1. Introduction

Improved hydrodesulfurization (HDS) catalysts are needed to satisfy the more and more stringent environmental restrictions imposed on the sulfur content of commercial fuels, prompting research to rapidly identify more active and selective catalyst formulations. Basically the approach has concentrated on (a) new supports; (b) noble metal-based catalysts; (c) zeolites; and (d) new compositions. In particular, several studies suggested that replacing the conventional alumina support with titania or alumina-titania mixed oxides is a promising method. Indeed, Mo catalysts supported on titania were 4.4 times more active than those supported on alumina for thiophene HDS.

However, the titania supports generally have not only a low specific surface area (70 m²/g) compared with alumina (250 m²/g) but also poor thermal stability of the anatase phase at high temperatures. Therefore, to overcome these problems, catalysts supported on TiO₂-Al₂O₃ mixed oxides were proposed as HDS catalysts to combine the advantages of the good properties of titania (high activity) and alumina (excellent texture, mechanical and thermal properties). However, use of titania-poor TiO₂-Al₂O₃ mixed oxides as supports for Mo-based catalysts does not enhance the HDS activity which remains close to that obtained with the corresponding titania-free catalyst. A significant activity increase can be expected only for catalysts based on titania-rich TiO₂-Al₂O₃ mixed oxides. Moreover, the surface of titania-rich carriers (generally prepared by the sol-gel method) is preferentially covered by alumina, contrary to the desired morphology. To overcome this problem, technologies to directly synthesize high specific surface area (SSA) TiO₂ were proposed and recently a titania support suitable for catalytic applications exhibiting a high surface area of 134 m²/g and excellent mechanical properties was synthesized by Chiyoda Corp., which allows the direct use of titania support in industrial catalytic applications.

Mo catalysts were prepared by impregnation of titania synthesized by the pH swing method which provides a TiO₂ carrier with a high specific surface area (134 m²/g) and excellent mechanical properties. Dibenzothiophene (DBT) hydrodesulfurization (HDS) activity was estimated over the obtained catalysts under typical HDS reaction conditions for various Mo contents. The activity increased linearly with Mo content up to ca. 16 wt% MoO₃ and then decreased for higher Mo loadings. The sulfur behavior on the sulfided Mo/TiO₂ catalysts was elucidated under the reaction working conditions using a 35S radioisotope tracer method, or the HDS of 35S-labeled DBT. The results indicated that at a given temperature the H₂S release rate constant (kRE) was almost constant irrespective of the Mo content, and the amount of labile sulfur (S₀) increased linearly with the Mo content in parallel with the activity up to ca. 16 wt% MoO₃. The optimal Mo dispersion was 5.2 atom/nm², which is higher than the optimal Mo dispersion on 70 m²/g TiO₂ (4.2 atom/nm²). Comparison of kRE and S₀ of the titania-based catalysts and the alumina-based catalysts suggested that the active phase consists of a TiMoS phase exhibiting a promoting effect similar to the well-known CoMoS phase (promotion of the MoS₂ active phase by Ti atoms).

Keywords
Hydrodesulfurization, High surface area titania, Molybdenum catalyst, Radioactive tracer method
the MoO₃ species on TiO₂ supports can be converted much more easily into MoS₂ than the MoO₃ species on Al₂O₃ supports during the sulfidation and reduction step. Another interesting observation was that the synergistic effect of the cobalt promoter in CoMo HDS catalysts supported on alumina is larger than in catalysts supported on titania. Therefore, the main beneficial effect of the TiO₂ support seems to involve modification of the Mo active phase rather than enhancement of the promoting effect of Co. We previously investigated the catalytic activity and sulfur behavior on Mo-based catalysts supported on TiO₂ with a relatively low surface area of ca. 70 m²·g⁻¹ (21–25). The catalytic activity increased linearly with the Mo content up to 6 wt%, which was not sufficient to compete with conventional alumina-based catalysts.

The present study evaluated the HDS catalytic performance of Mo supported on the new TiO₂ support with high specific surface area (134 m²·g⁻¹) and investigated the behavior of the sulfur on these catalysts using a ³⁵S radioisotope tracer method to monitor the HDS of ³⁵S-labeled dibenzothiophene (DBT) in situ.

2. Experimental

2.1. Catalysts

The TiO₂ support (anatase) used in this study was a solid with a surface area of 134 m²·g⁻¹ supplied by Chiyoda Corp. The Mo/TiO₂ catalysts were prepared by incipient wetness impregnation of the TiO₂ support with an aqueous solution containing the desired amount of ammonium heptamolybdate, followed by drying at 120°C for 3 h and calcining in air at 500°C for 15 h. The amounts of deposited molybdenum were checked with X-ray fluorescence measurements with an EDX-800 spectrometer (Shimadzu Corp.). The catalysts were named MT6, MT11, MT16, and MT20, in which the numerical values indicate the MoO₃ contents, i.e. 6, 11, 16, and 20 wt% MoO₃, respectively.

2.2. Apparatus and Procedure

The catalysts were packed in a reactor and presulfided under a flow of 5%H₂S/95%H₂ (5 l·h⁻¹, 0.1 MPa). After presulfiding, the reactor was cooled to room temperature and then pressurized with hydrogen. The reactant solution (DBT dissolved in decalin) was fed into the reactor pre-heated at the desired reaction temperature using a high-pressure liquid pump (Kyowa Seimitsu KHD-16). Typical HDS reaction conditions were as follows: H₂ flow rate 25 l·h⁻¹, WHSV 28 h⁻¹, reaction pressure 5 MPa, and concentration of DBT in decalin 1.0 wt%. The liquid products were collected every 15 min and analyzed using a gas chromatograph equipped with a FID detector (Shimadzu-17A, Shimadzu Corp.) and a commercial capillary column (DB-1). The same reaction conditions were used to characterize the solid catalyst properties with the [³⁵S]DBT radioisotope tracer method described elsewhere.

The rate constants (k_HDS) of the pseudo-first-order reactions of HDS of DBT were determined using the following equation:

\[ k_{HDS} = \frac{(F/W)}{x \ln(1-x)} \]  \hspace{1cm} (1)

where \( k_{HDS} \) is the rate constant of HDS (mol·h⁻¹·g·cat⁻¹), \( x \) is the conversion of DBT, \( F \) is the feed rate of the reactant (mol·h⁻¹), and \( W \) is the weight of the catalyst (g). Similarly, the formation of cyclohexylbenzene (CHB) was used to describe the hydrogenation (HYD) reaction of DBT. The rate constants (k_F) of the pseudo-first-order reaction of hydrogenation of DBT were determined from the formation of CHB.

3. Results

3.1. HDS Activities of Mo Catalysts Supported on High Specific Surface Area Titania

The DBT HDS activities of the Mo/TiO₂ catalysts with various Mo contents were measured at 320°C. The results are shown in Fig. 1, together with the activities of Mo/Al₂O₃ catalysts described in a previous study. The value of \( k_{HDS} \) for the Mo/TiO₂ catalysts increased linearly with increasing Mo content up to about 16 wt% MoO₃ and then decreased with further increasing Mo content (i.e. for 20 wt% Mo). The activation energies for HDS of DBT on the Mo/TiO₂ catalysts with various 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 that generally observed on Mo/Al₂O₃ catalysts at 84 ±8 kJ/mol. For the same Mo loading, the activities
observed over the high SSA titania were more than twice higher than those observed over the 256 m$^2$·g$^{-1}$ alumina.

The activity of the catalyst supported on alumina reached a maximum at about 4.2 Mo atoms per nm$^2$, similar to that observed in the case of 70 m$^2$·g$^{-1}$ TiO$_2$ support (Fig. 2). Using this latter support, a plateau was observed after the Mo content reached a value of 4.2 Mo atoms per nm$^2$ with only a relatively limited influence on the activity by a further increase in Mo loading. In contrast, using the 134 m$^2$·g$^{-1}$ titania support, an increase in Mo loading from 4 atom·nm$^{-2}$ to 5.2 atom·nm$^{-2}$ led to a drastic increase in activity (+60%). This indicates that the high SSA titania exhibits some particular properties that were not observed in the low SSA titania and the $\gamma$-alumina.

3.2 Sulfur Behavior on Mo Catalysts Supported on High Specific Surface Area Titania

$[^{35}S]$DBT HDS was performed to investigate the sulfur behavior on Mo/TiO$_2$ catalysts with various Mo contents. Figure 3 shows a typical operation procedure for the $[^{35}S]$ tracer method. In this example, the HDS reaction of $[^{35}S]$DBT was carried out over sulfided 16% Mo/TiO$_2$ catalyst at 320°C. Initially, a decalin solution of 1 wt% $[^{32}S]$DBT was pumped into the reactor until the conversion of DBT became constant. The $[^{32}S]$DBT solution was then replaced with a decalin solution of 1 wt% $[^{35}S]$DBT, which was pumped until the amount of detected $[^{35}S]$H$_2$S became constant. After the $[^{35}S]$DBT was introduced, the radioactivity of unreacted $[^{35}S]$DBT in the liquid product increased and approached the steady state almost immediately. In contrast, the radioactivity of the produced $[^{35}S]$H$_2$S reached the steady state after ca. 120 min. Then, the $[^{35}S]$DBT solution was replaced by decalin. When decalin and H$_2$ were used to purge the catalyst, the amount of released $[^{35}S]$H$_2$S drastically decreased and a certain quantity of $[^{35}S]$S remained on the catalyst. This quantity is represented by the shaded area A in Fig. 3. The delay observed before the quantity of released $[^{35}S]$H$_2$S attained the equilibrium (steady state) corresponded to the progressive incorporation in the active phase of $[^{35}S]$ atoms released by the desulfurization of $[^{35}S]$DBT molecules (exchange between $^{32}S$ atoms of MoS$_2$ and $^{35}S$ atoms of $[^{35}S]$DBT). Then, the cumulative difference between the amount of radioactivity of $[^{35}S]$H$_2$S detected at the steady state and the amount of radioactivity of $[^{35}S]$H$_2$S detected at each time before reaching the steady state represents the total amount of radioactivity that was incorporated in the active phase. When the reactant solution was replaced by $[^{32}S]$DBT again, incorporated $^{35}S$ could be released as $[^{35}S]$H$_2$S, as shown in Fig. 3 (shaded area B). This $[^{35}S]$H$_2$S release corresponds to the exchange of $^{35}S$ atoms incorporated in the active phase with $^{32}S$ atoms from $[^{32}S]$DBT. Since there is no isotopic effect between $^{32}S$ and $^{35}S$, the quantity of released radioactivity represented by area B is approximately equal to that of area A. These areas correspond to the radioactivity of the total amount of labile sulfur atoms on the catalysts$^{26,31}$. The amount of labile sulfur (S$_0$) could be calculated from the total radioactivity of the $[^{35}S]$H$_2$S released after $[^{35}S]$DBT was reintroduced, i.e., from the shaded area B, according to the method reported elsewhere$^{26}$. To describe the $[^{35}S]$H$_2$S release kinetics more accurately, the $[^{35}S]$H$_2$S release rate constant was determined for each catalyst. As reported previously$^{26}$, the release of $[^{35}S]$H$_2$S in the range of area B shown in Fig. 3 can be interpreted with respect to a first-order reaction. A linear relationship was obtained for the plot of ln$Ra$ as a function of $t$, where $Ra$ is the radioactivity of $[^{35}S]$H$_2$S released in the range of area B, and $t$
is the reaction time. The \([^{35}\text{S}]\text{H}_2\text{S}\) release rate constant, \(k_{\text{RE}}\), can be determined from the slope of the obtained line.

In addition to the experiments at 320°C, radioisotope tracer experiments were also conducted over the MT16 catalyst at 280 and 300°C to investigate the effect of the reaction temperature on the sulfur behavior over the Mo/TiO\(_2\) catalysts. The amount of labile sulfur (\(S_0\)) and the rate constant of \(\text{H}_2\text{S}\) release (\(k_{\text{RE}}\)) were determined. All results are summarized in Table 1. With increasing temperature, the increase in activity was associated with an increase in both the amount of labile sulfur and the \(\text{H}_2\text{S}\) release rate constant. Over MT16 catalyst, the amounts of labile sulfur atoms for 280, 300 and 320°C were 4.51, 7.29 and 10.1 mg·g-cat.\(^{-1}\), respectively, and the \(\text{H}_2\text{S}\) release rate constants were \(2.60 \times 10^{-2}\) min\(^{-1}\), \(3.69 \times 10^{-2}\) min\(^{-1}\) and \(4.85 \times 10^{-2}\) min\(^{-1}\), respectively.

The effect of the Mo content on the sulfur behavior over the Mo/TiO\(_2\) catalysts was investigated at 320°C. The results are summarized in Table 1 and Fig. 4.

### Table 1  Kinetic Parameters at Various Temperatures for Mo/TiO\(_2\) Catalysts

<table>
<thead>
<tr>
<th>MoO(_3) [wt%]</th>
<th>6</th>
<th>11</th>
<th>12*</th>
<th>16</th>
<th>16</th>
<th>16</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>320</td>
<td>320</td>
<td>320</td>
<td>280</td>
<td>300</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Conversion [%]</td>
<td>39.4</td>
<td>60.5</td>
<td>26.2</td>
<td>19.0</td>
<td>57.0</td>
<td>77.5</td>
<td>75.0</td>
</tr>
<tr>
<td>Selectivity CHB(^a) [%]</td>
<td>43.2</td>
<td>60.5</td>
<td>—</td>
<td>63.9</td>
<td>71.4</td>
<td>73.9</td>
<td>70.0</td>
</tr>
<tr>
<td>(S_0)(^b) [mg·g-cat.(^{-1})]</td>
<td>4.13</td>
<td>6.84</td>
<td>7.82</td>
<td>4.51</td>
<td>7.29</td>
<td>10.1</td>
<td>8.14</td>
</tr>
<tr>
<td>(k_{\text{RE}})(^c) [10(^{-2}) min(^{-1})]</td>
<td>4.80</td>
<td>4.62</td>
<td>2.63</td>
<td>2.60</td>
<td>3.69</td>
<td>4.85</td>
<td>4.47</td>
</tr>
<tr>
<td>(k_{\text{HDS}})(^d) [10(^{-4}) mol·h(^{-1}·\text{g}(^{-1})]</td>
<td>7.31</td>
<td>14.2</td>
<td>4.65</td>
<td>3.22</td>
<td>12.9</td>
<td>22.8</td>
<td>21.2</td>
</tr>
</tbody>
</table>

\(*\)Data for Mo/Al\(_2\)O\(_3\) catalyst cited in reference 29.

\(^a\) Selectivity of cyclohexylbenzene (CHB).

\(^b\) Amount of labile sulfur.

\(^c\) Release constant of \([^{35}\text{S}]\text{H}_2\text{S}\).

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

\(\triangleright\) Rate constant of pseudo-first-order reaction for hydrogenation.

The \(\text{H}_2\text{S}\) 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 we proposed previously\(^{26}\), 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)\(^{31}\). Therefore, at a given temperature, the increase in HDS activity with the content of molybdenum for this series of Mo/TiO\(_2\) catalysts was due to an increase in the total number of active sites participating in the reaction and not to a modification of their intrinsic properties. In addition, the decrease in the activity of the catalysts observed for a higher Mo content (20%) was also directly linked with the decrease in \(S_0\), i.e. a decrease in the number of active sites.

## 4. Discussion

### 4.1. Optimal Mo Dispersion and Sulfur Behavior on MoO\(_3\) Catalysts Supported on High Specific Surface Area Titania

Several studies have investigated the coverage of TiO\(_2\) by Mo species as a function of the molybdenum content in the case of sulfided catalysts\(^{9,30,32}\). Most structural studies showed that the MoS\(_2\) crystallites in the sulfided state are present in the form of a monolayer. Further, the coverage of titania by Mo species is generally observed to increase linearly with the Mo content up to a certain limit, and then levels off, suggesting the presence of bulk-like MoS\(_2\) structures, of which the size somewhat increases with increasing molybdenum content. Thus, in our case, the MoS\(_2\) crystallites were present as a monolayer up to 16 wt% Mo. Indeed, the catalytic activities of the series of Mo/TiO\(_2\) catalysts increased linearly with molybdenum content up to ca. 5.2 atom/nm\(^2\) (16 wt% MoO\(_3\)) and then slightly decreased beyond this value.
4.2. Comparison of Optimal Mo Dispersion over High SSA Titania (134 m²·g⁻¹), Low SSA Titania (70 m²·g⁻¹) and γ-Alumina (256 m²·g⁻¹)

We previously showed that the HDS activity of Mo catalysts supported on 70 m²·g⁻¹ titania increased linearly with the Mo content up to 6 wt% MoO₃ and then slightly leveled off for higher Mo contents²¹,²². Therefore, Mo monolayer dispersion was obtained at 4.2 atom·nm⁻², which is lower than the value of the present study (5.2 atom·nm⁻²) over the high SSA TiO₂. Presumably the pH swing method used to prepare the high SSA titania, which is known to give a solid with a great homogeneity, provides a carrier with a controlled morphology suitable to optimize the Mo dispersion as suggested elsewhere³³.

The optimal Mo density on alumina for the same experimental conditions can be evaluated from the results presented in Fig. 1. Among the tested solids, the best activity was obtained for 20 wt% Mo, which corresponds to a Mo density of ca. 3.9 atom·nm⁻². Nevertheless, for this catalyst the H₂S release rate constant kₘₒ was (7.32 × 10⁻⁴ s⁻¹) evaluated at 360°C, which is slightly decreased as compared to that of other catalysts with lower Mo loadings (about 7.8 × 10⁻⁴ s⁻¹ for 6, 12 and 16 wt% Mo)²⁹. Therefore, the percentage of labile sulfur S₀ was 17.4% on the 20 wt% Mo catalyst but 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% MoO₃, i.e. the optimal Mo density is between 2.9 and 3.9 atom·nm⁻², which is less than the value obtained on the high SSA titania carrier.

Further, over a Mo/Al₂O₃ catalyst prepared by the sol-gel method, which provides solids with very high SSA and allows loading of exceptionally high Mo contents, the optimal activity for thiophene HDS was obtained for MoO₃~45 wt% (SSA ~500 m²·g⁻¹)³⁴. This corresponds to a Mo density of ~3.8 atom·nm⁻², which is in good agreement with the above result. Previously we proposed that although MoS₂ (100) epitactic surfaces might be formed on both Al₂O₃ and TiO₂ carriers, the morphology of the optimal phase is different³³. The active sites are located on the edge of MoS₂ slabs on alumina, so the ratio edge Mo atoms to total Mo atoms is a determining factor for the catalytic performance³⁵, with an expected maximum of 30-40 Mo atoms per MoS₂ slab. As a consequence, a uniform MoS₂ monolayer on alumina might exhibit a lower activity than MoS₂ slabs optimally dispersed on the surface. In contrast, the MoS bonds on TiO₂ are weakened due to the formation of a TiMoS₂ phase (see 4.3.2, for detailed explanation) and the active sites might be distributed all over the MoS₂ surface, giving optimal activity when a MoS₂ monolayer is formed. The value of 5.2 atom·nm² obtained for the optimal Mo dispersion on the high SSA titania is equivalent to the Mo density of perfect MoS₂ (100) planes³³.

4.3. Interpretation of the Activity Results

4.3.1. Influence of the TiO₂ Carrier Specific Surface Area

The activity results at 320°C were compared for optimal Mo/TiO₂ catalysts (i.e. with an optimal Mo loading) supported on the relatively low SSA titania used in a previous study and on the high SSA of the present study (Cat1: 6 wt% Mo on 70 m²·g⁻¹ titania²³; and Cat2: 16 wt% Mo on 134 m²·g⁻¹ titania). When using the high SSA titania instead of the low SSA titania, the optimal Mo loading increased of about 2.7 times (6 wt% and 16 wt%, respectively), but the increase in kₘₒ was only 1.9 times, with values of 12.0 × 10⁻⁴ mol·h⁻¹·g⁻¹ and 22.8 × 10⁻⁴ mol·h⁻¹·g⁻¹ for Cat1 and Cat2, respectively. S₀ exhibited a reasonable increase of about 2.35 times (Cat1: S₀ = 4.3 mg·g⁻¹·cat⁻¹; Cat2: S₀ = 10.1 mg·g⁻¹·cat⁻¹). The use of the high SSA TiO₂ allowed a higher optimal Mo surface density (5.2 atom·nm⁻² versus 4.2 atom·nm⁻²), but had a detrimental effect on kₘₒ, which decreased from 6.3 × 10⁻² min⁻¹ for Cat1 to 4.85 × 10⁻² min⁻¹ for Cat2. The activity ratio calculated as [kₘₒ]Cat₂/[kₘₒ]Cat₁ for 20% MoO₃ was 1.83, which is in very good agreement with that directly calculated as (kₘₒ)Cat₂/(kₘₒ)Cat₁ = 1.9.

Therefore, a higher optimal Mo density was obtained on the 134 m²·g⁻¹ titania, but the increase in the number of sulfur vacancies S₀ was not as pronounced as expected (S₀ = 2.35 times higher for a Mo wt% increase of 2.7 times). Further, kₘₒ, the H₂S release rate constant, decreased when compared to that obtained for a conventional low SSA TiO₂. Therefore, the beneficial effect of the larger Mo loading was not as high as expected. Nevertheless, the global activity increased by a factor of almost 2 when compared with the ‘low’ SSA titania-supported catalyst, so the high SSA TiO₂ is more effective. Moreover, kₘₒ obtained for 256 m²·g⁻¹ alumina loaded with 16 wt% of MoO₃ was only about 9.3 × 10⁻⁴ mol·h⁻¹·g⁻¹ (11.4 × 10⁻⁴ mol·h⁻¹·g⁻¹ for 20 wt% MoO₃)²⁹ for the same experimental conditions (see Fig. 1), clearly illustrating again the superiority of the high SSA TiO₂ carrier (kₘₒ = 22.8 × 10⁻⁴ mol·h⁻¹·g⁻¹).

4.3.2. Comparison of the Performances of the Catalysts Supported on Alumina and on High SSA TiO₂

The HDS activity of the Mo/TiO₂ catalysts was about 2.5 times higher than that of the Mo/Al₂O₃ catalysts with the same Mo wt% at the same temperature (for example, 9.3 × 10⁻⁴ mol·h⁻¹ versus 22.8 × 10⁻⁴ mol·h⁻¹·g⁻¹ for 16 wt% Mo at 320°C), indicating that the Ti species may also act as a ‘promoter’ of the MoS₂ phase. To clarify the promoting effect of the TiO₂ support on the Mo species under the reaction working conditions, the amount of labile sulfur and the rate constant of H₂S release for a 12% MoO₃/Al₂O₃ catalyst cited in a previous study²⁰ are also given in Table 1.
The 11% MoO₃/TiO₂ catalyst had an amount of labile sulfur equivalent to that of the 12 wt% MoO₃/Al₂O₃ catalyst, but the H₂S release rate constant was roughly two times higher. Therefore, the results indicate that the use of TiO₂ as a support instead of Al₂O₃ mobilizes the sulfur on the sulfided Mo/TiO₂ catalysts rather than inducing an increase in the number of active sites. In a recent study, we proposed that the promoting effect of cobalt for Mo-based catalysts on an alumina support is due to increased mobility of the sulfur in the so-called "CoMoS" phase, in which we supposed that the strength of the Mo-S bond was weakened. A structural model was accordingly built. Similarly, the promoting effect of TiO₂ on Mo catalysts can be discussed in terms of bond strength in the metal sulfide. The strength of the Mo-S bond on TiO₂-supported catalysts is assumed to be weaker (increase in \( k_{\text{rel}} \), i.e. increase in the S mobility) than that on Al₂O₃-supported catalysts. In other words, the TiO₂ in Mo catalysts not only acts as a support but also as an electronic promoter of the Mo sulfidic phase.

Unlike Al₂O₃ supports, TiO₂ supports can be plus or minus extensively sulfided during the catalyst pre-sulfiding procedure and the sulfided Ti species can be further reduced into Ti³⁺ species under a H₂ atmosphere. This reduction involves the formation of sulfur anion vacancies containing trapped electrons. The structure of the sulfided Mo/TiO₂ catalysts is accordingly proposed in Fig. 5. In this model, the structure of MoS₅ is a deformed tetrahedral structure as on Al₂O₃ supports. As represented in Fig. 5, the TiO₂ support is sulfided into TiS₂ simultaneously to the active phase during the pre-sulfiding procedure. Then, under a high pressure H₂ atmosphere (i.e. for conventional HDS reaction conditions) reduction occurs and Ti(III) species are created, involving the formation of sulfur anion vacancies containing trapped electrons. Due to the formation of sulfur anion vacancies and the possibility of an electron transfer from Ti(III) to Mo, the S' sulfur in the vicinity of the formed sulfur anion vacancy might be weakly bonded with the two neighboring Ti atoms. This leads to the formation of a new 'TiMoS' active phase in which the Mo-S' bond strength is weakened making the S' sulfur more labile. This proposal is in good agreement with the radiotracer method results that suggested an increase in sulfur mobility when using titania instead of alumina (in Table 1, the H₂S release rate constant for the catalyst supported on titania is two times higher than that for the catalyst supported on alumina). In brief, the electronic promotion of the Mo active phase brought by the TiO₂ carrier phase is similar to that induced by the classical Co promoter. Indeed, the strength of the Mo-S bond is also subsequently decreased in this case due to the formation of a 'TiMoS' active phase acting in the same way as the 'CoMoS' phase.

5. Conclusions

(1) The HDS activities over the Mo catalysts supported on high specific surface area TiO₂ (134 m²·g⁻¹) increased linearly with Mo loading up to ca. 5.2 atom·nm⁻² (16 wt%) and then decreased beyond this value, which indicates that the monolayer dispersion of MoO₃ on the TiO₂ support could be maintained up to a density of 5.2 atoms of Mo per nm². This value is higher than that obtained over 70 m²·g⁻¹ TiO₂ (4.2 atoms of Mo per nm²) prepared by a classical method. This suggests that 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. In addition, the HDS activity of the Mo/TiO₂ catalyst with 16 wt% Mo was about 2.5 times higher than that observed over the Mo/Al₂O₃ catalyst with the same Mo loading. The optimal Mo density observed for catalysts supported on alumina is lower (2.9-3.9 atom·nm⁻²) suggesting that the morphology of the active phase might be different on alumina and titania.

(2) 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 \( k_{\text{rel}} \) was about two times higher. These results indicate that the presence of TiO₂ enhances the activity by increasing the sulfur atom mobility rather than inducing an increase in the number of active sites. This result, together with the other results, was consistent with the presence of a 'TiMoS' phase on the high SSA TiO₂ carrier, which behaves like a 'CoMoS' phase.

Acknowledgments

This work was entrusted by the New Energy and Industrial Technology Development Organization under a subsidy of the Ministry of Economy, Trade and Industry.

References

要  旨

³⁵Sトレーサー法を用いた高表面積チタニア担持モリブデン系水素化脱硫触媒上における硫黄挙動の解析

石原 篤⑴, Franck DUMEIGNIL⑵, 王 丹紅⑶, 李 相国⑷, 荒川 久⑸

⑴ 東京農工大学工学部化学システム工学科, 184-8588 東京都小金井市中町2-24-16
⑵ 千代田化工建設(株)研究開発センター, 221-0022 横浜市神奈川区守屋町3-13

pHスイング法で調製した高表面積で機械的挙動特性の優れたTiO₂担体（134 m²·g⁻¹）の上に含浸法によりMoを担持させた調製した触媒を用いて、Mo/TiO₂触媒のジベンゾチオフェン（DBT）の水素化脱硫活性に及ぼすMo担持量の影響を検討した。その結果、16 wt％Moまで活性が直線的に向上するが、Mo担持量をさらに増やすと活性が若干低下することが分かった。さらに、³⁵Sアイソトープトレーサー法（すなわち³⁵SJDBTの水素化脱硫反応）により、硫黄化したMo/TiO₂触媒上における硫黄の挙動を解析した。同じ温度においてはMo担持量によらずH₂Sの放出速度定数（k₈₁）はほぼ同様な値を示したのに対し、Mo担持量の増加とともに移動可能な硫黄の量(S₀)は16 wt％Moまで直線的に増加することが分かった。

また、高表面積チタニア担持触媒上のMoの最適分散度（5.2 atom/nm²）は低表面積（70 m²·g⁻¹）チタニア担体上にMoを担持したときの最適分散度（4.2 atom/nm²）より高い値を示すことが分かった。さらに、k₈₁およびS₀の値はMoS₂/TiO₂触媒の活性相がTiMoS₂相であり、CoMoS₂相と同種の活性向上効果をもたらすことを示唆した（Ti原子によるMoS₂活性相の活性向上）。

J. Jpn. Petrol. Inst., Vol. 48, No. 1, 2005