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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^{1),2)}. 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^{3)~5)}. Fuel consumption and carbon dioxide (CO₂) emissions of diesel vehicles are superior to those of gasoline vehicles⁶⁾. However, emissions of nitrogen oxides (NO_x) and particulate matter (PM) from diesel engines exceed those from gasoline engines. Since the aromatic compounds in diesel fuel are impor-

tant 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^{7)~11)}.

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^{12)~15)}. Previously, we reported that noble metals, especially platinum, supported on mesoporous silicates, such as FSM-16¹⁶⁾, MCM-41^{17)~19)} and SBA-15^{20),21)}, showed high activities in the HDS of thiophene (TP). However, diesel fuel contains benzothiophenes and dibenzothiophenes, which are larger molecules than TP.

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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)₁₁N(CH₃)₃Br (Aldrich), (CH₃CH₂CH₂)₄NBr (Aldrich) and 25 wt% C₁₆H₃₃N(CH₃)₃Cl (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 H₂PtCl₆·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 263-30, FID) with a silicone DC-550 column (2 m, 190°C). The reaction conditions were catalyst weight = 0.1 g and *W/F* = 218 g·h/mol. The rate constant as a pseudo first order reaction was calculated from the following equation.

$$k_{\text{HDS}} = \frac{-\ln(1 - x/100)}{W/F} \quad (1)$$

In which, k_{HDS} is the reaction rate of BT HDS (mol/h·g), and x is conversion at 10 h (%).

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 followed 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°C. 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

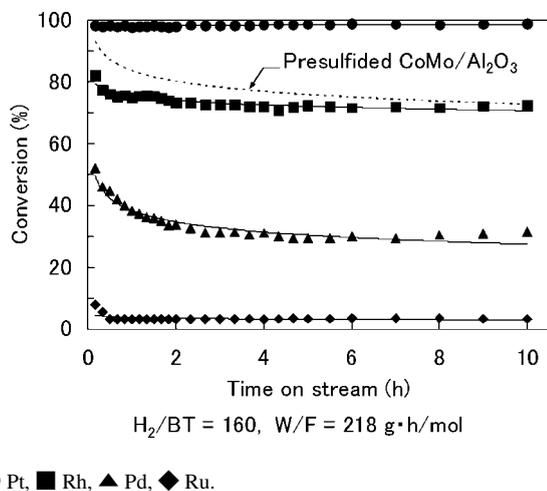


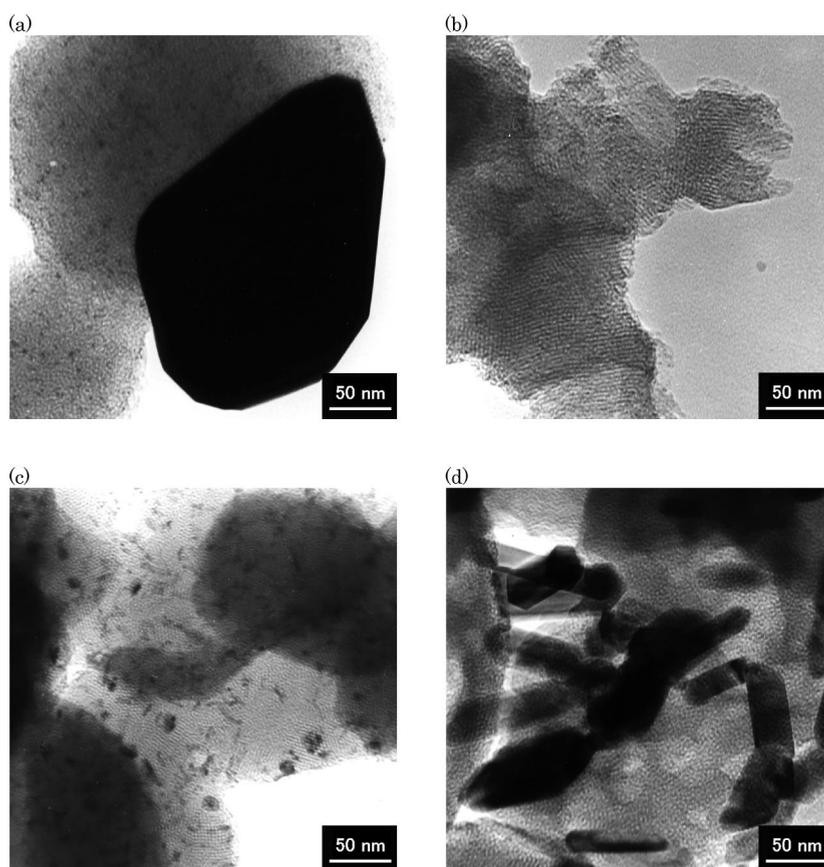
Fig. 1 Hydrodesulfurization of Benzothiophene over Noble Metal/MCM-41 Catalysts at 350°C

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



(a) Pt, (b) Rh, (c) Pd, (d) Ru.

Fig. 2 TEM Images of Noble Metal/MCM-41 Catalysts after Calcination at 500°C

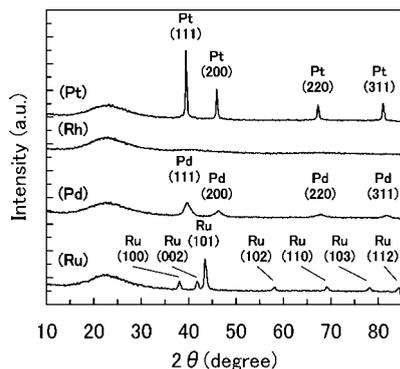
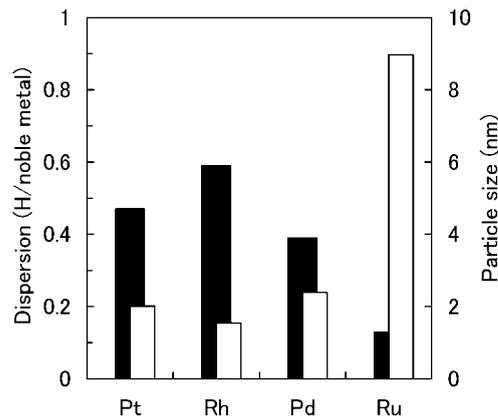


Fig. 3 XRD Patterns of Noble Metal Supported on MCM-41 after Reduction at 450°C

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 particles²⁶. 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



■ Dispersion, □ Particle size.

Fig. 4 Dispersion and Particle Size of Noble Metal on MCM-41 Measured by Hydrogen Adsorption at 25°C

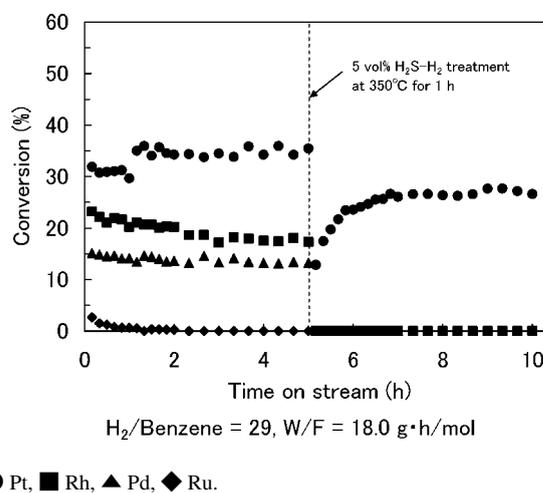


Fig. 5 Catalytic Activities of Noble Metal/MCM-41 for Benzene Hydrogenation at 300°C

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 ≈ Ir²². The Rh/MCM-41 catalyst showed cracking ac-

Table 1 Catalytic Activities of Noble Metal Supported on MCM-41 for Benzene Hydrogenation at 300°C before H₂S Treatment (after reaction for 5 h)

Noble metal	Yield of cyclohexane [%]	Yield of cracking products [%]	TOF for hydrogenation [h ⁻¹]
Pt	35.5	0.0	16.4
Rh	14.8	2.5	2.9
Pd	13.3	0.0	4.0
Ru	0.0	0.0	0.0

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

Precursor	Conversion of BT [%]	Dispersion of Pt (H/Pt)	Particle size of Pt [nm]	TOF [h ⁻¹]
H ₂ PtCl ₆ ·6H ₂ O	98.6	0.47	2.0	3.77
(NH ₄) ₂ PtCl ₆	7.9	0.14	6.8	1.01
K ₂ PtCl ₆	5.5	0.20	4.8	0.50

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 character³⁷. 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% H₂S-H₂ mixture gas are shown in **Fig. 5**. The catalytic activities of noble metal/MCM-41, except Pt, for benzene hydrogenation were remarkably decreased by H₂S treatment, but that of Pt/MCM-41 was regenerated with time on stream. Thus, Pt/MCM-41 catalyst has remarkably higher hydrogenation activity and sulfur tolerance than other noble metal/MCM-41 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/Al₂O₃ 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: H₂PtCl₆·6H₂O ≫ (NH₄)₂PtCl₆ > K₂PtCl₆. On the other hand, the order of the Pt dispersion was as follows; H₂PtCl₆·6H₂O > K₂PtCl₆ ≈ (NH₄)₂PtCl₆. The

Table 3 Dispersion and Particle Size of Pt on MCM-41 and SiO₂ Measured by the Hydrogen Adsorption Method

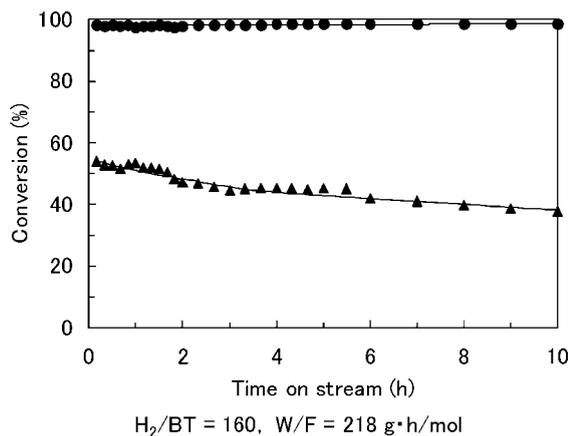
Catalyst	Dispersion of Pt (H/Pt)	Particle size of Pt [nm]
Pt/MCM-41	0.47	2.01
Pt/SiO ₂	0.43	2.21

isoelectric point of SiO₂ is pH ≈ 2, whereas the pH of H₂PtCl₆·6H₂O aqueous solution is 1. Since the SiO₂ surface is positively charged in H₂PtCl₆·6H₂O aqueous solution, anionic Pt precursor ([PtCl₆]²⁻) may electrostatically interact with the SiO₂ surface. However, the pH of K₂PtCl₆ and (NH₄)₂PtCl₆ aqueous solutions were both about 2, respectively. Thus, Pt dispersion in Pt/MCM-41 catalyst prepared from H₂PtCl₆·6H₂O was higher than in those from other Pt precursors. Therefore, the HDS activity of Pt/MCM-41 prepared from H₂PtCl₆·6H₂O was remarkably higher than in those from other Pt precursors. However, although the dispersion of Pt in Pt/MCM-41 prepared from K₂PtCl₆ was the same as that prepared from (NH₄)₂PtCl₆, the HDS activity of Pt/MCM-41 catalyst prepared from K₂PtCl₆ was the same as that from (NH₄)₂PtCl₆. 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/SiO₂

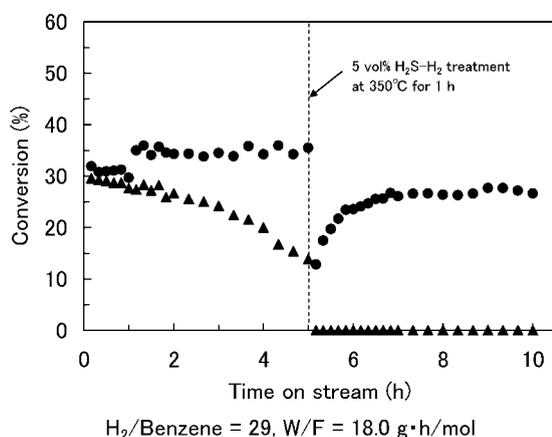
3.4.1. HDS Activity and Properties of Pt/SiO₂ Catalyst

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 SiO₂ as shown in **Table 3**. Thus, the HDS activity and properties of Pt/MCM-41 catalyst were compared with those of Pt/SiO₂ 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 SiO₂ at 350°C. The Pt/MCM-41 catalyst showed remarkably higher activity than Pt/SiO₂ catalyst for the HDS of BT and the activity of Pt/SiO₂ catalyst decreased with time on stream. Furthermore, the benzene hydrogenation



● Pt/MCM-41, ▲ Pt/SiO₂.

Fig. 6 Hydrodesulfurization of Benzothiophene over Supported Pt Catalysts at 350°C



● Pt/MCM-41, ▲ Pt/SiO₂.

Fig. 7 Hydrogenation of Benzene over Supported Pt Catalysts at 300°C

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°C), 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 sites^{23)~26)}. The 2-PA molecule is dehydrated to propylene at acid sites of catalyst surface. Therefore,

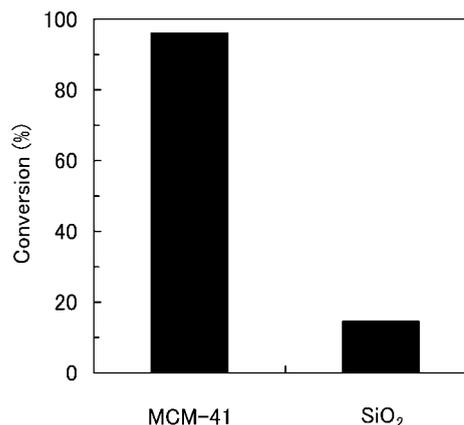


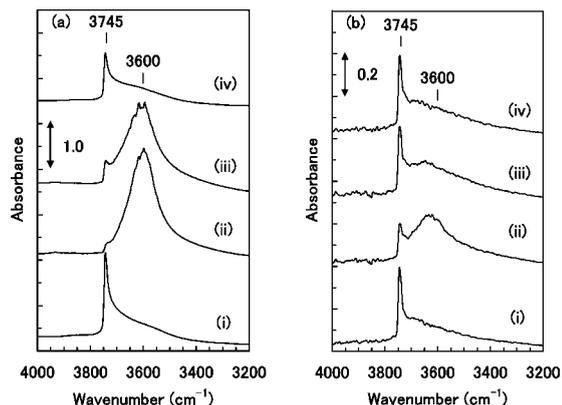
Fig. 8 Catalytic Activities of MCM-41 and SiO₂ for 2-Propanol Dehydration at 300°C

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°C. 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 catalysts^{27)~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 reported^{16)~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°C 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°C, 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 25°C for 0.5 h. On the other hand, the decreased absorbance of silanol groups was not completely regenerated by evacuation at 150°C, with a



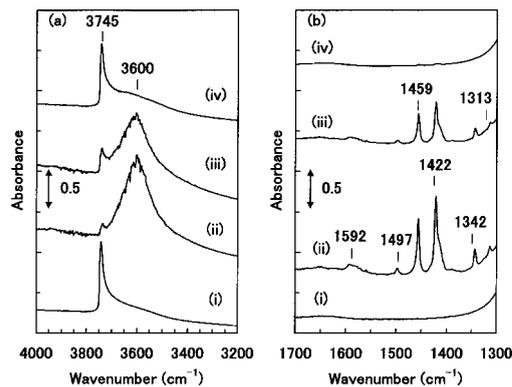
(i) After evacuation at 500°C for 2 h, (ii) in the presence of benzothiophene (0.07 kPa) at 25°C, (iii) after evacuation at 25°C for 0.5 h, (iv) after evacuation at 150°C for 0.5 h.

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 SiO₂ evacuated at 500°C 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 SiO₂ at 25°C, 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°C, 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 Al₂O₃-modified MCM-41 (Al₂O₃-MCM-41) was higher than that of Al-incorporated MCM-41 (AlMCM-41), so the strength of interaction between Al₂O₃-MCM-41 and TP was stronger than that of AlMCM-41¹⁹). These results indicate that the interaction between BT and MCM-41 with acid sites is stronger than that with SiO₂ 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°C¹⁹). Thus, BT interacted more strongly with MCM-41 than TP.

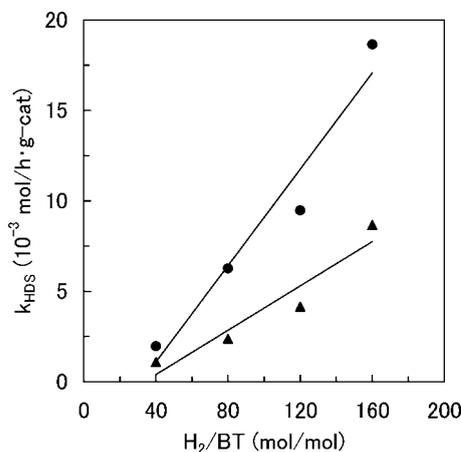
Figure 10 shows the FT-IR spectra of BT adsorbed on Pt/MCM-41 after reduction at 450°C (Fig. 10 (a)). The spectra were similar to those of MCM-41. Furthermore, the bands of BT adsorbed on Pt/MCM-41 occurred at 1592, 1497, 1456, 1422, 1343 and 1313, which were attributed to vibration of the aromatic ring. After evacuation at 150°C 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.

(i) After evacuation at 500°C for 2 h, (ii) in the presence of benzothiophene (0.07 kPa) at 25°C, (iii) after evacuation at 25°C for 0.5 h, (iv) after evacuation at 150°C for 0.5 h.

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



● Pt/MCM-41, ▲ CoMo/Al₂O₃.

Fig. 11 Effect of H₂/BT Ratio on the HDS Activities of Pt/MCM-41 and CoMo/Al₂O₃ Catalysts

3. 4. 3. Active Sites in Pt/MCM-41 Catalyst for HDS of BT

We examined the effect of H₂/BT ratio on the HDS activity of Pt/MCM-41 catalyst. Figure 11 shows the effect of H₂/BT ratio on the pseudo first order HDS rates of Pt/MCM-41 and CoMo/Al₂O₃ catalysts. The HDS rate constant was enhanced with increasing H₂/BT ratio on Pt/MCM-41 catalyst. In addition, the HDS rate constant of Pt/MCM-41 was higher than that of CoMo/Al₂O₃ catalyst at any H₂/BT ratio. This indicates that the HDS rate constant of Pt/MCM-41 catalyst is significantly dependent on the H₂/BT ratio compared with that of CoMo/Al₂O₃. 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

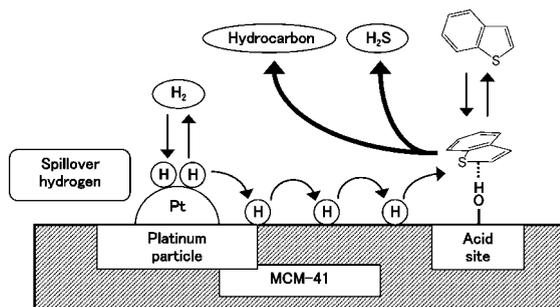


Fig. 12 Bifunctional Route of Benzothiophene HDS over Highly Active Pt/MCM-41 Catalyst

Figs. 1 and 5. These results indicate that the remarkable HDS activity of Pt/MCM-41 catalyst depended on the high hydrogenation activity and sulfur tolerance of Pt. Thus, the reaction mechanism of HDS of BT over Pt/MCM-41 catalyst may differ from that over CoMo/Al₂O₃ catalyst. 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, respectively³⁸. 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^{30,31}, Pt/Al₂O₃-modified SiO₂ (Al₂O₃-SiO₂)³⁴, Pt/Al₂O₃-modified MCM-41 (Al₂O₃-MCM-41)^{18,19} and Pt/AlSBA-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 surface³⁶. 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

- 1) Topsøe, H., Clausen, B. S., Massoth, F. E., *Catal.-Sci. Tech.*, **11**, 1 (1996).
- 2) Whitehurst, D. D., Isoda, T., Mochida, I., *Adv. Catal.*, **4**, 345 (1998).
- 3) Sugioka, M., *PETROTECH*, **19**, 458 (1996).
- 4) Kabe, T., Ishihara, A., Qian, W., "Hydrodesulfurization and Hydrodenitrogenation," Kodansha Scientific, Wiley-VCH, Tokyo, New York, Berlin (1999), p. 266.
- 5) Okamoto, Y., *J. Jpn. Petrol. Inst.*, **46**, (6), 343 (2003).
- 6) Fujikawa, T., *J. Jpn. Petrol. Inst.*, **50**, (5), 249 (2007).
- 7) Yoshimura, Y., Toba, M., Farag, H., Sakanishi, K., *Catal. Surv. Asia*, **8**, 47 (2003).
- 8) Barrio, V. L., Arias, P. L., Cambra, J. F., Güemez, M. B., Pawelec, B., Fierro, J. L. G., *Fuel*, **82**, 501 (2003).
- 9) Ishihara, A., Dumeignil, F., Lee, J., Mitsuhashi, K., Qian, E. W., Kabe, T., *Appl. Catal. A: General*, **289**, 163 (2005).
- 10) Vít, Z., Gulková, D., Kaluža, L., Zdražil, M., *J. Catal.*, **232**, 447 (2005).
- 11) Niquille-Röthlisberger, A., Prins, R., *J. Catal.*, **242**, 207 (2006).
- 12) Song, C., Reddy, K. M., *Appl. Catal. A: General*, **176**, 1 (1999).
- 13) Li, X., Wang, A., Sun, Z., Li, C., Ren, J., Zhao, B., Wang, Y., Chen, Y., Hu, Y., *Appl. Catal. A: General*, **254**, 319 (2003).
- 14) Muthu Kumaran, G., Garg, S., Soni, K., Kumar, M., Sharma, L. D., Murali Dhar, G., Rama Rao, K. S., *Appl. Catal. A: General*, **305**, 123 (2006).

- 15) Li, X., Wang, A., Zhang, S., Chen, Y., Hu, Y., *Appl. Catal. A: General*, **316**, 134 (2007).
- 16) Sugioka, M., Andalaluna, L., Morishita, S., Kurosaka, T., *Catal. Today*, **39**, 61 (1997).
- 17) Sugioka, M., Morishita, S., Kurosaka, T., Seino, A., Nakagawa, M., Namba, S., *Stud. Surf. Sci. Catal.*, **125**, 531 (1999).
- 18) Kanda, Y., Uemichi, Y., Kobayashi, T., Andalaluna, L., Sugioka, M., *Stud. Surf. Sci. Catal.*, **156**, 747 (2005).
- 19) Kanda, Y., Kobayashi, T., Uemichi, Y., Namba, S., Sugioka, M., *Appl. Catal. A: General*, **308**, 111 (2006).
- 20) Sugioka, M., Aizawa, T., Kanda, Y., Kurosaka, T., Uemichi, Y., Namba, S., *Stud. Surf. Sci. Catal.*, **142**, 739 (2002).
- 21) Kanda, Y., Aizawa, T., Uemichi, Y., Sugioka, M., Namba, S., *Appl. Catal. B: Environment*, **77**, 117 (2007).
- 22) Albertazzi, S., Ganzerla, R., Gobbi, C., Lenarda, M., Mndreoli, M., Salatelli, E., Savini, P., Storaro, L., Vaccari, A., *J. Mol. Catal. A*, **200**, 261 (2003).
- 23) Yasuda, H., Sato, T., Yoshimura, Y., *Catal. Today*, **50**, 63 (1999).
- 24) Navarro, R., Pawelec, B., Fierro, J. L. G., Vasudevan, P. T., Cambra, J. F., Guemez, M. B., Arias, P. L., *Fuel Proc. Technol.*, **61**, 73 (1999).
- 25) Reinhoudt, H. R., Troost, R., van Schalkwijk, S., van Langeveld, A. D., Sie, S. T., van Veen, J. A. R., Moulijn, J. A., *Fuel Proc. Technol.*, **61**, 117 (1999).
- 26) Matsui, T., Harada, M., Ichihashi, Y., Bando, K. K., Matsubayashi, N., Toba, M., Yoshimura, Y., *Appl. Catal. A: General*, **286**, 249 (2005).
- 27) Simon, L. J., van Ommen, J. G., Jentys, A., Lecher, J. A., *J. Catal.*, **201**, 60 (2001).
- 28) Simon, L. J., van Ommen, J. G., Jentys, A., Lecher, J. A., *J. Catal.*, **203**, 434 (2001).
- 29) Simon, L. J., van Ommen, J. G., Jentys, A., Lecher, J. A., *Catal. Today*, **73**, 105 (2002).
- 30) Sugioka, M., Sado, F., Kurosaka, T., Wang, X., *Catal. Today*, **45**, 327 (1998).
- 31) Sugioka, M., Kurosaka, T., *J. Jpn. Petrol. Inst.*, **45**, (6), 342 (2002).
- 32) Topsøe, H., Hinnemann, B., Nørskov, J. K., Lauritsen, J. V., Besenbacher, F., Hansen, P. L., Hytoft, G., Egeberg, R. G., Knudsen, K. G., *Catal. Today*, **107-108**, 12 (2005).
- 33) Egorova, M., Prins, R., *J. Catal.*, **241**, 162 (2006).
- 34) Kanda, Y., Kobayashi, T., Uemichi, Y., Sugioka, M., *J. Jpn. Petrol. Inst.*, **49**, (2), 49 (2006).
- 35) Kanda, Y., Ooka, Y., Kobayashi, T., Uemichi, Y., Sugioka, M., *J. Jpn. Petrol. Inst.*, **50**, (1), 61 (2007).
- 36) Miller, J. T., Meyers, B. L., Modica, F. S., Lane, G. S., Vaarkamp, M., Koningsberger, D. C., *J. Catal.*, **143**, 395 (1993).
- 37) Boudart, M., Ptak, L. D., *J. Catal.*, **16**, 90 (1970).
- 38) Yoshimura, Y., Toba, M., Matsui, T., Harada, M., Ichihashi, Y., Bando, K. K., Yasuda, H., Ishihara, H., Morita, Y., Kameoka, T., *Appl. Catal. A: General*, **322**, 152 (2007).

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 担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) 担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 触媒よりも高く, 安定であった。担持貴金属触媒のベンゼ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 触媒上での 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。