[Regular Paper]

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

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The catalytic activities and properties of noble metals (Pt, Pd, Rh, Ru) supported on silica gel (SiO_2) and alumina-modified silica gel (Al_2O_3–SiO_2) were investigated for the hydrodesulfurization of thiophene. Al_2O_3–SiO_2 was prepared by an impregnation method using aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) aqueous solution. Pt/8 wt%Al_2O_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_2O_3 hydrodesulfurization catalyst. The sulfur tolerance of noble metal/SiO_2 was enhanced by Al_2O_3 modification of SiO_2 and Pt/8 wt%Al_2O_3–SiO_2 catalyst showed the highest sulfur tolerance among the supported noble metal catalysts. Pt/8 wt%Al_2O_3–SiO_2 catalyst had high hydrogenating ability for unsaturated C_4 hydrocarbons formed in the hydrodesulfurization of thiophene. The catalysts were characterized by 2-propanol dehydration, cumene cracking, XRD, H_2 adsorption and FT-IR. Dispersion of Pt on 8 wt%Al_2O_3–SiO_2 was remarkably higher than that on SiO_2 and the particle size of Pt on 8 wt%Al_2O_3–SiO_2 was the lowest among the supported noble metal catalysts. The acidity of 8 wt%Al_2O_3–SiO_2 was higher than that of SiO_2. Furthermore, Brönsted acid sites were present on 8 wt%Al_2O_3–SiO_2. FT-IR spectroscopy of thiophene adsorbed on 8 wt%Al_2O_3–SiO_2 support indicated that the thiophene molecule interacts with the Brönsted acid site on 8 wt%Al_2O_3–SiO_2. The activity of the double-layer (Pt/SiO_2 + 8 wt%Al_2O_3–SiO_2) catalyst obtained experimentally was higher than that calculated. This suggests that spillover hydrogen was present on Pt/Al_2O_3–SiO_2 in the hydrodesulfurization of thiophene. Both the Brönsted acid sites of Al_2O_3–SiO_2 and the Pt particles in the Pt/Al_2O_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_2O_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_2O_3–MCM-41)[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_2O_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

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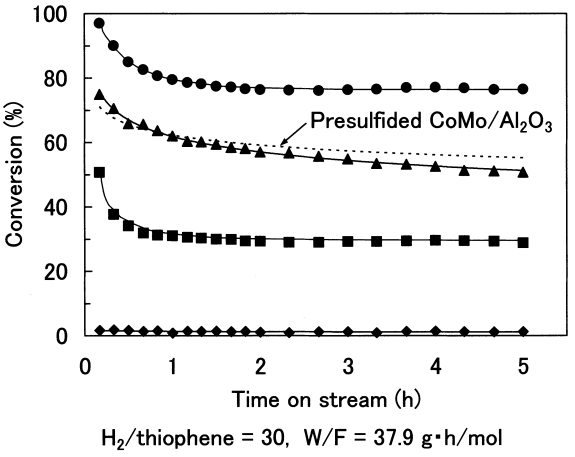
supplied from Nippon Aerosil Co., and Al_2O_3 (JRC-ALO-2) and $SiO_2 \cdot Al_2O_3$ (JRC-SAH-1) from the Catalysis Society of Japan. Alumina-modified silica gel (Al_2O_3–SiO_2) was prepared by an impregnation method using aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Wako Pure Chemical Industries, Ltd., 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 $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, $RhCl_3 \cdot 3H_2O$ and $RuCl_3 \cdot 3H_2O$ aqueous solutions, to obtain a noble metal loading of 5 wt%. However, $PdCl_2$ was dissolved in 1.0 mol/*l* HCl aqueous solution because $PdCl_2$ 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 m*l*/min) through a thiophene trap cooled at 0°C. Reaction conditions were as follows: catalyst weight = 0.1 g, H_2/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 Al_2O_3–SiO_2 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 Al_2O_3–SiO_2 was measured by XRD analysis and hydrogen adsorption. XRD analysis used a Rigaku diffractometer with Cu K_α 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%Al_2O_3–SiO_2 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 SiO_2 and 8 wt% Al_2O_3–SiO_2 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.



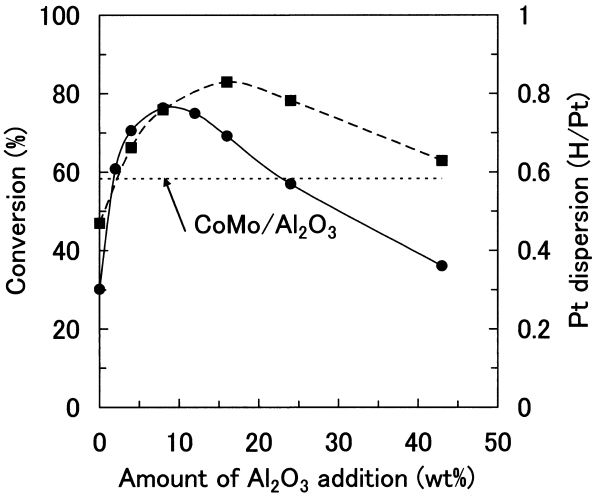
● Pt, ▲ Pd, ■ Rh, ◆ Ru.

Fig. 1 Hydrodesulfurization of Thiophene over 8 wt%Al_2O_3–SiO_2-supported Noble Metal Catalysts at 350°C

3. Results and Discussion

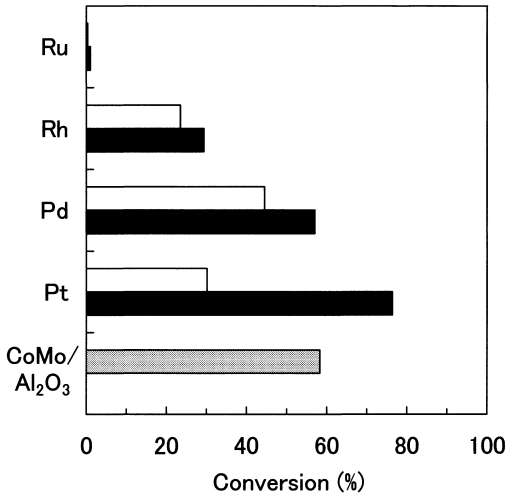
3. 1. Catalytic Activities of Noble Metal Supported on Al_2O_3-SiO_2

The catalytic activities of various noble metals (Pt, Pd, Rh, Ru) supported on 8 wt%Al_2O_3–SiO_2 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%Al_2O_3–SiO_2 was the highest and was higher than that of commercial presulfided CoMo/Al_2O_3 HDS catalyst. Previously[22], we reported that dispersion of Pt on Al_2O_3–MCM-41 was the highest and particle size was the lowest among noble metals supported on Al_2O_3–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[14]. 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[14]. 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[25]. 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%Al_2O_3–SiO_2 can be explained by dispersion, hydrogenation ability and sulfur tolerance of the noble metal. The catalytic activities of noble metal/8 wt%Al_2O_3–SiO_2, except Ru/8 wt%Al_2O_3–SiO_2, in the HDS of thiophene decreased



● HDS conversion, ■ Pt dispersion.

Fig. 2 Effect of Al_2O_3-modification of SiO_2 on HDS Activities of Pt/Al_2O_3–SiO_2 Catalysts and Dispersion of Pt on Al_2O_3–SiO_2



□ Noble metal/SiO_2, ■ Noble metal/8 wt%Al_2O_3–SiO_2.

Fig. 3 Activities of SiO_2- and 8 wt%Al_2O_3–SiO_2-supported Noble Metal Catalysts for HDS of Thiophene at 350°C

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_2O_3 loading for the HDS of thiophene revealed an optimal Al_2O_3 loading for the activity of Pt/Al_2O_3–SiO_2 of 8 wt% as shown in **Fig. 2**. The BET surface area of Al_2O_3–SiO_2 decreased with increasing Al_2O_3 loading. However, the BET surface area of 8 wt%Al_2O_3–SiO_2 was remained high (246 m^2/g) after Al_2O_3 modification. Dispersion of Pt on Al_2O_3–SiO_2 was about 0.8 with Al_2O_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_2O_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_2O_3–SiO_2 catalysts for HDS of thiophene at 350°C. The activities of noble metal/8 wt%Al_2O_3–SiO_2 catalysts were higher than those of noble metal/SiO_2 catalysts and Pt supported on 8 wt%Al_2O_3–SiO_2 had the highest catalytic activity.

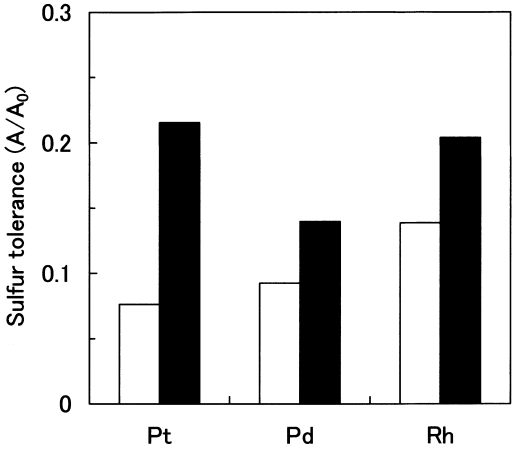
The sulfur tolerance (A/A_0) of Pt, Pd and Rh supported on SiO_2 and 8 wt%Al_2O_3–SiO_2 was evaluated as HDS activity before (A_0) and after (A) hydrogen sulfide introduction for 1 h. Hydrogen sulfide (3 m*l*/min) was introduced using micro feeder with a glass syringe for 1 h. HDS activities of noble 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[30], 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_2O_3 modification of SiO_2. The sulfur tolerance of Pt/8 wt%Al_2O_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[11),26),29)]. Thus, increased sulfur tolerance of supported noble metal catalyst was attributed to electron attraction from the noble metal by the acid sites of Al_2O_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_2O_3 modification of SiO_2, the effect of Al_2O_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_2O_3–SiO_2 were mainly C_4 hydrocarbons (butane 88%, butenes 11%) and trace amounts of C_1-C_3 hydrocarbons, whereas those over Pt/SiO_2 were C_4 hydrocarbons (butane 72%, butenes 27%) as shown in **Table 1**. These results indicate that Pt/Al_2O_3–SiO_2 catalyst has higher hydrogenating ability than Pt/SiO_2 catalyst for unsaturated C_4 hydrocarbons formed in the HDS of thiophene.

3. 2. Catalytic Properties of Pt/Al_2O_3–SiO_2

Pt/8 wt%Al_2O_3–SiO_2 was investigated in detail to understand the causes of the high activity of Pt/8 wt%Al_2O_3–SiO_2 for the HDS of thiophene. **Figure 5** shows the XRD patterns of Pt/SiO_2 and Pt/8 wt%Al_2O_3–SiO_2 after reduction at 450°C. The peak height of Pt on SiO_2 was significant but decreased remarkably on 8 wt%Al_2O_3–SiO_2. This indicates that the dispersion of Pt on 8 wt%Al_2O_3–SiO_2 was higher than that on SiO_2. **Table 2** shows the dispersion and particle sizes of various noble metals on SiO_2 and 8 wt%Al_2O_3–SiO_2 measured by the hydrogen adsorption method. Pt dispersion (0.76) on 8 wt%Al_2O_3–SiO_2 was the highest and particle size (1.24 nm) was the lowest among the noble metal/SiO_2 and noble metal/8 wt%Al_2O_3–SiO_2 catalysts. Dispersions of noble metals (except Ru) on 8 wt%Al_2O_3–SiO_2 were higher than on SiO_2. $[PtCl_6]^{2-}$ and $[RhCl_3(H_2O)_3]$ react with the hydroxyl groups on the Al_2O_3 surface[23),27)]. We showed that dispersion of Pt on ZSM-5 zeolite increased with higher proton content[15)]. This result indicates that anionic noble metal precursors such as $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ electrostatically interact with the Brönsted acid sites of the Al_2O_3–SiO_2 surface. Therefore, dispersion of noble metals (except Ru) on SiO_2 was enhanced by Al_2O_3 modification of SiO_2. The surface sulfur tolerance of small Pt and Pd particles (< 2 nm) is higher than that of large particles[24)]. Thus, small Pt and Rh particles on 8 wt%Al_2O_3–SiO_2 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 SiO_2 and 8 wt%Al_2O_3–SiO_2 by the reaction of 2-PA dehydration (200°C) and cumene cracking (400°C) using a pulse reactor. SiO_2 showed very low activity for both reactions whereas 8 wt%Al_2O_3–SiO_2 showed high activity for these reactions (see **Table 3**). These results indicate that 8 wt%Al_2O_3–SiO_2 has high acidity and Brönsted acid sites are present on 8 wt%Al_2O_3–SiO_2.



A_0: HDS activity before introduction of hydrogen sulfide.
A: HDS activity after introduction of hydrogen sulfide for 1 h (Rh/SiO_2; 5 min).
□ Noble metal/SiO_2, ■ Noble metal/8 wt%Al_2O_3–SiO_2.

Fig. 4 Sulfur Tolerance (A/A_0) of SiO_2- and 8 wt%Al_2O_3–SiO_2-supported Noble Metal Catalysts

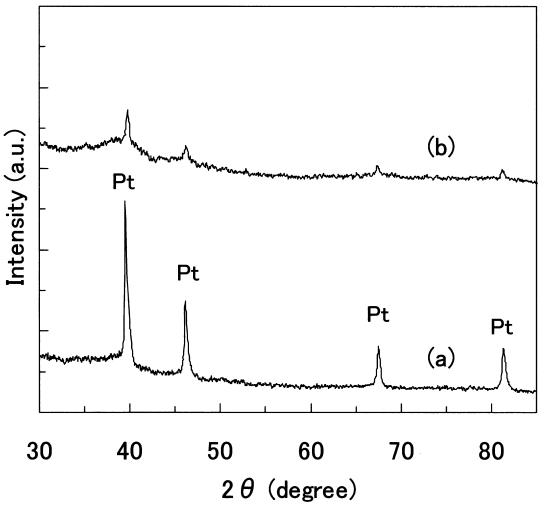


Fig. 5 XRD Patterns of Pt Supported on (a) SiO_2 and (b) 8 wt%Al_2O_3–SiO_2 after Reduction at 450°C

Table 1 Product Distribution in HDS of Thiophene over Reduced SiO_2-supported Noble Metal and 8 wt%Al_2O_3–SiO_2-supported Noble Metal Catalysts at 350°C

Catalyst	HDS [%]	< C_3[a)] [%]	C_4[b)] [%]	$C_4^=$[c)] [%]	1,3-$C_4^=$[d)] [%]
Pt/SiO_2	30.1	1.0	71.7	27.3	0.0
Pt/8 wt%Al_2O_3–SiO_2	79.5	0.8	88.3	10.9	0.0
Pd/SiO_2	44.5	0.2	28.5	71.3	0.0
Pd/8 wt%Al_2O_3–SiO_2	57.0	0.7	18.0	81.3	0.0
Rh/SiO_2	23.5	0.7	11.4	87.9	0.0
Rh/8 wt%Al_2O_3–SiO_2	29.3	1.7	13.8	84.5	0.0
Ru/SiO_2	0.3	22.8	0.0	66.6	10.6
Ru/8 wt%Al_2O_3–SiO_2	1.1	18.4	1.6	80.0	0.0

a) C_1-C_3 hydrocarbons. b) Butanes. c) Butenes. d) 1,3-Butadiene.

Table 3 shows the catalytic properties of Pt/8 wt% Al_2O_3–SiO_2 and other supported Pt catalysts such as Pt/SiO_2, Pt/Al_2O_3 and Pt/$SiO_2 \cdot Al_2O_3$. Pt/8 wt% Al_2O_3–SiO_2 catalyst had the highest HDS activity, with high Pt dispersion and Brönsted acidity. Evaluation of the HDS activities of the supported Pt catalysts by turnover frequency (TOF) showed the TOF of Pt/$SiO_2 \cdot Al_2O_3$ catalyst was remarkably higher than those of Pt/SiO_2 and Pt/Al_2O_3 catalysts. The relationship between dispersion of Pt on Al_2O_3 and TOF is negative in HDS of thiophene[28]. However, this cannot explain why the TOF of Pt/$SiO_2 \cdot Al_2O_3$ catalyst is so high. Moreover, TOF of Pt/8 wt%Al_2O_3–SiO_2 catalyst with high Pt dispersion was higher than that of Pt/Al_2O_3 catalyst with similar Pt dispersion. Thus, the high TOF of Pt/$SiO_2 \cdot Al_2O_3$ and Pt/8 wt%Al_2O_3–SiO_2 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/Al_2O_3–SiO_2 Catalyst

Pt/8 wt%Al_2O_3–SiO_2 catalyst had the highest activity among noble metal/8 wt%Al_2O_3–SiO_2 catalysts for the HDS of thiophene. We studied the reaction mechanism of HDS of thiophene over Pt/Al_2O_3–SiO_2 catalyst.

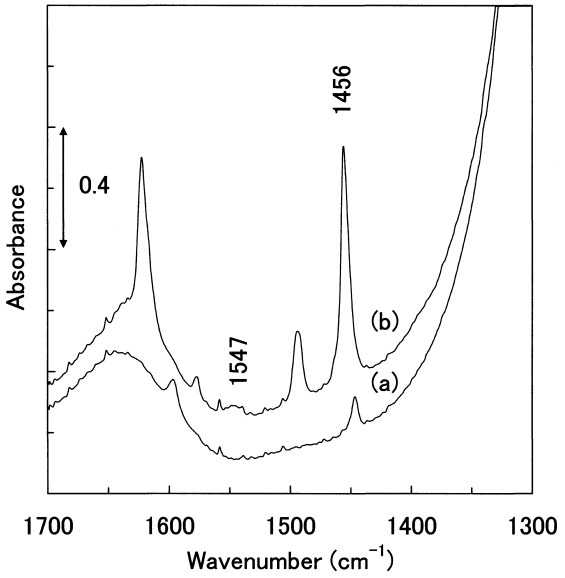
We previously found[13)~15),18)~22)] that Brönsted acid sites on the support of noble metal catalysts act as sites for the activation of thiophene. We supposed that the Brönsted acid sites on Al_2O_3–SiO_2 are also active for the activation of thiophene, whereas Pt particles are active for the activation of hydrogen in the HDS of thiophene. We confirmed the presence of the Brönsted acid sites on 8 wt%Al_2O_3–SiO_2 by the observation of the FT-IR spectra of pyridine at 1547 cm^{-1} adsorbed on 8 wt%Al_2O_3–SiO_2 as shown in spectrum (b) in **Fig. 6**. Presumably the surface silanol group (Si–OH) on 8 wt%Al_2O_3–SiO_2 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% Al_2O_3–SiO_2 were observed to clarify the interaction of the silanol group with the thiophene molecule. In the background spectra of 8 wt%Al_2O_3–SiO_2 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%Al_2O_3–SiO_2 in the

Table 2 Dispersion and Particle Size of Noble Metals on SiO_2 and 8 wt%Al_2O_3–SiO_2[a)]

Catalyst	Dispersion (H/noble metal)	Particle size [nm]
Pt/SiO_2	0.47	2.01
Pt/8 wt%Al_2O_3–SiO_2	0.76	1.24
Pd/SiO_2	0.21	4.46
Pd/8 wt%Al_2O_3–SiO_2	0.23	3.98
Rh/SiO_2	0.39	2.36
Rh/8 wt%Al_2O_3–SiO_2	0.74	1.24
Ru/SiO_2	0.24	4.82
Ru/8 wt%Al_2O_3–SiO_2	0.20	5.81

a) Measured by the hydrogen adsorption method.



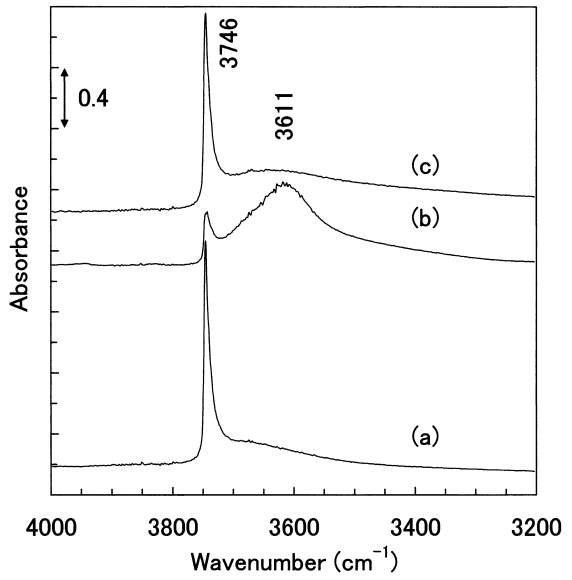
Pyridine was adsorbed at 150°C followed by evacuation at 150°C for 0.5 h.

Fig. 6 FT-IR Spectra of Pyridine Adsorbed on (a) SiO_2 and (b) 8 wt%Al_2O_3–SiO_2

Table 3 Catalytic Properties of Pt Supported on Various Metal Oxides

Catalyst	HDS conv.[a)] [%]	Dispersion [H/Pt]	TOF[b)] [h^{-1}]	Dehydration of 2-PA[c)] [%]	Cracking of cumene[c)] [%]
Pt/8 wt%Al_2O_3–SiO_2	76.4	0.76	10.4	39.7	5.2
Pt/Al_2O_3	40.3	0.82	5.0	62.4	0.0
Pt/$SiO_2 \cdot Al_2O_3$	38.0	0.12	32.0	98.4	44.7
Pt/SiO_2	30.1	0.47	6.6	0.0	0.0

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



(a) After evacuation at 500°C for 2 h, (b) In the presence of thiophene (2 kPa), (c) After evacuation at room temperature for 0.5 h.

Fig. 7 FT-IR Spectra of Thiophene Adsorbed on 8 wt%Al_2O_3–SiO_2

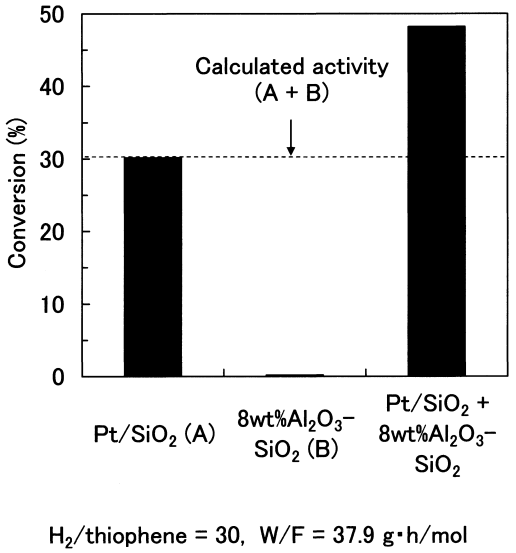


Fig. 8 Hydrodesulfurization of Thiophene over Double-layer (Pt/SiO_2 + 8 wt%Al_2O_3–SiO_2) Catalyst at 350°C

HDS of thiophene over Pt/8 wt%Al_2O_3–SiO_2 catalyst.

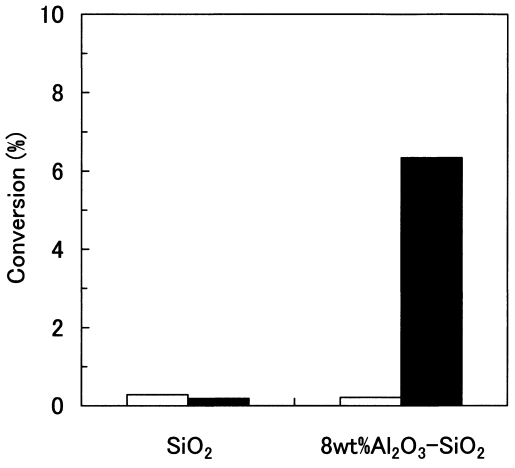
Furthermore, we tried to confirm the existence of spillover hydrogen in the HDS of thiophene over Pt/Al_2O_3–SiO_2 catalyst. The HDS activity of double-layer catalyst (0.1 g of Pt/SiO_2 (A, upper layer) and 0.1 g of 8 wt%Al_2O_3–SiO_2 (B, lower layer)) was examined. The activity of double-layer catalyst 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/SiO_2 to form spillover hydrogen, and thiophene was activated on the Brönsted acid sites of 8 wt%Al_2O_3–SiO_2. This suggests that spillover hydrogen is present on Pt/Al_2O_3–SiO_2 in the HDS of thiophene.

On the basis of these results, we propose a possible mechanism for the HDS of thiophene over Pt/Al_2O_3–SiO_2 catalyst. Previously[31], 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/SiO_2 and Pt/Al_2O_3 showed remarkably lower activity than Pt/8 wt%Al_2O_3–SiO_2 catalyst with Brönsted acid sites as shown in **Table 3**. Therefore, we propose two reaction routes for thiophene HDS over the highly active Pt/Al_2O_3–SiO_2 catalyst: (i) monofunctional route (on Pt particles) and (ii) bifunctional route (on Brönsted acid sites). In reaction route (ii), thiophene is activated on the Brönsted acid sites of Al_2O_3–SiO_2 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 Al_2O_3 modification of SiO_2, 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 sulfidation[24]. The Pt particle in high sulfur tolerant Pt/Al_2O_3–SiO_2 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 Al_2O_3–SiO_2. We also observed trace amounts of tetrahydrothiophene (THT) in the HDS products. **Figure 9** shows the catalytic activities of thiophene and THT cracking over SiO_2 and 8 wt%Al_2O_3–SiO_2 at 400°C. Both SiO_2 and 8 wt%Al_2O_3–SiO_2 catalysts showed very low activities for thiophene cracking. However, the catalytic activity of 8 wt%Al_2O_3–SiO_2 for THT cracking was higher than that of SiO_2. The main product in THT cracking over 8 wt%Al_2O_3–SiO_2 catalyst was hydrocarbons (*ca.* 70%).

Thus, the activated thiophene is hydrogenated into THT and the H_2S and C_4 hydrocarbon species were formed on acid site by cleavage of the C–S bond in the THT molecule.

4. Conclusions

Pt/8 wt%Al_2O_3–SiO_2 catalyst showed high activity for the HDS of thiophene, and both the Pt particles and Brönsted acid sites on the Pt/Al_2O_3–SiO_2 catalyst act as active sites for the HDS of thiophene. Pt/8 wt%Al_2O_3–SiO_2 has high potential as an industrial HDS cat-



□ Cracking of thiophene, ■ Cracking of THT.

Fig. 9 Catalytic Activities of SiO_2 and 8 wt%Al_2O_3–SiO_2 for Cracking of Thiophene and Tetrahydrothiophene (THT) at 400°C

alyst for organic sulfur compounds in petroleum feedstocks.

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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

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貴金属担持シリカゲル（SiO_2）およびアルミナ修飾シリカゲル（Al_2O_3–SiO_2）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。Al_2O_3–SiO_2は硝酸アルミニウム（$Al(NO_3)_3 \cdot 9H_2O$）水溶液を用いた含浸法により調製した。Pt/8 wt% Al_2O_3–SiO_2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$CoMo/Al_2O_3$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硫黄性について検討した結果，SiO_2にAl_2O_3修飾を施すことによって担持貴金属触媒の耐硫黄性は向上し，とくに担持Pt触媒において著しい耐硫黄性の向上が見られた。Pt/Al_2O_3–SiO_2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C_4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，クメンの分解反応，XRD，水素吸着およびFT-IRによりキャラクタリゼーションした。その結果，Pt/8 wt% Al_2O_3–SiO_2の白金の分散度はPt/SiO_2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% Al_2O_3–SiO_2はSiO_2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% Al_2O_3–SiO_2上にはBrönsted酸点が存在することが分かった。8 wt% Al_2O_3–SiO_2担体に吸着させたチオフェンのFT-IRスペクトルより，チオフェン分子と8 wt% Al_2O_3–SiO_2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/SiO_2および8 wt% Al_2O_3–SiO_2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/Al_2O_3–SiO_2触媒におけるHDS反応にはスピルオーバー水素が関与していることが考えられる。Pt/Al_2O_3–SiO_2触媒によるチオフェンの水素化脱硫反応では，Al_2O_3–SiO_2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。

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