Catalytic Performance of Noble Metals Supported on Alumina-modified Silica Gel for Hydrodesulfurization Reaction

Yasuharu KANDA *, Takao KOBAYASHI, Yoshio UEMICHI, and Masatoshi SUGIOKA

Dept. of Applied Chemistry, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, JAPAN

(Received April 21, 2005)

The catalytic activities and properties of noble metals (Pt, Pd, Rh, Ru) supported on silica gel (SiO$_2$) and alumina-modified silica gel (Al$_2$O$_3$·SiO$_2$) were investigated for the hydrodesulfurization of thiophene. Al$_2$O$_3$·SiO$_2$ was prepared by an impregnation method using aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O) aqueous solution. Pt/8 wt%Al$_2$O$_3$·SiO$_2$ catalyst showed the highest activity for hydrodesulfurization of thiophene among various supported noble metal catalysts and this activity was higher than that of commercial CoMo/Al$_2$O$_3$ hydrodesulfurization catalyst. The sulfur tolerance of noble metal/SiO$_2$ was enhanced by Al$_2$O$_3$ modification of SiO$_2$ and Pt/8 wt%Al$_2$O$_3$·SiO$_2$ catalyst showed the highest sulfur tolerance among the supported noble metal catalysts. Pt/8 wt%Al$_2$O$_3$·SiO$_2$ catalyst had high hydrogenating ability for unsaturated C$_3$ hydrocarbons formed in the hydrodesulfurization of thiophene. The catalysts were characterized by XRD, H$_2$ adsorption and FT-IR. Dispersion of Pt on 8 wt%Al$_2$O$_3$·SiO$_2$ was remarkably higher than that on SiO$_2$ and the particle size of Pt on 8 wt%Al$_2$O$_3$·SiO$_2$ was the lowest among the supported noble metal catalysts. The acidity of 8 wt%Al$_2$O$_3$·SiO$_2$ was higher than that of SiO$_2$. Furthermore, Brønsted acid sites were present on 8 wt%Al$_2$O$_3$·SiO$_2$. FT-IR spectroscopy of thiophene adsorbed on 8 wt%Al$_2$O$_3$·SiO$_2$ support indicated that the thiophene molecule interacting with the Brønsted acid site on 8 wt%Al$_2$O$_3$·SiO$_2$. The activity of the double-layer (Pt/SiO$_2$ + 8 wt%Al$_2$O$_3$·SiO$_2$) catalyst obtained experimentally was higher than that calculated. This suggests that spillover hydrogen was present on Pt/Al$_2$O$_3$·SiO$_2$ in the hydrodesulfurization of thiophene. Both the Brønsted acid sites of Al$_2$O$_3$·SiO$_2$ and the Pt particles in the Pt/Al$_2$O$_3$·SiO$_2$ catalyst act as active sites for the hydrodesulfurization of thiophene.

Keywords
Hydrodesulfurization, Thiophene, Noble metal catalyst, Alumina modification, Bifunctional catalysis

1. Introduction

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the important processes used in the petroleum industry to produce clean fuels$^{1-4}$. Highly active HDS catalysts, which exhibit higher activity than commercial CoMo/Al$_2$O$_3$ HDS catalyst, have been developed to produce lower sulfur content fuels$^{5,6}$. Noble metal catalysts are believed to have high potential as new HDS catalysts$^{7-12}$. We previously investigated the development of highly active noble metal HDS catalysts supported on zeolites$^{13-15}$. Recently, mesoporous silicate materials such as FSM-16, MCM-41 and SBA-15, which have larger mean pore diameter than zeolites, have attracted attention as new materials for catalysts and catalyst supports. Some attempts have been made to develop new HDS catalysts based on mesoporous silicates$^{16,17}$. We previously reported$^{18-22}$ that noble metals, especially platinum, supported on mesoporous silicates such as FSM-16$^{18}$, MCM-41$^{19}$, SBA-15$^{20}$ and alumina-modified MCM-41 (Al$_2$O$_3$·MCM-41)$^{21,22}$ showed high and stable activity for the HDS of thiophene, and noble metals supported on mesoporous silicates have high potential as new HDS catalysts for petroleum feedstocks. However, mesoporous silicates are not easy to produce on the industrial scale as the support for noble metal HDS catalysts.

In the present study, we examined the catalytic performance of noble metals supported on alumina-modified silica gel (Al$_2$O$_3$·SiO$_2$) for the HDS of thiophene to develop highly active noble metal HDS catalysts supported on metal oxides, which can be produced in large quantities.

2. Experimental

2.1. Preparation of Catalysts

Silica gel (SiO$_2$, BET surface area 295 m$^2$/g) was...
supplied from Nippon Aerosil Co., and Al₂O₃ (JRC-ALO-2) and SiO₂·Al₂O₃ (JRC-SA-1) from the Catalysis Society of Japan. Alumina-modified silica gel (Al₂O₃·SiO₂) was prepared by an impregnation method using aluminum nitrate (Al(NO₃)₃·9H₂O, Wako Pure Chemical Industries, Ltd., GR grade) aqueous solution. After aluminum nitrate impregnation, supports were dried at 120°C and then calcined at 500°C (10°C/min) for 4 h in air. Supported noble metal catalysts were prepared by an impregnation method using noble metal chlorides (Kanto Chemical Co., Inc., GR grade) such as H₃PtCl₆·6H₂O, PdCl₂, RhCl₃·3H₂O and RuCl₃·3H₂O aqueous solutions, to obtain a noble metal loading of 5 wt%. However, PdCl₂ was dissolved in 1.0 mol/l HCl aqueous solution because PdCl₂ did not dissolve completely in water. All catalysts were dried at 120°C and then calcined at 500°C (10°C/min) for 4 h in air. The catalysts were pretreated with helium at 500°C for 1 h and then reduced with hydrogen at 450°C for 1 h prior to the reaction.

2. 2. Hydrodesulfurization of Thiophene

HDS of thiophene was carried out at 350°C under 0.1 MPa in a conventional fixed bed flow reactor. Thiophene (ca. 3 vol%) was introduced into the reactor by passing hydrogen (30 ml/min) through a thiophene trap cooled at 0°C. Reaction conditions were as follows: catalyst weight = 0.1 g, H₂/thiophene = 30 mol/mol, W/F = 37.9 g·h/mol. The reaction products were analyzed by gas chromatography (FID) with silicone DC-550 (2 m, 150°C) and VZ-7 (4 m, 0°C) columns, respectively.

2. 3. Characterization of Catalysts

The acidity of Al₂O₃·SiO₂ was evaluated by 2-propanol (2-PA) dehydration (200°C) and cumene cracking (400°C) using a pulse reactor with helium carrier gas. In both reactions, catalysts (0.03 g) were charged into reactor and were pretreated at 500°C for 1 h before the reaction. The dispersion of the noble metal on Al₂O₃·SiO₂ was measured by XRD analysis and hydrogen adsorption. XRD analysis used a Rigaku diffractometer with Cu Kα radiation. Adsorption of hydrogen on the noble metal catalysts was carried out in a Pyrex glass vacuum system at 25°C. The supported noble metal catalysts were evacuated at 500°C for 1 h followed by reduction with hydrogen (26.7 kPa) at 450°C for 1 h and evacuation at the same temperature for 1 h before hydrogen adsorption. FT-IR spectra of pyridine and thiophene adsorbed on 8 wt%Al₂O₃·SiO₂ were observed using a Jasco FT-IR spectrometer. The catalysts were evacuated at 500°C for 2 h prior to the measurement. Catalytic activities of SiO₂ and 8 wt% Al₂O₃·SiO₂ for thiophene and tetrahydrothiophene (THT) cracking at 400°C were evaluated using a pulse reactor with helium carrier gas. The catalysts (0.05 g) were charged into the reactor and pretreated at 500°C for 1 h before the reaction.

3. Results and Discussion

3.1. Catalytic Activities of Noble Metal Supported on Al₂O₃·SiO₂

The catalytic activities of various noble metals (Pt, Pd, Rh, Ru) supported on 8 wt%Al₂O₃·SiO₂ for the HDS of thiophene were examined at 350°C. The catalytic activities remarkably varied with the noble metal as shown in Fig. 1. The order of the activities of these catalysts after 2 h reaction was as follows: Pt > Pd > Rh > Ru. The activity of Pt/8 wt%Al₂O₃·SiO₂ was the highest and was higher than that of commercial presulfided CoMo/Al₂O₃ HDS catalyst. Previously, we reported that dispersion of Pt on Al₂O₃·MCM-41 was the highest and the particle size was the lowest among noble metals supported on Al₂O₃·MCM-41. We also reported that the catalytic activity of noble metal/HZSM-5 except Pt/HZSM-5 for the hydrocracking of benzene was completely poisoned by the introduction of hydrogen sulfide, but that of Pt/HZSM-5 almost completely regenerated with time on stream. This result suggests that Pt/HZSM-5 catalyst does not lose hydrogenation activity, i.e., ability to dissociate hydrogen, even after the introduction of hydrogen sulfide. Furthermore, Pt containing MCM-41 catalyst showed the highest naphthalene hydrogenation activity among the noble metal (Pt, Rh, Pd, Ru, Ir) containing MCM-41 catalysts and only Pt catalyst was reversibly poisoned by dibenzothiophene. Therefore, the supported Pt catalyst showed the highest activity among supported noble metal catalysts and the order of the catalytic activities of noble metal supported on 8 wt%Al₂O₃·SiO₂ can be explained by dispersion, hydrogenation ability and sulfur tolerance of the noble metal. The catalytic activities of noble metal/8 wt%Al₂O₃·SiO₂, except Ru/8 wt%Al₂O₃·SiO₂, in the HDS of thiophene decreased.

with reaction time and attained steady activity after reaction for 2 h.

Examination of the catalytic activities of Pt supported on SiO$_2$ modified with various amounts of Al$_2$O$_3$ loading for the HDS of thiophene revealed an optimal Al$_2$O$_3$ loading for the activity of Pt/Al$_2$O$_3$-SiO$_2$ of 8 wt% as shown in Fig. 2. The BET surface area of Al$_2$O$_3$-SiO$_2$ decreased with increasing Al$_2$O$_3$ loading. However, the BET surface area of 8 wt% Al$_2$O$_3$-SiO$_2$ was remained high (246 m$^2$/g) after Al$_2$O$_3$ modification. Dispersion of Pt on Al$_2$O$_3$-SiO$_2$ was about 0.8 with Al$_2$O$_3$ loading from 8 to 24 wt% as shown in Fig. 2. These results indicate that high Pt dispersion with high BET surface area after Al$_2$O$_3$ modification is one of the important factors in the high activity for HDS of thiophene.

Figure 3 shows the activities of noble metal/SiO$_2$ and noble metal/8 wt% Al$_2$O$_3$-SiO$_2$ catalysts for HDS of thiophene at 350°C. The activities of noble metal/8 wt% Al$_2$O$_3$-SiO$_2$ catalysts were higher than those of noble metal/SiO$_2$ catalysts and Pt supported on 8 wt% Al$_2$O$_3$-SiO$_2$ had the highest catalytic activity.

The sulfur tolerance (A/A$_0$) of Pt, Pd and Rh supported on SiO$_2$ and 8 wt% Al$_2$O$_3$-SiO$_2$ was evaluated as HDS activity before (A$_0$) and after (A) hydrogen sulfide introduction for 1 h. Hydrogen sulfide (3 ml/min) was introduced using micro feeder with a glass syringe for 1 h. HDS activities of noble metal catalysts were decreased by introduction of hydrogen sulfide. However, the HDS activities of supported noble metal catalysts (except Rh/SiO$_2$ catalyst) were completely regenerated by cutting off the flow of hydrogen sulfide. The HDS activity of Rh/SiO$_2$ catalyst after cutting off the flow of hydrogen sulfide was higher than that before the introduction of hydrogen sulfide. Previously, we have reported that HDS activity of Rh/SiO$_2$ catalyst was enhanced by presulfidation. Increased HDS activity of Rh/SiO$_2$ after the introduction of hydrogen sulfide was explained by sulfidation of Rh. Since Rh/SiO$_2$ catalyst was sulfided by introduction of hydrogen sulfide for 1 h, the A/A$_0$ of reduced Rh/SiO$_2$ catalyst was based on the HDS activity after introduction of hydrogen sulfide for 5 min taken as A. The sulfur tolerance of supported noble metal catalysts were enhanced by Al$_2$O$_3$ modification of SiO$_2$. The sulfur tolerance of Pt/8 wt% Al$_2$O$_3$-SiO$_2$ catalyst was remarkably higher than that of Pt/SiO$_2$ and was the highest among the supported noble metal catalysts as shown in Fig. 4. Generally, the positive effect of acidity of support on the sulfur tolerance of noble metals can be explained by the electron deficiency. Thus, increased sulfur tolerance of supported noble metal catalyst was attributed to electron attraction from the noble metal by the acid sites of Al$_2$O$_3$-SiO$_2$. This indicates that enhancement of sulfur tolerance was important to increase the HDS activity of supported noble metal catalyst. Since the sulfur tolerance of Pt/SiO$_2$ catalyst was remarkably enhanced by Al$_2$O$_3$ modification of SiO$_2$, the effect of Al$_2$O$_3$ modification on HDS activity of supported Pt catalyst was more significant than for other supported noble metal catalysts.

The reaction products of the HDS of thiophene over Pt/8 wt% Al$_2$O$_3$-SiO$_2$ were mainly C$_5$ hydrocarbons (butane 88%, butenes 11%) and trace amounts of C$_6$-C$_9$ hydrocarbons, whereas those over Pt/SiO$_2$ were C$_7$ hydrocarbons (butane 72%, butenes 27%) as shown in Table 1. These results indicate that Pt/Al$_2$O$_3$-SiO$_2$ catalyst has higher hydrogenating ability than Pt/SiO$_2$ catalyst for unsaturated C$_7$ hydrocarbons formed in the HDS of thiophene.
3.2. Catalytic Properties of Pt/Al₂O₃-SiO₂

Pt/8 wt% Al₂O₃-SiO₂ was investigated in detail to understand the causes of the high activity of Pt/8 wt% Al₂O₃-SiO₂ for the HDS of thiophene. Figure 5 shows the XRD patterns of Pt/SiO₂ and Pt/8 wt% Al₂O₃-SiO₂ after reduction at 450°C. The peak height of Pt on SiO₂ was significant but decreased remarkably on 8 wt% Al₂O₃-SiO₂. This indicates that the dispersion of Pt on 8 wt% Al₂O₃-SiO₂ was higher than that on SiO₂. Table 2 shows the dispersion and particle sizes of various noble metals on SiO₂ and 8 wt% Al₂O₃-SiO₂ measured by the hydrogen adsorption method. Pt dispersion (0.76) on 8 wt% Al₂O₃-SiO₂ was the highest and particle size (1.24 nm) was the lowest among the noble metal/SiO₂ and noble metal/8 wt% Al₂O₃-SiO₂ catalysts. Dispersions of noble metals (except Ru) on 8 wt% Al₂O₃-SiO₂ were higher than on SiO₂. [PtCl₆]²⁻ and [RhCl₃(H₂O)₃] react with the hydroxyl groups on the Al₂O₃ surface. We showed that dispersion of Pt on ZSM-5 zeolite increased with higher proton content. This result indicates that anionic noble metal precursors such as [PtCl₆]²⁻ and [PdCl₄]²⁻ electrostatically interact with the Brönsted acid sites of the Al₂O₃-SiO₂ surface. Therefore, dispersion of noble metals (except Ru) on SiO₂ was enhanced by Al₂O₃ modification of SiO₂. The surface sulfur tolerance of small Pt and Rh particles (< 2 nm) is higher than that of large particles. Thus, small Pt and Rh particles on 8 wt% Al₂O₃-SiO₂ showed high sulfur tolerance as shown in Fig. 4.

Since the dehydration of 2-propanol (2-PA) proceeds on both Lewis and Brönsted acid sites and cumene cracking proceeds on Brönsted acid sites, the acidic properties of supports can be evaluated by 2-PA dehydration and cumene cracking. We also evaluated the acidic properties of SiO₂ and 8 wt% Al₂O₃-SiO₂ by the reaction of 2-PA dehydration (200°C) and cumene cracking (400°C) using a pulse reactor. SiO₂ showed very low activity for both reactions whereas 8 wt% Al₂O₃-SiO₂ showed high activity for these reactions (see Table 3). These results indicate that 8 wt% Al₂O₃-SiO₂ has high acidity and Brönsted acid sites are present on 8 wt% Al₂O₃-SiO₂.

![Figure 4: Sulfur Tolerance](image)

*Fig. 4: Sulfur tolerance (A/Ao) of SiO₂ and 8 wt% Al₂O₃-SiO₂-supported Noble Metal Catalysts*

![Figure 5: XRD Patterns](image)

*Fig. 5: XRD Patterns of Pt Supported on (a) SiO₂ and (b) 8 wt% Al₂O₃-SiO₂ after Reduction at 450°C*

**Table 1: Product Distribution in HDS of Thiophene over Reduced SiO₂-supported Noble Metal and 8 wt% Al₂O₃-SiO₂-supported Noble Metal Catalysts at 350°C**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HDS [%]</th>
<th>C₅⁺ [%]</th>
<th>C₆⁺ [%]</th>
<th>C₇⁺ [%]</th>
<th>1,3-C₄⁻ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO₂</td>
<td>30.1</td>
<td>1.0</td>
<td>71.7</td>
<td>27.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt/8 wt% Al₂O₃-SiO₂</td>
<td>79.5</td>
<td>0.8</td>
<td>88.3</td>
<td>10.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Pd/SiO₂</td>
<td>44.5</td>
<td>0.2</td>
<td>28.5</td>
<td>71.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Pd/8 wt% Al₂O₃-SiO₂</td>
<td>57.0</td>
<td>0.7</td>
<td>81.3</td>
<td>18.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Rh/SiO₂</td>
<td>23.5</td>
<td>0.7</td>
<td>11.4</td>
<td>87.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Rh/8 wt% Al₂O₃-SiO₂</td>
<td>29.3</td>
<td>1.7</td>
<td>84.5</td>
<td>13.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Ru/SiO₂</td>
<td>0.3</td>
<td>22.8</td>
<td>0.0</td>
<td>66.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Ru/8 wt% Al₂O₃-SiO₂</td>
<td>1.1</td>
<td>18.4</td>
<td>1.6</td>
<td>80.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

a) C₅-C₇ hydrocarbons.  b) Butanes.  c) Butenes.  d) 1,3-Butadiene.
Table 3 shows the catalytic properties of Pt/8 wt% Al₂O₃·SiO₂ and other supported Pt catalysts such as Pt/ SiO₂, Pt/Al₂O₃, and Pt/SiO₂·Al₂O₃. Pt/8 wt% Al₂O₃·SiO₂ catalyst had the highest HDS activity, with high Pt dispersion and Brönsted acidity. Evaluation of the HDS activities of the supported Pt catalysts by turn-over frequency (TOF) showed the TOF of Pt/SiO₂·Al₂O₃ catalyst was remarkably higher than those of Pt/SiO₂ and Pt/Al₂O₃ catalysts. The relationship between dispersion of Pt on Al₂O₃ and TOF is negative in HDS of thiophene²⁰. However, this cannot explain why the TOF of Pt/SiO₂·Al₂O₃ catalyst is so high. Moreover, TOF of Pt/8 wt% Al₂O₃·SiO₂ catalyst with high Pt dispersion was higher than that of Pt/Al₂O₃ catalyst with similar Pt dispersion. Thus, the high TOF of Pt/SiO₂·Al₂O₃ and Pt/8 wt% Al₂O₃·SiO₂ catalysts with Brönsted acid sites were attributed to the electron deficiency of the Pt particles caused by the Brönsted acid sites and/or direct participation of the Brönsted acid sites in the HDS of thiophene.

3.3. Mechanism of HDS of Thiophene on Pt/Al₂O₃·SiO₂ Catalyst

Pt/8 wt% Al₂O₃·SiO₂ catalyst had the highest activity among noble metal/8 wt% Al₂O₃·SiO₂ catalysts for the HDS of thiophene. We studied the reaction mechanism of HDS of thiophene over Pt/Al₂O₃·SiO₂ catalyst.

We previously found²⁰⁻²² that Brönsted acid sites on the support of noble metal catalysts act as sites for the activation of thiophene. We supposed that the Brönsted acid sites on Al₂O₃·SiO₂ are also active for the activation of thiophene, whereas Pt particles are active for the activation of hydrogen in the HDS of thiophene. We confirmed the presence of the Brönsted acid sites on 8 wt% Al₂O₃·SiO₂ by the observation of the FT-IR spectra of pyridine at 1547 cm⁻¹ adsorbed on 8 wt% Al₂O₃·SiO₂ as shown in spectrum (b) in Fig. 6. Presumably the surface silanol group (Si-ÖH) on 8 wt% Al₂O₃·SiO₂ acts as a Brönsted acid site and is the site for the activation of thiophene in the HDS of thiophene.

The FT-IR spectra of thiophene adsorbed on 8 wt% Al₂O₃·SiO₂ were observed to clarify the interaction of the silanol group with the thiophene molecule. In the background spectra of 8 wt% Al₂O₃·SiO₂ evacuated at 500°C for 2 h, the silanol group was observed at 3746 cm⁻¹ as shown in spectrum (a) in Fig. 7. After introduction of 2 kPa of thiophene, the absorption band at 3746 cm⁻¹ decreased and shifted to 3611 cm⁻¹ as shown in spectrum (b). The decreased absorbance of silanol group was almost regenerated by evacuation at room temperature as shown in spectrum (c). These findings confirmed that thiophene is adsorbed and activated smoothly on the Brönsted acid sites on 8 wt% Al₂O₃·SiO₂ in the

Table 2  Dispersion and Particle Size of Noble Metals on SiO₂ and 8 wt% Al₂O₃·SiO₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion (H/noble metal)</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO₂</td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>Pt/8 wt% Al₂O₃·SiO₂</td>
<td></td>
<td>0.76</td>
</tr>
<tr>
<td>Pd/SiO₂</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>Pt/8 wt% Al₂O₃·SiO₂</td>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td>Rh/SiO₂</td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Rh/8 wt% Al₂O₃·SiO₂</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>Ru/SiO₂</td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>Ru/8 wt% Al₂O₃·SiO₂</td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

a) Measured by the hydrogen adsorption method.

Table 3  Catalytic Properties of Pt Supported on Various Metal Oxides

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HDS conv. [%]</th>
<th>Dispersion [H/Pt]</th>
<th>TOF[¹] [h⁻¹]</th>
<th>Dehydration of 2-PA² [%]</th>
<th>Cracking of cumene³ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/8 wt% Al₂O₃·SiO₂</td>
<td>76.4</td>
<td>0.76</td>
<td>10.4</td>
<td>39.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>40.3</td>
<td>0.82</td>
<td>5.0</td>
<td>62.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt/SiO₂·Al₂O₃</td>
<td>38.0</td>
<td>0.12</td>
<td>32.0</td>
<td>98.4</td>
<td>44.7</td>
</tr>
<tr>
<td>Pt/SiO₂</td>
<td>30.1</td>
<td>0.47</td>
<td>6.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

a) Supported Pt catalyst.  b) Calculated by Pt dispersion.  c) Activity of support (0.03 g).

Fig. 6 FT-IR Spectra of Pyridine Adsorbed on (a) SiO₂ and (b) 8 wt% Al₂O₃·SiO₂.

Pyridine was adsorbed at 150°C followed by evacuation at 150°C for 0.5 h.
HDS of thiophene over Pt/8 wt%Al₂O₃·SiO₂ catalyst.

Furthermore, we tried to confirm the existence of spillover hydrogen in the HDS of thiophene over Pt/Al₂O₃·SiO₂ catalyst. The HDS activity of double-layer catalyst (0.1 g of Pt/SiO₂ (A, upper layer) and 0.1 g of 8 wt%Al₂O₃·SiO₂ (B, lower layer)) was examined. The activity of double-layer catalyst obtained experimentally was higher than that calculated (A+B) as shown in Fig. 8. This result indicates that hydrogen was activated on the Pt particles of Pt/SiO₂ to form spillover hydrogen, and thiophene was activated on the Brönsted acid sites of 8 wt%Al₂O₃·SiO₂. This suggests that spillover hydrogen is present on Pt/Al₂O₃·SiO₂ in the HDS of thiophene.

On the basis of these results, we propose a possible mechanism for the HDS of thiophene over Pt/Al₂O₃·SiO₂ catalyst. Previously⁴¹, we reported that the HDS activities of metal oxide-supported Pt catalysts were strongly correlated with the dispersion of Pt on metal oxide, implying that the thiophene molecule reacts with hydrogen on the Pt particle. However, the metal oxide-supported Pt catalysts such as Pt/SiO₂ and Pt/Al₂O₃ showed remarkably lower activity than Pt/8 wt%Al₂O₃·SiO₂ catalyst with Brönsted acid sites as shown in Table 3. Therefore, we propose two reaction routes for thiophene HDS over the highly active Pt/Al₂O₃·SiO₂ catalyst: (i) monofunctional route (on Pt particles) and (ii) bifunctional route (on Brönsted acid sites). In reaction route (ii), the thiophene is activated on the Brönsted acid sites of Al₂O₃·SiO₂ and hydrogen is activated on the Pt particles to form spillover hydrogen. Since the dispersion of Pt and acidity of the support were enhanced by Al₂O₃ modification of SiO₂, the sulfur tolerance property of Pt was remarkably enhanced. Small Pt and Pd particles on high silica USY zeolite showed high sulfur tolerance and the metallic phase was still present in Pt and Pd particles even after sulfidation⁴¹. The Pt particle in high sulfur tolerant Pt/Al₂O₃·SiO₂ catalyst would partly retain the metallic state even in the HDS reaction. The metallic Pt particle or surface is important to form spillover hydrogen and hydrogenation of unsaturated hydrocarbons in the HDS of thiophene. The spillover hydrogen formed on the Pt particles attacks the activated thiophene on the Brönsted acid sites of Al₂O₃·SiO₂. We also observed trace amounts of tetrahydrothiophene (THT) in the HDS products. Figure 9 shows the catalytic activities of thiophene and THT cracking over SiO₂ and 8 wt%Al₂O₃·SiO₂ at 400°C. Both SiO₂ and 8 wt%Al₂O₃·SiO₂ catalysts showed very low activities for thiophene cracking. However, the catalytic activity of 8 wt%Al₂O₃·SiO₂ for THT cracking was higher than that of SiO₂. The main product in THT cracking over 8 wt%Al₂O₃·SiO₂ catalyst was hydrocarbons (ca. 70%). Thus, the activated thiophene is hydrogenated into THT and the H₂S and C₆ hydrocarbon species were formed on acid site by cleavage of the C-S bond in the THT molecule.

4. Conclusions

Pt/8 wt%Al₂O₃·SiO₂ catalyst showed high activity for the HDS of thiophene, and both the Pt particles and Brönsted acid sites on the Pt/Al₂O₃·SiO₂ catalyst act as active sites for the HDS of thiophene. Pt/8 wt%Al₂O₃·SiO₂ has high potential as an industrial HDS cat-
Aerosil Co. for supplying the silica gel.

We thank Nippon for Scientific Research, Japan.

Acknowledgment

This work was partly supported by a Grant-in-Aid for Scientific Research, Japan. We thank Nippon Aerosil Co. for supplying the silica gel.

References


Fig. 9 Catalytic Activities of SiO2 and 8 wt%Al2O3-SiO2 for Cracking of Thiophene and Tetrahydrothiophene (THT) at 400°C.
要 旨
アルミナ修飾シリカゲル担持貴金属の水素化脱硫反応に対する触媒特性

神田 康晴，小林 弘夫，上道 芳夫，杉岡 正敬

室蘭工業大学応用化学科，050-8585 北海道室蘭市水元町27-1

貴金属担持シリカゲル（SiO₂）およびアルミナ修飾シリカゲル（Al₂O₃ SiO₂）のチオフェンの水素化脱硫反応に対する活性と触媒特性について検討した。Al₂O₃ SiO₂を硝酸アルミニウム（Al(NO₃)₃・9H₂O）水溶液を用いた合浸法により調製した。Pt/8 wt% Al₂O₃ SiO₂触媒は種々の担持貴金属触媒において高い水素化脱硫活性を示し、この活性は市販のCoMo/Al₂O₃系脱硫触媒の活性を上回るものであった。また、担持貴金属触媒の耐酸性について検討した結果、SiO₂にPtを修飾を施すことによって担持貴金属触媒の耐酸性強化を向上し、特に担持Pt触媒において著しい耐酸性の向上が見られた。Pt/Al₂O₃ SiO₂触媒はチオフェンの水素化脱硫反応において、生成した不飽和C₄炭化水素に対して高い水素化能を有していた。触媒は2-プロパノールの脱水反応、クエンの分解反応、XRD、水素吸着およびFT-IRによりキャラクタリゼーションを行った。その結果、Pt/8 wt% Al₂O₃ SiO₂の白金の分散度はPt/SiO₂よりも著しく高く、その白金の粒子径は種々の担持貴金属触媒において最小となることが分かった。また、8 wt% Al₂O₃ SiO₂はSiO₂よりも高い酸性質を有していることが明らかとなった。さらに、8 wt% Al₂O₃ SiO₂上にBrönsted酸点が存在することが分かった。8 wt% Al₂O₃ SiO₂担体に吸着させたチオフェンのFT-IRスペクトールより、チオフェン分子と8 wt% Al₂O₃ SiO₂のBrönsted酸点との間には相互作用があることが明らかとなった。Pt/SiO₂および8 wt% Al₂O₃ SiO₂を用いた2層型触媒のHDS活性は、これらの触媒のHDS活性を合わせたものよりも高いことが分かった。これより、Pt/Al₂O₃ SiO₂触媒におけるHDS反応にはスピールオーバー水素が関与していることが考えられる。Pt/Al₂O₃ SiO₂触媒によるチオフェンの水素化脱硫反応では、Al₂O₃ SiO₂上のBrönsted酸点およびPt粒子が活性点として作用することが明らかとなった。