detected. If the reactant solution was replaced by [^{32}S]DBT again, a portion of ^{35}S was released as [^{35}S]H $_2$ S as shown in **Fig. 5** (shaded area B). This portion of ^{35}S was approximately equal to shaded area A, and represented the total amount of labile sulfur on the catalyst under this reaction condition. The amount of labile sulfur can be calculated from the total radioactivity of the [^{35}S]H $_2$ S released after [^{32}S]DBT was re-introduced, *i.e.*, shaded area B as reported previously²⁸.

To evaluate the release process of [^{35}S]H $_2$ S more accurately, the rate constant of [^{35}S]H $_2$ S release from ^{35}S -labeled catalyst was determined. The release of [^{35}S]H $_2$ S in the range of area B shown in **Fig. 5** can be explained as a first-order reaction, and the rate constant of [^{35}S]H $_2$ S release, k_{RE} , was determined. To understand the promoting effect of TiO $_2$ support on Mo species under reaction conditions, the changes in the amount of labile sulfur (S_0) and the rate constant of H $_2$ S release (k_{RE}) for MT(6) catalyst and MA(6) catalyst⁴⁴ at various temperatures are shown in **Fig. 6**.

Fig. 6 S_0 and k_{RE} over Mo/TiO $_2$ and Mo/Al $_2$ O $_3$ Catalysts at Various Temperatures

Compared with the Mo/Al $_2$ O $_3$ catalyst, the Mo/TiO $_2$ catalyst shows a slightly higher amount of labile sulfur (S_0), whereas the rate constant of H $_2$ S release (k_{RE}) was about 2 times higher on the Mo/TiO $_2$ catalyst. We previously proposed that the amount of labile sulfur (S_0) represents the number of active sites and the rate constant of H $_2$ S release (k_{RE}) represents the mobility of active sites on the surface of the catalyst, *i.e.*, the turn-over frequency in the HDS reaction⁴⁵. Therefore, the present results indicate that the presence of TiO $_2$ increases the mobility of the sulfur on the sulfided Mo/TiO $_2$ catalyst as well as increases the number of active sites. We have also proposed that the promoting effect of cobalt for molybdenum catalyst is due to increased mobility of the sulfur in the so-called 'CoMoS' phase, in which the strength of the Mo-S bond is weakened^{46,47}. Similarly, the promoting effect of TiO $_2$ on Mo catalyst is presumably the formation of a new mobile 'TiMoS' phase (**Fig. 7**), resulting in decreased strength of the Mo-S bond, since the sulfur mobility on the catalyst depends on the bond strength of the metal sulfide. The strength of the Mo-S bond on TiO $_2$ -supported catalyst is assumed to be weaker than that on Al $_2$ O $_3$ -supported catalyst, since Ti species can be reduced to Ti $^{3+}$ under H $_2$ atmosphere, and the transfer of electrons from Ti to Mo will decrease the Mo-S bond energy as discussed above. Therefore, TiO $_2$ in Mo catalyst both acts as a conventional support and as an electronic promoter of the molybdenum sulfide phase.

5. HDS Activities and Sulfur Mobility of Mo Catalysts Supported on High Specific Surface Area Titania³⁰

The DBT HDS activities of the Mo/TiO $_2$ catalysts with high specific surface area were measured at 320°C. **Figure 8** shows the effect of Mo content on HDS activity. The activities of Mo/Al $_2$ O $_3$ catalysts described in a previous study are also shown in **Fig. 8**⁴⁴. The value of k_{HDS} for the Mo/TiO $_2$ catalysts increased linearly with increasing Mo content up to about 16 wt% MoO $_3$, and then decreased with further increasing Mo content (*i.e.* for 20 wt% Mo). The activation energies for HDS of DBT over the Mo/TiO $_2$ catalysts with vari-

□ : sulfur anion vacancy with trapped electron.

Fig. 7 Schematic View of the Structure of 'TiMoS' Phase on Mo/TiO $_2$ Catalyst

Specific surface area: TiO₂ 134 m²·g⁻¹; Al₂O₃ 256 m²·g⁻¹.

Fig. 8 Effect of Mo Content on HDS Activities of Catalysts Supported on High SSA TiO₂ and on γ -Alumina at 320°C

MT (70 m²/g), MA (256 m²/g).

Fig. 9 Effect of Mo Content on HDS Activities

ous Mo contents were calculated from the Arrhenius plots ($\ln k_{HDS}$ as a function of $1/T$; not shown here). The activation energy for HDS of DBT over the Mo/TiO₂ catalysts was almost constant at 92 ± 8 kJ/mol, irrespective of the Mo loading, which is close to the 84 ± 8 kJ/mol generally observed for Mo/Al₂O₃ catalysts⁴⁴). For the same Mo loading, the activities observed over the high SSA titania were more than twice higher than those observed over the 256 m²·g⁻¹ alumina.

As shown in **Fig. 9**, the activity of the catalyst supported on alumina increased to about 3.9 Mo atoms per nm², similar to that observed with 70 m²·g⁻¹ TiO₂ support. A plateau was observed after the Mo content reached a value of 4.2 Mo atoms per nm² with only a relatively limited influence on the activity by a further increase in Mo loading using the 70 m²·g⁻¹ TiO₂ support. In contrast, an increase in Mo loading from ~ 4 atom·nm⁻² to ~ 5.2 atom·nm⁻² led to a drastic increase in activity (+60%) using the 134 m²·g⁻¹ titania support. This indicates that high SSA titania may

Specific surface area of TiO₂: 134 m²·g⁻¹.

Fig. 10 Effect of Mo Content on S_0 and k_{RE} over Mo/TiO₂ Catalysts at 320°C

exhibit some particular properties not observed in low SSA titania and γ -alumina. Presumably the pH swing method used to prepare the high SSA titania, which is known to give a solid with great homogeneity, provides a carrier with controlled morphology suitable to optimize the Mo dispersion as previously suggested⁴⁸).

Several studies have investigated the coverage of TiO₂ by Mo species as a function of the molybdenum content in sulfided catalysts^{9),49),50}). Most structural studies showed that the MoS₂ crystallites in the sulfided state are present as a monolayer. Further, the coverage of titania by Mo species generally increases linearly with the Mo content up to a certain limit, and then levels off, suggesting the presence of bulk-like MoS₂ structures, of which the size somewhat increases with increasing molybdenum content. Thus, in our study, the MoS₂ crystallites were present as a monolayer up to 16 wt% Mo. Indeed, the catalytic activities of our series of Mo/TiO₂ catalysts increased linearly with molybdenum content up to ca. 5.2 atom/nm² (16 wt% MoO₃) and then slightly decreased beyond this value.

[³⁵S]DBT HDS was performed to investigate the sulfur behavior on Mo/TiO₂ catalysts with various Mo contents as summarized in **Fig. 10**. The H₂S release rate constant did not vary significantly with the molybdenum content, but the amount of labile sulfur varied proportionally to the HDS rate up to 16 wt%. As proposed above²⁷), the amount of labile sulfur represents the number of active sites whereas the release rate constant indicates the regeneration efficiency of the coordinatively unsaturated sites (CUS)⁵¹). Therefore, at a given temperature, the increase in HDS activity with greater molybdenum content for this series of Mo/TiO₂ catalysts was due to an increase in the total number of active sites participating in the reaction and not to any modification of their intrinsic properties. In addition, the decrease in activity of the catalysts observed at higher Mo content (20%) was also directly linked with

the decrease in S_o , i.e. a decrease in the number of active sites.

The optimal Mo density on alumina for any specified conditions can be evaluated from the results presented in **Fig. 8**. The highest activity was obtained for 20 wt% Mo, which corresponds to a Mo density of *ca.* $3.9 \text{ atom} \cdot \text{nm}^{-2}$. Nevertheless, the H_2S release rate constant k_{RE} ($7.32 \times 10^{-4} \text{ s}^{-1}$) for this catalyst evaluated at 360°C was slightly lower compared to other catalysts with lower Mo loadings (about $7.8 \times 10^{-4} \text{ s}^{-1}$ for 6, 12 and 16 wt% Mo)⁴⁴. In addition, the percentage of labile sulfur S_o against the total amount of sulfur in MoS_2 was 17.4% on the 20 wt% Mo catalyst but was almost constant at *ca.* 21.5% on the other catalysts. Therefore, the optimal Mo wt% on this alumina is between 16 wt% and 20 wt% MoO_3 ⁴⁸, so the optimal Mo density is between 2.9 and $3.9 \text{ atom} \cdot \text{nm}^{-2}$ (**Fig. 9**), which is less than that for the high SSA titania carrier. The optimal activity for thiophene HDS was obtained at $\text{MoO}_3 \sim 45 \text{ wt\%}$ ($\text{SSA} \sim 500 \text{ m}^2 \cdot \text{g}^{-1}$) for a $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst prepared by the sol-gel method, which provides solids with very high SSAs and allows loading of exceptionally high Mo contents⁵². This corresponds to a Mo density of $\sim 3.8 \text{ atom} \cdot \text{nm}^{-2}$, which is in good agreement with the above result. We have proposed that although MoS_2 (100) epitactic surfaces might be formed on both Al_2O_3 and TiO_2 carriers, the morphology of the optimal active phase is different⁵⁰. The active sites are located on the edge of MoS_2 slabs on alumina, so the ratio of 'edge Mo atoms'/'total Mo atoms' is the determining factor for the catalytic performance⁵³, with an expected maximum of 30-40 Mo atoms per MoS_2 slab. Consequently, a uniform MoS_2 monolayer on alumina might exhibit lower activity than MoS_2 slabs optimally dispersed on the surface. In contrast, the MoS bonds on TiO_2 are weakened due to the formation of TiMoS phase (**Fig. 7**), and the active sites may be distributed all over the MoS_2 surface, so optimal activity is achieved by a MoS_2 monolayer. The Mo density of $5.2 \text{ atom} \cdot \text{nm}^{-2}$ obtained for optimal Mo dispersion on high SSA titania is equivalent to the Mo density of perfect MoS_2 (100) planes⁵⁰.

6. HDS Activities and Sulfur Mobility of CoMo Catalysts Supported on High Specific Surface Area Titania^{31,32}

Figure 11 compares the activity for DBT HDS of Mo/TiO_2 , CoMo/TiO_2 and NiMo/TiO_2 . The promotion effects of cobalt and nickel were observed and the activity increased in the order $\text{Mo}/\text{TiO}_2 < \text{CoMo}/\text{TiO}_2 < \text{NiMo}/\text{TiO}_2$. However, the synergetic effect of a cobalt or a nickel promoter in CoMo and NiMo HDS catalysts supported on alumina is greater than in catalysts supported on titania^{8,24}. Therefore, the main beneficial effect of the TiO_2 support appears to occur

Co(Ni)Mo ratio, 0.4; 16% $\text{MoO}_3/\text{TiO}_2$ 0.2 g, 0.01 wt% DBT in decalin, WHSV 70 h^{-1} , H_2 18 l/h, presulfiding 400°C 3 h (4% H_2S).

Fig. 11 Comparison of Activity for DBT HDS of Mo/TiO_2 , CoMo/TiO_2 and NiMo/TiO_2

on the Mo phases rather than on the Co promoter. To investigate the origin of this effect on the TiO_2 -supported catalysts, [^{35}S]DBT HDS on CoMo/TiO_2 was performed.

S_o , the amount of labile sulfur^{29,51}, and k_{RE} , the H_2S release rate constant, were determined for all catalysts from the results of the [^{35}S]DBT HDS experiments using the method described elsewhere⁵¹. The effect of the Co/Mo ratio on the sulfur behavior was investigated for the series of CMT16 catalysts (CoMo/TiO_2 , MoO_3 16 wt%) at 300°C . Note that 16 wt% was the optimal MoO_3 loading for non-promoted catalysts supported on the high SSA titania as shown above³⁰. The results are plotted in **Table 2**. The HDS reaction rate constant k_{HDS} increased with the higher cobalt content up to a Co/Mo molar ratio of 0.4 and then decreased. A similar trend was observed for the amount of labile sulfur atoms, which increased almost linearly with Co content up to a Co/Mo molar ratio of 0.4 and then decreased. In contrast, the variation of k_{RE} values with the change in the Co/Mo ratio was very small of $\sim 4.1 \times 10^{-2} \pm 0.2 \times 10^{-2} \text{ min}^{-1}$, although k_{RE} only slightly decreased at Co/Mo = 0.6. Further, k_{RE} of the Co-promoted catalysts was only a little higher than that of the corresponding non-promoted catalyst at the same temperature. Therefore, the variation in S_o significantly affected the activity of CoMo/TiO_2 catalysts. In contrast, the introduction of cobalt to Mo catalysts supported on Al_2O_3 increases k_{RE} by a factor of more than 3⁴⁸. This suggests a limit to the promoting effect of cobalt on the mobility of sulfur atoms over CoMo/TiO_2 catalysts, which was also observed over low SSA titania²⁴) with a maximum increase in k_{RE} of less than 10% at 320°C . In contrast, a significant increase in k_{RE} in the case of Co-promoted Mo catalysts supported on alumina⁴⁸) indicates that sulfur is significantly more mobile over $\text{CoMo}/\text{Al}_2\text{O}_3$ than over $\text{Mo}/\text{Al}_2\text{O}_3$. This finding agrees

Table 2 Kinetic Parameters at 300°C for CoMo/TiO₂ (MoO₃: 16 wt%) Catalysts

Co/Mo atom atom ⁻¹		0	0.2	0.4	0.6
Conversion	[%]	57.0	78.8	82.0	64.5
Selectivity CHB ^{a)}	[%]	71.4	34.6	26.8	29.0
S ₀ ^{b)}	[mg·g-cat ⁻¹]	7.29	8.28	9.20	7.49
k _{RE} ^{c)}	[10 ⁻² min ⁻¹]	3.69	4.13	4.32	3.96
k _{HDS} ^{d)}	[10 ⁻⁴ mol·h ⁻¹ ·g ⁻¹]	12.9	23.8	26.2	15.7
k _{HYD} ^{e)}	[10 ⁻⁴ mol·h ⁻¹ ·g ⁻¹]	7.99	4.87	3.80	3.15

a) Selectivity for cyclohexylbenzene (CHB).

b) Amount of labile sulfur.

c) Release constant of [³⁵S]H₂S.

d) Rate constant of pseudo-first-order reaction for hydrodesulfurization.

e) Rate constant of pseudo-first-order reaction for hydrogenation.

with the formation of an active phase providing enhanced intrinsic activity, *i.e.* the so-called CoMoS phase^{54),55)}.

The present study has described the promoting effect of TiO₂ on the MoS₂ phase by the formation of a 'TiMoS' phase (see Fig. 7). However, addition of Co to the present catalysts did not result in any significant increase in sulfur mobility (very low variation in k_{RE}). This suggests that the promotion effect on MoS₂ induced by the TiO₂ carrier is similar (increase in k_{RE}) to the promotion effect induced by Co addition to Mo/Al₂O₃ catalysts, with formation of the TiMoS and CoMoS phases, respectively. This suggests why the increase in sulfur mobility observed upon Co addition on the TiMoS phase is insignificant compared to that observed when promoting MoS₂/Al₂O₃ catalysts with Co. **Figure 12** represents the Co-promoted TiMoS phase under a reducing atmosphere²⁴⁾. In the non-promoted catalyst (equivalent to the structure in the right hand side of Fig. 7), the S* sulfur atom is shared by the Mo and Ti atoms, which induces weakening of the Mo-S* bonds. Therefore, the mobility of the S* atom is enhanced. In the Co-promoted catalyst (Fig. 12), the Mo-S* bonds together with the electronic interaction between S* and Ti atoms increases the electronic density on the Mo atoms (transfer of electrons from the Ti³⁺ species to the Mo4d conduction band). Therefore, the expected promoting effect of Co on mobility of created S_a sulfur atoms is reduced in Fig. 12. In addition, the S* and S_a sulfur atoms in Fig. 12 are supposedly both labile, but if both the S* and S_a atoms of a pyramidal structure are removed at the same time, the structure presented in Fig. 12 becomes unstable, which suggests another important reason for the observation of a much lower promoting effect than expected.

Conclusions

The [³⁵S]H₂S radioisotope tracer method was used to determine the sulfidation state of Mo/TiO₂ catalysts. MoO₃ was almost completely sulfided to MoS₂ at low temperatures such as 300°C. Part of the sulfided Mo/

Fig. 12 Schematic of the Structure of Co-promoted 'TiMoS' Phase in a Reductive Atmosphere (adapted from *Appl. Catal. A: General*, **238**, (1), 109 (2003))

TiO₂ catalyst could be reduced by H₂ at a lower temperature of 200°C.

HDS of [³⁵S]DBT was performed to determine the mobility of sulfur on the working Mo/TiO₂ and CoMo/TiO₂ catalysts. The Mo/TiO₂ catalysts exhibited almost the same amount of labile sulfur (S₀) as the Mo/Al₂O₃ catalysts with the same Mo loading, whereas the H₂S release rate constant (k_{RE}) was about two times higher. These results indicate that the presence of TiO₂ enhances the catalytic activity by increasing sulfur atom mobility rather than increasing the number of active sites. These results were consistent with the presence of a 'TiMoS' phase on TiO₂ carrier, which behaves like a 'CoMoS' phase.

The HDS activities and sulfur mobility of the Mo catalysts supported on high specific surface area TiO₂ (134 m²·g⁻¹) were investigated to clarify the properties of pH swing TiO₂. The catalytic activity increased linearly with Mo loading up to *ca.* 5.2 atom·nm⁻² (16 wt%) and then decreased, which indicates that monolayer dispersion of MoO₃ on the TiO₂ support

could be maintained up to a density of 5.2 atoms of Mo per nm². Therefore, the pH swing method used to prepare the high SSA titania provides very homogeneous titania with surface morphology suitable for optimized Mo dispersion in the sulfide state.

The HDS activity of the CoMo catalysts supported on TiO₂ increased with addition of cobalt up to a Co/Mo molar ratio of 0.4 but then decreased, irrespective of the MoO₃ loading. The amount of labile sulfur (*S*_o) also increased with the addition of cobalt up to a Co/Mo ratio of 0.4. In contrast, only very slight increase in the H₂S release rate constant (*k*_{RE}) was observed after Co promotion.

Acknowledgment

A part of this work was entrusted by the New Energy and Industrial Technology Development Organization under a subsidy of the Ministry of Economy, Trade and Industry. The author thanks Dr. F. Dumeignil, Dr. D. Wang, Dr. W. Qian, Prof. T. Kabe (Tokyo University of Agriculture and Technology (TUAT)), Dr. S. Inoue and Mr. A. Muto (Chiyoda Corporation) for helpful discussion and collaborative works, and Mr. X. Li, Mr. H. Arakawa, Mr. K. Morimoto and many other students and collaborators in TUAT for their enthusiastic experimental efforts.

References

- 1) Kabe, T., Ishihara, A., Qian, W., "Hydrodesulfurization and Hydrodenitrogenation," Kodansha, Tokyo and Wiley-VCH, New York (1999).
- 2) Ishihara, A., Lee, J., Dumeignil, F., Higashi, R., Wang, A., Qian, E. W., Kabe, T., *J. Catal.*, **217**, 59 (2003).
- 3) Ishihara, A., Lee, J., Dumeignil, F., Higashi, R., Wang, A., Qian, E. W., Kabe, T., *J. Catal.*, **224**, (2), 243 (2004).
- 4) Lee, J., Ishihara, A., Dumeignil, F., Qian, E. W., Kabe, T., *J. Mol. Cat.*, **213**, (2), 207 (2004).
- 5) Lee, J., Ishihara, A., Dumeignil, F., Miyazaki, K., Oomori, Y., Qian, E. W., Kabe, T., *J. Mol. Cat.*, **209**, 155 (2004).
- 6) Ishihara, A., Lee, J., Dumeignil, F., Qian, E. W., Kabe, T., Proceedings of the 13rd International Congress on Catalysis, (2004).
- 7) Ishihara, A., Lee, J., Dumeignil, F., Qian, E. W., Kabe, T., Proceedings of the 10th APChE Congress, (2004).
- 8) Ramirez, J., Fuentes, S., Diaz, G., Vrinat, M., Breyse, M., Lacroix, M., *Appl. Catal.*, **52**, 211 (1989).
- 9) Okamoto, Y., Maezawa, A., Imanaka, T., *J. Catal.*, **120**, 29 (1989).
- 10) Olguin, E., Vrinat, M., Cedeno, L., Ramirez, J., Borque, M., Lopez-Agudo, A., *Appl. Catal. A: General*, **165**, 1 (1997).
- 11) Ramirez, J., Ruiz-Ramirez, L., Cedeno, L., Harle, V., Vrinat, M., Breyse, M., *Appl. Catal. A: General*, **93**, 163 (1993).
- 12) Ramirez, J., Gutierrez, A., *J. Catal.*, **170**, 108 (1997).
- 13) Lecrenay, E., Sakanishi, K., Nagamatsu, T., Mochida, I., Suzuka, T., *Appl. Catal. B: Environment*, **18**, 325 (1998).
- 14) Yoshinaka, S., Segawa, K., *Catal. Today*, **45**, 293 (1998).
- 15) Kaneko, E. Y., Pulcinelli, S. H., Teixeira da Silva, V., Santilli, C. V., *Appl. Catal. A: General*, **235**, 71 (2002).
- 16) Inoue, S., Kudou, H., Muto, A., Ono, T., Proceedings of 225th ACS National Meeting, (2003), p. 88.
- 17) Inoue, S., Muto, A., Kudou, H., Ono, T., Proceedings of 226th ACS National Meeting, (2003), p. 496.
- 18) Wei, Z. B., Wei, C. D., Xin, Q., *Acta Physico-chemica Sinica*, **10**, 402 (1994).
- 19) Wei, Z. B., Xin, Q., Guo, X. X., Grange, P., Delmon, B., Yoshida, S., *Catal. Sci. Technol.*, **1**, 147 (1991).
- 20) Pophal, C., Kameda, F., Hoshino, K., Yoshinaka, S., Segawa, K., *Catal. Today*, **39**, 21 (1997).
- 21) Ookubo, A., Kanezaki, E., Ooi, K., *Langmuir*, **6**, 206 (1990).
- 22) Wang, D. H., Qian, W., Ishihara, A., Kabe, T., *Appl. Catal. A: General*, **224**, 191 (2002).
- 23) Ishihara, A., Wang, D. H., Qian, W., Kabe, T., Proceedings of 226th ACS National Meeting, **48**, (2), 607 (2003).
- 24) Wang, D. H., Li, X. G., Qian, W., Ishihara, A., Kabe, T., *Appl. Catal. A: General*, **238**, 109 (2003).
- 25) Wang, D. H., Qian, W., Ishihara, A., Kabe, T., *J. Catal.*, **209**, 266 (2002).
- 26) Kabe, T., Qian, W., Tanihata, K., Ishihara, A., Godo, M., *J. Chem. Soc., Faraday Trans.*, **93**, 3709 (1997).
- 27) Kabe, T., Qian, W., Ishihara, A., *J. Phys. Chem.*, **98**, 912 (1994).
- 28) Kabe, T., Qian, W., Ishihara, A., *J. Catal.*, **149**, 171 (1994).
- 29) Qian, W., Ishihara, A., Ogawa, S., Kabe, T., *J. Phys. Chem.*, **98**, 907 (1994).
- 30) Ishihara, A., Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., *J. Jpn. Petrol. Inst.*, **48**, (1), 37 (2005).
- 31) Ishihara, A., Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., *Appl. Catal. A: General*, **292**, 50 (2005).
- 32) Ishihara, A., Dumeignil, F., Morimoto, K., Qian, E. W., Kabe, T., Inoue, S., Muto, A., *J. Jpn. Petrol. Inst.*, **50**, (3), 154 (2007).
- 33) Wang, D., Qian, W., Ishihara, A., Kabe, T., *J. Catal.*, **203**, 322 (2001).
- 34) Johnson, M. F. L., Andrew, P. V., Bauer, S. H., Chiu, N. S., *J. Catal.*, **98**, 51 (1986).
- 35) Brauer, H. E., Starnberg, H. I., Holleboom, L. J., Hughes, H. P., *Surf. Sci.*, **331**, 419 (1995).
- 36) Faba, M. G., Gonbeau, D., Pfister-Guillouzo, G., *J. Electron. Spectrosc. Relat. Phenom.*, **73**, 65 (1995).
- 37) Wei, Z. B., Yan, W. H., Zhang, H., Ren, T. L., Xin, Q., Li, Z. C., *Appl. Catal. A: General*, **167**, 39 (1998).
- 38) Lacroix, M., Dumonteil, C., Breyse, M., Kasztelan, S., *J. Catal.*, **185**, 219 (1999).
- 39) Ramirez, J., Cedeno, L., Busca, G., *J. Catal.*, **184**, 59 (1999).
- 40) Harris, S., Chianelli, R. R., *J. Catal.*, **86**, 400 (1984).
- 41) Harris, S., Chianelli, R. R., *J. Catal.*, **98**, 17 (1986).
- 42) Shimada, H., Sato, T., Yoshimura, Y., Hiraishi, J., Nishijima, A., *J. Catal.*, **110**, 275 (1988).
- 43) Byskov, L. S., Norskov, J. K., Calusen, B. S., Topsøe, H., *Preprints Symposia Recent Advances in Heteroatom Removal*, **43**, 12 (1988).
- 44) Qian, W., Zhang, Q., Okoshi, Y., Ishihara, A., Kabe, T., *J. Chem. Soc., Faraday Trans.*, **93**, 1821 (1997).
- 45) Qian, W., Ishihara, A., Wang, G., Tsuzuki, T., Godo, M., Kabe, T., *J. Catal.*, **170**, 286 (1997).
- 46) Qian, W., Ishihara, A., Okoshi, Y., Nakakami, W., Kabe, T., *J. Chem. Soc., Faraday Trans.*, **93**, (24), 4395 (1997).
- 47) Kabe, T., Qian, W., Funato, A., Okoshi, Y., Ishihara, A., *Phys. Chem. Chem. Phys.*, **1**, 921 (1999).
- 48) Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., Ishihara, A., *Res. Chem. Intermed.*, **31**, (9), 759 (2005).
- 49) Vrinat, M., Breyse, M., Fuentes, S., Lacroix, M., Ramirez, J., Proceedings of the IX Simposio, Iberoamericano de Catalisis, ed. by Cossio, F., (1988), p. 1029.
- 50) Ng, K. Y. S., Gulari, E., *J. Catal.*, **92**, 340 (1985).

- 51) Dumeignil, F., Paul, J.-F., Qian, W. E., Ishihara, A., Payen, E., Kabe, T., *Res. Chem. Inter.*, **29**, (6), 589 (2003).
- 52) Lebihan, L., Mauchassé, C., Duhamel, L., Grimblot, J., *J. Sol-Gel Sci. and Technol.*, **2**, 837 (1994).
- 53) Kasztelan, S., Toulhoat, H., Grimblot, J., Bonnelle, J.-P., *Appl. Catal.*, **13**, 127 (1984).
- 54) Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., Morup, S., *J. Catal.*, **68**, 433 (1981).
- 55) Topsøe, N. Y., Topsøe, H., *J. Catal.*, **139**, 631 (1993).

要 旨

³⁵S トレーサー法を用いたチタニア担持モリブデン系水素化脱硫触媒の硫化状態と硫黄挙動の解析

石原 篤

東京農工大学大学院, 184-8588 東京都小金井市中町2-24-16

(現在) 三重大学大学院工学研究科分子素材工学専攻, 514-8507 津市栗真町屋町1577

一連の TiO₂ 担持 Mo 系触媒硫化状態を調べるために, ³⁵S で標識した H₂S を用いた ³⁵S トレーサー法を行った。Al₂O₃ 担持触媒とは異なり, 300℃ で TiO₂ 担持触媒の TiO₂ 表面が MoO₃ に覆われていたとしても硫化された。また, 硫化された触媒は水素雰囲気下で還元された。作動状態での硫化 Mo/TiO₂ 触媒上での硫黄の移動挙動を定量するために, ³⁵S で標識したジベンゾチオフェン ([³⁵S]DBT) の脱硫反応を行った。この方法では, 触媒上の活性点の量を示すと考えられる移動可能な硫黄量 (S₀) および一つの活性点の反応性を示すと考えられる H₂S の放出速度定数 (k_{RE}) の値を評価した。MoO₃/TiO₂ では, S₀ の値は MoO₃/Al₂O₃ 触媒よりわずかに高いだけであったが, k_{RE} の値は MoO₃/Al₂O₃ の値よりも約2倍高く, このことは TiO₂ が助触媒として作用しており, Mo 上の硫黄の移動能力を TiMoS 相を形

成することで増加させていることを示唆した。

pH スイング法による高表面積 TiO₂ (134 m²·g⁻¹) 担持触媒を調製し, DBT の HDS を検討した結果, Mo の担持量が 16 wt% まで直線的に向上し, それ以上では活性が低下した。この値は Al₂O₃ 担持触媒の場合よりも高く, pH スイング法による高表面積チタニアでは活性相のモルフォロジーがアルミナや通常の TiO₂ と異なる可能性がある。高表面積 TiO₂ 上に担持した CoMo 触媒の活性は Co の添加量の増加に伴い Co/Mo 比が 0.4 まで向上したが, それ以上の添加では減少した。移動可能な硫黄量 (S₀) も Co の添加に伴い Co/Mo 比 0.4 まで増加した。これに対して, H₂S 放出の速度定数 (k_{RE}) は Co の添加に伴いわずかに変化しただけであった。Mo/TiO₂ 触媒への Co の添加効果は Al₂O₃ 担持触媒に比べて小さいものであった。