Catalytic Performance of Noble Metals Supported on Mesoporous Silica MCM-41 for Hydrodesulfurization of Benzothiophene

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The catalytic performances of noble metals (Pt, Rh, Pd, Ru) supported on mesoporous silica MCM-41 were investigated for the hydrodesulfurization (HDS) of benzothiophene (BT). The order of HDS activities of noble metal/MCM-41 catalysts was Pt > Rh > Pd > Ru. Pt/MCM-41 catalyst showed high HDS activity, which was higher than that of commercial CoMo/Al₂O₃ catalyst. The supported noble metal catalysts were characterized by TEM, XRD, hydrogen adsorption and benzene hydrogenation. The order of dispersion of noble metal on MCM-41 was Rh > Pt > Pd > Ru, which was not the same as that of HDS activities. On the other hand, the order of the activities of noble metal/MCM-41 catalysts for benzene hydrogenation was Pt > Rh > Pd > Ru. The hydrogenation activity of Pt/MCM-41 catalyst was regenerated after H₂S treatment, but the activities of other catalysts were not regenerated. Thus, high hydrogenation activity and sulfur tolerance are important factors to prepare highly active noble metal/MCM-41 catalysts. Pt/MCM-41 catalyst showed remarkably high and stable activity for the HDS of BT, but Pt/SiO₂ catalyst, with similar Pt dispersion on MCM-41, showed low activity which decreased with time on stream. Since MCM-41 showed higher acidity than SiO₂, hydrogenation activity and sulfur tolerance of Pt/MCM-41 catalyst were higher than those of Pt/SiO₂ catalyst. The results of FT-IR analysis indicated that the strength of interaction between BT and MCM-41 was stronger than that of SiO₂, suggesting that both acid sites of MCM-41 and Pt particles in the Pt/MCM-41 catalyst act as active sites for the HDS of BT. Furthermore, FT-IR spectra of BT adsorbed on Pt/MCM-41 revealed that BT interacts with the silanol group on the MCM-41 surface rather than the Pt surface. Therefore, we concluded that the high HDS activity of Pt/MCM-41 catalyst could be attributed to the high hydrogenation activity of Pt and the acidity of the support.

Keywords
Hydrodesulfurization, Benzothiophene, Noble metal catalyst, MCM-41, Bifunctional catalysis

1. Introduction

Hydrodesulfurization (HDS) is one of the most important processes in the petroleum industry for the production of clean fuel. CoMo/Al₂O₃ catalyst is widely used in the HDS process. But the recent development of HDS catalysts, with higher activity than commercial CoMo/Al₂O₃ HDS catalyst, have been claimed in the petroleum industry, and are considered to reduce the problem of acid rain affecting the global environment. Fuel consumption and carbon dioxide (CO₂) emissions of diesel vehicles are superior to those of gasoline vehicles. However, emissions of nitrogen oxides (NOₓ) and particulate matter (PM) from diesel engines exceed those from gasoline engines. Since the aromatic compounds in diesel fuel are important in the formation of PM, reduction of aromatic compounds in diesel fuel is required. Noble metal catalysts have high HDS and hydrogenation activities to produce sulfur-free diesel fuel containing fewer aromatic compounds. Therefore, noble metal catalysts have drawn much attention as a new HDS catalyst.

Recently, mesoporous silicates such as FSM-16, MCM-41 and SBA-15, which have larger pore diameters and higher surface areas than zeolites, have been attracting much attention as new materials for catalysts and catalyst supports. Some researchers have attempted to develop new HDS catalysts based on mesoporous materials. Previously, we reported that noble metals, especially platinum, supported on mesoporous silicates, such as FSM-16, MCM-41 and SBA-15, showed high activities in the HDS of thiophene (TP). However, diesel fuel contains benzo thiophenes and dibenzothiophenes, which are larger molecules than TP.
The present study examined the catalytic activities of various noble metals supported on mesoporous silica MCM-41 for the HDS of benzothiophene (BT) in order to develop highly active new HDS catalysts. Furthermore, we compared the HDS activity and properties of Pt/MCM-41 with those of Pt/amorphous silica (SiO2) to obtain information about the active sites of Pt/MCM-41 catalyst for the HDS reaction.

2. Experimental

2.1. Preparation of Catalysts

Siliceous MCM-41 was prepared using Ludox colloidal silica (Du Pont Co.) and surfactants such as CH3(CH2)nI(N(CH3))2Br (Aldrich), (CH3CH2CH2)6NBBr (Aldrich) and 25 wt% C10H15N(CH3)Cl (Aldrich) in aqueous solution. The product was washed with water and dried at 120°C. The templates were removed by calcination in air at 540°C for 10 h. Mesoporous silica MCM-41 with BET surface area of 1057 m2/g and BJH pore diameter of 3.1 nm was used. Amorphous silica (SiO2, JRC-SIO-1) was supplied by the Catalysis Society of Japan, with BET surface area of 111 m2/g and BJH pore diameter of 18.2 nm. Supported noble metal catalysts were prepared by the impregnation method using noble metal chlorides (Kanto Chemical Co., Inc.) such as H2PtCl6, 6H2O, PdCl2, RhCl3·3H2O and RuCl3·3H2O in aqueous solutions, to a metal loading of 5 wt%. However, PdCl2 was dissolved in 1.0 mol/l HCl aqueous solution because PdCl2 does not dissolve completely in water. The Pt/MCM-41 catalyst was prepared using various Pt precursors such as H2PtCl6·H2O, (NH4)2PtCl6 and K2PtCl6 aqueous solutions to evaluate the effect of Pt precursor on the HDS activity of Pt/MCM-41 catalyst. Pt/SiO2 catalyst was prepared using H3PtCl6·H2O aqueous solution. Supported noble metal catalysts were calcined at 500°C for 4 h in air and were reduced at 450°C for 1 h prior to the reaction.

2.2. Hydrodesulfurization of Benzothiophene

Hydrodesulfurization of benzothiophene over noble metal/MCM-41 catalyst was carried out at 350°C under 0.1 MPa using a conventional fixed-bed flow reactor. Benzothiophene was dissolved in n-decane and this solution (5 mol% BT) was introduced into the reactor using a microfeeder. Reaction products and BT were analyzed by gas chromatography (Hitachi G-3000, FID) with a TC-1 capillary column (60 m, 35°C). The reaction conditions were catalyst weight = 0.05 g and W/F = 18.0 g·h/mol.

2.3. Hydrogenation of Benzene

Hydrogenation of benzene over noble metal/MCM-41 catalyst was carried out at 300°C under 0.1 MPa using a conventional fixed-bed flow reactor. Benzene was introduced into the reactor using a hydrogen stream (30 ml/min) passed through a saturator containing liquid benzene at 0°C. Reaction products and benzene were analyzed by gas chromatography (Hitachi G-3000, FID) with a TC-1 capillary column (60 m, 35°C). The reaction conditions were catalyst weight = 0.05 g and W/F = 18.0 g·h/mol.

2.4. Characterization of Catalysts

Supported noble metal catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and hydrogen adsorption. TEM observation used a JEOL JEM-2000FX with acceleration voltage 200 kV and magnification ×120000. XRD analysis of the supported noble metal catalysts was carried out using a Rigaku diffractometer with CuKα radiation. Dispersion and particle diameter of the noble metal on MCM-41 and SiO2 were measured by the hydrogen adsorption method using a Pyrex glass vacuum system at 25°C. Supported noble metal catalyst was 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. The acidities of MCM-41 and SiO2 were evaluated by 2-propanol (2-PA) dehydration using a pulse reactor with helium carrier gas. Catalysts (0.03 g) were charged into the reactor and were pretreated at 500°C for 1 h before the reaction. 2-PA (2 μl) was introduced into the reactor using a microsyringe. The reaction products of 2-PA dehydration were separated using a PEG-1000 column (2 m, 80°C). However, the reaction products of 2-PA dehydration were trapped by liquid nitrogen and were flashed by boiling water before separation. After separation, the reactant and products were analyzed by thermal conductivity detector (TCD). FT-IR spectroscopy of BT adsorbed on MCM-41 and SiO2 was performed using a Jasco FT-IR spectrometer. The FT-IR spectra were recorded with 200 scans and 2 cm−1 resolution. The supports were pressed into wafers and were evacuated at 500°C for 2 h prior to measurement. Pt/MCM-41 was evacuated at 500°C for 2 h following by reduction with hydrogen (26.7 kPa) at 450°C for 1 h. Furthermore, reduced Pt/MCM-41 was evacuated at the same temperature for 1 h before measurement.

3. Results and Discussion

3.1. Catalytic Activities of Noble Metals Supported on MCM-41 for HDS of BT

The catalytic activities of noble metals (Pt, Rh, Pd,
Ru) supported on MCM-41 for HDS of BT were examined at 350℃. The catalytic activities of noble metal/MCM-41 depended greatly on the noble metal as shown in Fig. 1. The HDS activity for BT of Rh/MCM-41 catalyst was the same as that of commercial presulfided CoMo/Al₂O₃ HDS catalyst, whereas Pt/MCM-41 catalyst showed higher and stable activity. The order of the activities of these catalysts for the HDS of BT was as follows: Pt/MCM-41 > Rh/MCM-41 > Pd/MCM-41 > Ru/MCM-41. HDS of BT over Pt/MCM-41 catalyst formed mainly ethylbenzene and small amounts of unidentified hydrocarbons. These results indicate that Pt/MCM-41 catalyst has high hydrogenating ability for styrene and low hydrocracking activity for ethylbenzene in the HDS of BT.

We characterized the noble metal/MCM-41 catalysts to clarify the reasons for the above order of HDS activities.

### 3.2. Catalytic Properties of Noble Metals Supported on MCM-41

Figure 2 shows the TEM images of noble metal/MCM-41 catalysts after calcination. The particle size of Rh on MCM-41 was the smallest among the noble metal/MCM-41 catalysts. Large Pt particles as well as many small Pt particles were observed on Pt/MCM-41 catalyst. However, the particle size of Ru on MCM-41 was considerably larger than on other noble metal catalysts and no small Ru particles were observed in Fig. 2 (d). Furthermore, a wide distribution of particle sizes

![Figure 2](image2.png)

**Fig. 2** TEM Images of Noble Metal/MCM-41 Catalysts after Calcination at 500℃
of Pd was observed on MCM-41 in Fig. 2 (c). Figure 3 shows the XRD patterns of reduced noble metal/MCM-41 catalysts. No diffraction peaks assigned to Rh species were observed on Rh/MCM-41 catalyst. However, large diffraction peaks were observed on other supported noble metal catalysts, and the intensity of the diffraction peak of Pt was the highest among the noble metal/MCM-41 catalysts, probably due to the large Pt particles as shown in Fig. 2 (a). The broad peaks in the XRD pattern of Pd/MCM-41 were due to the non-uniform particle size of Pd as shown in Fig. 2 (c). These results imply that Rh occurs on MCM-41 as small particles, whereas Pt, Pd and Ru, especially Pt, occur on MCM-41 as large particles. These results agreed with the findings of TEM observation as shown in Fig. 2.

Generally, since hydrogen adsorption on noble metals is remarkably decreased by sulfidation, the dispersion and particle size of noble metal calculated by hydrogen adsorption cannot be accurate. Furthermore, small noble metal particles showed higher sulfur tolerance than large particles. The high activity of noble metal catalyst for the HDS reaction is probably due to the small noble metal particles supported on the carrier. Therefore, we used particle size calculated by hydrogen adsorption as one of the important parameters to evaluate the HDS activity of supported noble metal catalyst. Figure 4 shows the extent of dispersion of noble metal on MCM-41 calculated from the amount of adsorbed hydrogen as Rh/MCM-41 > Pt/MCM-41 > Pd/MCM-41 > Ru/MCM-41. However, the catalytic activities of noble metal supported on MCM-41 for the HDS of BT are independent of the dispersion of noble metal on MCM-41. The particle sizes of noble metals calculated from the amount of hydrogen adsorption are also shown in Fig. 4. The particle sizes of the noble metals were ca. 2 nm on MCM-41-supported Pt, Pd and Rh catalysts. In contrast, the particle size of Ru was about 4.5 times larger than those of other noble metals. The XRD pattern of Ru/MCM-41 catalyst after calcination detected significant peaks of RuO₂. These results can be explained by the formation and aggregation of ruthenium oxide species in the calcination step. Therefore, the low activity of Ru/MCM-41 catalyst for the HDS of BT was caused by the low dispersion of Ru on MCM-41.

The hydrogenation activities of noble metal/MCM-41 catalysts were evaluated using the activity for benzene hydrogenation at 300°C. Pt/MCM-41 catalyst showed the highest activity for the hydrogenation of benzene among the noble metal catalysts as shown in Fig. 5 and Table 1.

The order of the catalytic activities of noble metal/MCM-41 catalysts for benzene hydrogenation was Pt/MCM-41 > Rh/MCM-41 > Pd/MCM-41 > Ru/MCM-41. The order of catalytic activities of noble metal containing MCM-41 for naphthalene hydrogenation in the presence of BT is also Pt > Rh > Pd > Ru = Ir. The Rh/MCM-41 catalyst showed cracking ac-
tivity in benzene hydrogenation, and showed low activity for benzene hydrogenation, so cracking products were only observed as reaction products. Rh and Ru/MCM-41 catalysts showed higher hydrogenolysis activities than other noble metal catalysts, explained by percentage of Pauling d-bond character. The hydrogenation activities of the noble metal/MCM-41 catalysts evaluated by TOF (turnover frequency) are shown in Table 1. The TOF of supported Pt catalyst for the hydrogenation reaction was remarkably higher than that of other noble metal catalysts. The hydrogenation activities of supported noble metal catalysts after treatment using 5 vol% \( H_2S - H_2 \) mixture gas are shown in Fig. 5. The catalytic activities of noble metal/MCM-41, except Pt, for benzene hydrogenation were remarkably decreased by \( H_2S \) treatment, but that of Pt/MCM-41 was regenerated with time on stream. Thus, Pt/MCM-41 catalyst has remarkably higher hydrogenation reaction was remarkably higher than that of other noble metal catalysts. Therefore, high hydrogenation activity and sulfur tolerance are important factors to prepare highly active Pt/MCM-41 catalyst for BT HDS. Therefore, the Pt/MCM-41 catalyst was investigated in detail.

3.3. Effect of Pt Precursor on Catalytic Properties of Pt/MCM-41 for HDS of BT

The Pt/MCM-41 catalyst showed the highest activity for HDS of BT among the supported noble metal catalysts, and this activity was higher than that of the commercial CoMo/Al\(_2\)O\(_3\) catalyst. Therefore, the effect of Pt precursors on the HDS activity of Pt/MCM-41 was examined in detail to identify the causes of the high activity of Pt/MCM-41 catalyst for HDS of BT.

Table 2 shows the effect of Pt precursor on HDS activity and dispersion of Pt on Pt/MCM-41 catalyst. The HDS activities of the Pt/MCM-41 catalysts were remarkably changed with type of Pt precursor as follows: \( H_2PtCl_6 \cdot 6H_2O \succ (NH_4)\_2PtCl_6 \succ K_2PtCl_6 \). On the other hand, the order of the Pt dispersion was as follows: \( H_2PtCl_6 \cdot 6H_2O \succ K_2PtCl_6 = (NH_4)\_2PtCl_6 \). The isoelectric point of SiO\(_2\) is pH ≈ 2, whereas the pH of \( H_2PtCl_6 \cdot 6H_2O \) aqueous solution is 1. Since the SiO\(_2\) surface is positively charged in \( H_2PtCl_6 \cdot 6H_2O \) aqueous solution, anionic Pt precursor ([PtCl\(_6\)]\(^2\)) may electrostatically interact with the SiO\(_2\) surface. However, the pH of \( K_2PtCl_6 \) and \((NH_4)\_2PtCl_6\) aqueous solutions were both about 2, respectively. Thus, Pt dispersion in Pt/MCM-41 catalyst prepared from \( H_2PtCl_6 \cdot 6H_2O \) was higher than in those from other Pt precursors. Therefore, the HDS activity of Pt/MCM-41 prepared from \( H_2PtCl_6 \cdot 6H_2O \) was remarkably higher than in those from other Pt precursors. However, although the dispersion of Pt in Pt/MCM-41 prepared from \( K_2PtCl_6 \) was the same as that prepared from \((NH_4)\_2PtCl_6\), the HDS activity of Pt/MCM-41 catalyst prepared from \( K_2PtCl_6 \) was the same as that from \((NH_4)\_2PtCl_6\). This result indicates that the HDS activity of Pt/MCM-41 was not determined by only Pt dispersion.

3.4. Comparison of Pt/MCM-41 and Pt/SiO\(_2\)

3.4.1. HDS Activity and Properties of Pt/SiO\(_2\) Catalyst

The HDS activity of supported Pt catalyst was not determined by only Pt dispersion. The dispersion of Pt on MCM-41 was the same as that on SiO\(_2\) as shown in Table 3. Thus, the HDS activity and properties of Pt/MCM-41 catalyst were compared with those of Pt/SiO\(_2\) catalyst to discover why the Pt/MCM-41 catalyst showed high HDS activity. Figure 6 shows the HDS of BT over Pt supported on MCM-41 and SiO\(_2\) at 350°C. The Pt/MCM-41 catalyst showed remarkably higher activity than Pt/SiO\(_2\) catalyst for the HDS of BT and the activity of Pt/SiO\(_2\) catalyst decreased with time on stream. Furthermore, the benzene hydrogenation

### Table 1 Catalytic Activities of Noble Metal Supported on MCM-41 for Benzene Hydrogenation at 300°C before H\(_2S\) Treatment (after reaction for 5 h)

<table>
<thead>
<tr>
<th>Noble metal</th>
<th>Yield of cyclohexane [%]</th>
<th>Yield of cracking products [%]</th>
<th>TOF for hydrogenation [h(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>35.5</td>
<td>0.0</td>
<td>16.4</td>
</tr>
<tr>
<td>Rh</td>
<td>14.8</td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Pd</td>
<td>13.3</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

### Table 2 Effect of Pt Precursor on the HDS Activity and Dispersion of Pt in Pt/MCM-41 Catalyst

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Conversion of BT [%]</th>
<th>Dispersion of Pt (H/Pt)</th>
<th>Particle size of Pt [nm]</th>
<th>TOF [h(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2PtCl_6 \cdot 6H_2O )</td>
<td>98.6</td>
<td>0.47</td>
<td>2.0</td>
<td>3.77</td>
</tr>
<tr>
<td>((NH_4)_2PtCl_6)</td>
<td>7.9</td>
<td>0.14</td>
<td>6.8</td>
<td>1.01</td>
</tr>
<tr>
<td>( K_2PtCl_6 )</td>
<td>5.5</td>
<td>0.20</td>
<td>4.8</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### Table 3 Dispersion and Particle Size of Pt on MCM-41 and SiO\(_2\) Measured by the Hydrogen Adsorption Method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion of Pt (H/Pt)</th>
<th>Particle size of Pt [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MCM-41</td>
<td>0.47</td>
<td>2.01</td>
</tr>
<tr>
<td>Pt/SiO(_2)</td>
<td>0.43</td>
<td>2.21</td>
</tr>
</tbody>
</table>
activity of Pt/MCM-41 catalyst was remarkably higher than that of Pt/SiO2 catalyst as shown in Fig. 7. Significant deactivation was observed in Pt/SiO2 catalyst. This support contains a small amount of Al2O3 (ca. 1 wt%) as an impurity. Since this reaction was carried out at high temperature (300℃), the deactivation may be explained by coke formation on the impurity Al contained in the SiO2 support. The hydrogenation activity of Pt/SiO2 catalyst was remarkably decreased after H2S treatment. The hydrogenation activity of Pt/MCM-41 catalyst was also decreased by H2S treatment, but the activity was regenerated with time on stream. This indicates that Pt/MCM-41 catalyst has higher sulfur tolerance than Pt/SiO2 catalyst.

Generally, the sulfur tolerance of noble metal is attributed to the electron deficiency of noble metal by acid sites23)~26). The 2-PA molecule is dehydrated to propylene at acid sites of catalyst surface. Therefore, we evaluated the acidity of the support by 2-PA dehydration. Figure 8 shows the catalytic activities of MCM-41 and SiO2 for 2-PA dehydration at 300℃. The dehydration activity of MCM-41 was remarkably higher than that of SiO2. This result indicates that MCM-41 has higher acidity than SiO2. Two reaction routes are possible for benzene hydrogenation in the presence of organic sulfur compounds over sulfur tolerant Pt/zeolite catalysts27)~29). Benzene is hydrogenated into cyclohexane on the Pt particle and/or the Brønsted acid site. In benzene hydrogenation without organic sulfur compounds, the acid site would act as the active site. Since the acidity of MCM-41 was higher than that of SiO2, Pt/MCM-41 catalyst showed both higher hydrogenation activity and sulfur tolerance than Pt/SiO2. Thus, the high acidity and hydrogenation activity after catalyst poisoning by sulfur are important factors in the high HDS activity of Pt/MCM-41 catalyst. Furthermore, the stable activity of Pt/MCM-41 for HDS of BT was possible because of the high sulfur tolerance.

3.4.2. Interaction between Support and BT

We previously reported16)~21),30) that acid sites of the support interact with the TP molecule. Therefore, the strength of interaction between the support and BT is expected to change with the acidity of the support. We examined the effect of acidity on the strength of interaction between the support and BT by FT-IR.

The background spectra of MCM-41 evacuated at 500℃ for 2 h contained the silanol group signal at 3745 cm⁻¹ as shown in spectrum (i) in Fig. 9 (a). After introduction of 0.07 kPa of BT onto MCM-41 at 25℃, the absorption band of Si-OH at 3745 cm⁻¹ decreased considerably and a large and broad peak appeared at 3600 cm⁻¹, which was assigned to the silanol groups interacting with the BT molecules. Furthermore, the peak at 3600 cm⁻¹ persisted even after evacuation at 150℃ for 0.5 h. On the other hand, the decreased absorbance of silanol groups was not completely regenerated by evacuation at 150℃, with a
i) After evacuation at 500℃ for 2 h, (ii) in the presence of benzothiophene (0.07 kPa) at 25℃, (iii) after evacuation at 25℃ for 0.5 h, (iv) after evacuation at 150℃ for 0.5 h.

Fig. 9 FT-IR Spectra of Benzothiophene Adsorbed on (a) MCM-41 and (b) SiO2

small shoulder peak at around 3600 cm\(^{-1}\).

The background spectra of SiO\(_2\) evacuated at 500℃ for 2 h contained the silanol group signal at 3745 cm\(^{-1}\) as shown in spectrum (i) in Fig. 9 (b). After introduction of 0.07 kPa of BT onto SiO\(_2\) at 25℃, the absorption band at 3745 cm\(^{-1}\) decreased and shifted to around 3600 cm\(^{-1}\) as shown in spectrum (ii) in Fig. 9 (b). The decreased absorbance of the silanol group was completely regenerated by the evacuation at 25℃, with no shoulder peak at around 3600 cm\(^{-1}\) as shown in spectrum (iii) in Fig. 9 (b). We previously found that the acidity of Al\(_2\)O\(_3\)-modified MCM-41 (Al\(_2\)O\(_3\)-MCM-41) was higher than that of Al incorporated MCM-41 (AlMCM-41), so the strength of interaction between Al\(_2\)O\(_3\)-MCM-41 and TP was stronger than that of AlMCM-41\(^{19}\). These results indicate that the interaction between BT and MCM-41 with acid sites is stronger than that with SiO\(_2\) without acid sites. Furthermore, we observed that the shoulder peak at around 3600 cm\(^{-1}\) in the spectrum of TP adsorbed on MCM-41 was completely regenerated by evacuation at 25℃\(^{19}\). Thus, BT interacted more strongly with MCM-41 than TP.

Figure 10 shows the FT-IR spectra of BT adsorbed on Pt/MCM-41 after reduction at 450℃ (Fig. 10 (a)). The spectra were similar to those of MCM-41. Furthermore, the bands of BT adsorbed on Pt/MCM-41 occurred at 1592, 1497, 1456, 1422, 1343 and 1313, which were attributed to vibration of the aromatic ring. After evacuation at 150℃ for 0.5 h, these bands were not observed as shown in spectrum (iv) in Fig. 10 (b). These results indicate that BT interacts with the silanol group on the MCM-41 surface rather than the Pt surface.

(a) High frequency region, (b) low frequency region.

Fig. 10 FT-IR Spectra of Benzothiophene Adsorbed on Reduced Pt/MCM-41

3.4.3. Active Sites in Pt/MCM-41 Catalyst for HDS of BT

We examined the effect of H\(_2\)/BT ratio on the HDS activity of Pt/MCM-41 catalyst. Figure 11 shows the effect of H\(_2\)/BT ratio on the pseudo first order HDS rates of Pt/MCM-41 and CoMo/Al\(_2\)O\(_3\) catalysts. The HDS rate constant was enhanced with increasing H\(_2\)/BT ratio on Pt/MCM-41 catalyst. In addition, the HDS rate constant of Pt/MCM-41 was higher than that of CoMo/Al\(_2\)O\(_3\) catalyst at any H\(_2\)/BT ratio. This indicates that the HDS rate constant of Pt/MCM-41 catalyst is significantly dependent on the H\(_2\)/BT ratio compared with that of CoMo/Al\(_2\)O\(_3\). Furthermore, Pt/MCM-41 catalyst with high hydrogenation activity showed remarkably higher HDS activity and sulfur tolerance than other noble metal/MCM-41 catalysts as shown in
3.4.1. The interaction between the BT molecule and catalysts for the HDS of BT as described in section support remarkably affected the activity of supported Pt catalysts. The active site of CoMo/Al2O3 catalyst is widely accepted to involve the sulfur vacancy of metal sulfide[32,33]. In contrast to CoMo/Al2O3 catalyst, we supposed two reaction routes for HDS of TP over highly active supported Pt catalysts: a monofunctional route in which the HDS reaction proceeds only on Pt particles, and a bifunctional route in which both Pt particle and Brønsted acid sites are involved in HDS[19,21,34,35].

The active sites for HDS and hydrogenation reactions over Pt-Pd/USY catalyst were the coordinatively unsaturated site and metallic site of the sulfided Pd-Pt surface, respectively[30]. Thus, in the monofunctional route, coordinatively unsaturated sites of sulfided Pt particle act as active sites for HDS of BT over Pt/MCM-41 catalyst. In the bifunctional route, TP is adsorbed on the Brønsted acid sites of the support and the spillover hydrogen formed on the metallic Pt particle attacks the TP molecule on the acid site[19,21,34,35]. In the present study, the acidity of the support remarkably affected the activity of supported Pt catalysts for the HDS of BT as described in section 3.4.1. The interaction between the BT molecule and acidic MCM-41 was stronger than that of non-acidic SiO2 as shown in Fig. 9. Therefore, both the Pt particles and acid sites of the Pt/MCM-41 catalyst also act as active sites in the HDS of BT as well as HDS of TP over highly active Pt/HZSM-5[20,31], Pt/Al2O3-modified SiO2 (Al2O3-SiO2)34, Pt/Al2O3-modified MCM-41 (Al2O3-MCM-41)19,19 and Pt/AISBA-15[20,21] catalysts as shown in Fig. 12. Furthermore, the acid site is important for high HDS activity not only as the hydrogenolysis site of BT in the HDS reaction but also for enhancement of sulfur tolerance of the noble metal particles.

According to the bifunctional route, the low HDS activity of Pt/MCM-41 catalyst prepared from K2PtCl6 can be explained as follows. We evaluated the HDS activities of various Pt/MCM-41 catalysts by turnover frequency (TOF) calculated from Pt dispersion. The TOF of Pt/MCM-41 catalyst prepared from (NH4)2PtCl6 was 2 times higher than that prepared from K2PtCl6 as shown in Table 2. This indicates that the low TOF of Pt/MCM-41 catalyst prepared from K2PtCl6 was due to the decrease in acid sites acting as active sites for the HDS of BT in the presence of potassium ion (K+). The amount of spillover hydrogen over supported Pt catalysts was related to the number of hydroxyl groups on the support surface[30]. Furthermore, the spillover hydrogen was trapped by alkali metal ions[13,15]. That is, the hydrogenation activity is decreased in the presence of alkali metal ion. Therefore, the low HDS activity of Pt/MCM-41 catalyst prepared from K2PtCl6 can be attributed to decreased hydrogenation activity of Pt and acidity of MCM-41. These results indicate that high hydrogenating activity to form spillover hydrogen and acidity are important factors in the formulation of highly active supported Pt catalyst for the HDS reaction.

4. Conclusion

The Pt/MCM-41 catalyst showed high and stable activity for the HDS of BT, and this activity was the highest among the noble metal/MCM-41 catalysts. The characterization results revealed that hydrogenation activity and acidity of the support strongly affects the HDS activity of supported Pt catalyst. Both Pt particles and acid sites on highly active Pt/MCM-41 catalyst act as active sites for the HDS reaction.

References


要旨
ベンゾチオフェンの水素化脱硫反応に対するメソポーラスシリカ MCM-41 携持貴金属の触媒特性

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ベンゾチオフェン（BT）の水素化脱硫（HDS）反応に対する貴金属（Pt, Rh, Pd, Ru）携持メソポーラスシリカの触媒特性について検討した。貴金属/MCM-41触媒のHDS活性の序列はPt>Rh>Pd>Ruとなり, Pt/MCM-41触媒の活性はCoMo/Al₂O₃の触媒よりも高く, 安定であった。携持貴重金属触媒のベンゾチオフェン水素化活性の評価結果から, 貴金属/MCM-41触媒が高いHDS活性を示すためには高い水素化能と耐硫黄性が必要であると考えられる。また, Pt/MCM-41触媒はPt/SiO₂触媒よりも高い水素化能および耐硫黄性を示した。これはMCM-41がSiO₂よりも高い酸性質を有しているためであると考えられる。FT-IRスペクトルの測定結果から, BTとMCM-41との相互通用作用はSiO₂の場合よりも強いことが分かった。これより, Pt/MCM-41触媒上のHDS反応においてPtおよび酸点はいずれも活性点として働くと推測された。したがって, Pt/MCM-41が高いHDS活性を示したのは高い水素化能と酸性質を有しているためであると結論付けた。