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Abstract

Effect of Pt precursor and pretreatment on HDS activity of Pt/Al-PILM catalyst was examined to prepare highly active Pt-supported HDS catalyst. The order of hydrodesulfurization (HDS) activities of Pt/alumina-pillared clay montmorillonite (Al-PILM) catalysts prepared by various Pt precursors was $Pt(C_5H_7O_2)_2 >$ $H_2PtCl_6 \cdot 6H_2O > [Pt(NH_3)_4](NO_3)_2 > [Pt(NH_3)_4]Cl_2 \cdot H_2O > H_2Pt(OH)_6$. This order was in accordance with that of Pt dispersion. Thus, high Pt dispersion is essential factor to prepare highly active Pt/Al-PILM catalyst for HDS reaction. On the other hand, the effect of pretreatment on the HDS activities of Pt/Al-PILM catalysts prepared by various Pt precursors was also evaluated. The UC-TPS Pt/Al-PILM catalyst showed the highest HDS activity among various pretreated Pt/Al-PILM

catalysts, in which uncalcined (UC) catalyst was sulfided by temperature programmed sulfidation (TPS). We assumed that high HDS activity of UC-TPS Pt/Al-PILM catalyst is caused by partly sulfided Pt particle with high dispersion. It is concluded that the highly active Pt/Al-PILM catalyst for the HDS reaction could be prepared by using $Pt(C_5H_7O_2)_2$ as a precursor and UC-TPS treatment.

Keywords

Hydrodesulfurization • Supported Pt catalyst • Alumina-pillared clay montmorillonite • Pt precursor • Pretreatment effect

1. Introduction

Recently, the technologies to solve environmental problems such as acid rain and global warming on a global scale have been attracted much attention. Sulfur oxide (SO_X), which causes the acid rain, is formed by combustion of organic sulfur compounds in petroleum and coal used for boilers of power plants and engines of automobiles. Furthermore, it is well known that SO_X cause deactivation of automotive exhaust catalysts. Hydrodesulfurization (HDS) process is one of the important processes in the petroleum industry to produce clean fuel[1,2]. $CoMo/Al_2O_3$ catalyst has been widely used in the HDS process. Recently, the development of highly active HDS catalysts, which exhibit higher activity than commercial $CoMo/Al_2O_3$ HDS catalyst, have been claimed in the petroleum industry to prevent the acid rain and deactivation of automotive exhaust catalysts[3-5]. Fuel consumption and carbon dioxide (CO_2) emission of diesel vehicle are superior to those of gasoline vehicle[6]. However, the formation of nitrogen oxide (NO_X) and particulate matter (PM) emission by diesel engine are larger than those by gasoline engine. NO_X reduction activity of exhaust catalyst is lowered by

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the poisoning of sulfur compounds. Since aromatic compounds in diesel fuel is a one of important factors to form PM, reduction of aromatic compounds in diesel fuel has been claimed. On the other hand, noble metal catalysts show high HDS and hydrogenation activities for the production of sulfur free diesel fuel containing lower aromatic compounds. Thus, noble metal catalysts have been much attention as new HDS catalysts[7-12].

In the previous papers, we have reported that noble metals, especially platinum (Pt), supported on zeolites[13-15] and related materials such as mesoporous silicates[16-18] and clays[15] showed high and stable activity in HDS of thiophene. However, effect of Pt precursor and pretreatment on HDS activity of supported noble metal catalyst has not been reported. In the present study, we examined the effect of Pt precursor and pretreatment on catalytic activity of Pt supported on alumina-pillared clay montmorillonite (Al-PILM) for HDS of thiophene in order to prepare highly active HDS catalysts.

2. Experimental

2.1 Preparation of Catalysts

We used Al-PILM (Fluka, 163 m^2/g) as a catalyst support. Al-PILM-supported Pt catalysts were prepared by an impregnation method using hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), tetraammine platinum (II) nitrate ($[Pt(NH_3)_4](NO_3)_2$), tetraammine platinum (II) chloride monohydrate ($[Pt(NH_3)_4]Cl_2 \cdot H_2O$), hydrogen hexahydroxoplatinate (IV) ($H_2Pt(OH)_6$) aqueous solutions. However, platinum (II) acetylacetonato ($Pt(C_5H_7O_2)_2$) was dissolved in toluene. The amount of Pt loading was 5 wt.%. After impregnation, the catalysts were dried at 120 °C for 24 h followed by calcination in air at 500 °C for 4 h to obtain calcined (C) catalyst. Uncalcined (UC) catalysts were prepared by only

drying after impregnation.

C and UC catalysts were pretreated by four different methods (reduction (R), sulfidation (S), temperature programmed reduction (TPR) and temperature programmed sulfidation (TPS)) before HDS reaction. For example, Pt/Al-PILM catalyst treated by calcination followed by reduction is indicated as C-R Pt/Al-PILM. Reduction treatment was carried out as follows: Pt/Al-PILM catalyst was heated with 10 °C/min in helium stream from room temperature to 500 °C and was kept at 500 °C for 1h, followed by reduction with hydrogen at 450 °C for 1h. Sulfided Pt/Al-PILM catalyst was obtained by sulfidation in 5%H_2S-H_2 stream at 400 °C for 1h after reduction treatment. TPR and TPS treatments were carried out using hydrogen and 5%H_2S-H_2 mixture, respectively. Pt/Al-PILM catalyst was heated with 10 °C/min in hydrogen or 5%H_2S-H_2 stream from room temperature to 400 °C and was kept at 400 °C for 1h.

2.2 Hydrodesulfurization of Thiophene

HDS of thiophene was performed at 350 °C under 0.1 MPa by a conventional fixed-bed flow reactor. Thiophene was introduced into the reactor by passing hydrogen (30 ml/min) through a thiophene trap cooled at 0 °C. Reaction conditions were as follows: catalyst weight = 0.1 g, H_2/thiophene = 30 mol/mol, W/F = 37.9 g•h/mol. The reaction products were analyzed by gas chromatograph (FID) equipped with silicone DC-550 (2 m, 110 °C) and VZ-7 (4 m, 0 °C) columns, respectively. Commercial CoMo/Al_2O_3 catalyst (Nippon Cyanamid Co.) was used to compare with supported Pt catalysts.

2.3 Characterization of Catalysts

Supported Pt catalysts were characterized by transmission electron microscopy (TEM) technique, XRD and hydrogen adsorption. TEM observation was carried out using JEOL JEM-2000FX. The conditions of TEM operation was as follows;

acceleration voltage = 200 kV and magnification = 120000 or 300000. XRD analysis was performed using a Rigaku diffract meter with Cu K_α radiation. Adsorption of hydrogen on the Pt/Al-PILM catalyst was performed using a glass vacuum system at 25 °C. The Pt/Al-PILM 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. The amount of hydrogen adsorption was employed to determine the dispersion and particle size of Pt on Al-PILM. The particle size of Pt (d_{Pt}, assumed as spherical shape) was calculated by dispersion of Pt, according to equation d_{Pt} = 0.944/D (D = dispersion of Pt). The acidities of Al-PILM were 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 the reactor and were pretreated at 500 °C for 1 h before the reaction. 0.2 µl of 2-PA or cumene were introduced into the reactor. The reaction products of 2-PA dehydration and cumene cracking were separated using PEG-1000 column (2 m, 80°C) and silicone DC-550 (2 m, 130 °C) column, respectively. However, the reaction products of 2-PA dehydration were trapped by liquid nitrogen and were flashed by boiling water before the separation. After the separation, the reactant and products were analyzed by TCD. We used $SiO_2 \cdot Al_2O_3$ (JRC-SAH-1) as a reference solid acidic catalyst which was supplied from the Catalysis Society of Japan.

3. Results and Discussion

3.1 Hydrodesulfurization of Thiophene over C-R Pt/Al-PILM Catalyst

We have reported in the previous paper that the HDS activity of Pt/AlSBA-15 catalyst was enhanced by increasing Pt loading, but the activity of 5 wt.% Pt loaded catalyst was the same as that of 7 wt.% Pt loaded catalyst[18]. Thus, we evaluate the

HDS activities of Pt/Al-PILM catalysts with 5 wt.% Pt loading. **Figure 1** shows the HDS activities of C-R Pt/Al-PILM catalysts prepared by various Pt precursors. The HDS activities of Pt/Al-PILM catalysts were remarkably changed by the kind of Pt precursor and the order of HDS activities of these catalysts was $Pt(C_5H_7O_2)_2$ > $H_2PtCl_6 \cdot 6H_2O$ ≈ $CoMo/Al_2O_3$ > $[Pt(NH_3)_4](NO_3)_2$ > $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ > $H_2Pt(OH)_6$. The HDS activity of Pt/Al-PILM catalyst prepared by $Pt(C_5H_7O_2)_2$ was higher than that of sulfided $CoMo/Al_2O_3$ HDS catalyst.

The reaction products in the HDS of thiophene over C-R Pt/Al-PILM catalysts prepared by various Pt precursors are given in **Table 1**. It was found that C_4 hydrocarbons were formed as main reaction products in the HDS of thiophene and small amount of cracking products (C_1-C_3 hydrocarbons) were also formed. This indicates that Pt/Al-PILM catalysts have low cracking activities for hydrocarbons. The relationship between thiophene conversion over Pt/Al-PILM catalyst and selectivities of products in the thiophene HDS was shown in **Fig. 2**. The selectivity of butanes in thiophene HDS over Pt/Al-PILM catalyst was increased and selectivity of butenes was decreased with increasing thiophene conversion. On the other hand, selectivity of tetrahydrothiophene (THT) was higher at low conversion. In presulfided $CoMo/Al_2O_3$ HDS catalyst, selectivity of butanes was lower than that of Pt/Al-PILM prepared by $H_2PtCl_6 \cdot 6H_2O$ with similar activity as shown in **Table 1**. Furthermore, it was found that selectivity of THT in HDS over $CoMo/Al_2O_3$ catalyst (0.06 %) was remarkably lower that of Pt/Al-PILM prepared by $H_2PtCl_6 \cdot 6H_2O$ (0.99 %) (not shown). These results indicate that hydrogenation of thiophene into THT over Pt/Al-PILM catalyst proceeds preferentially than over $CoMo/Al_2O_3$ catalyst.

3.2 Characterization of C-R Pt/Al-PILM Catalysts

The particle size of Pt in C-R Pt/Al-PILM catalyst was characterized by TEM technique, XRD and hydrogen adsorption. Highly dispersed small Pt particles were observed in Pt/Al-PILM catalyst prepared by $Pt(C_5H_7O_2)_2$ as shown in **Fig. 3a**. However, particle size of Pt in Pt/Al-PILM catalyst prepared by $H_2Pt(OH)_6$ (**Fig. 3 (c)**), which showed the lowest HDS activity, were remarkably larger than those in Pt/Al-PILM catalyst prepared by $Pt(C_5H_7O_2)_2$ and $H_2PtCl_6\cdot6H_2O$ (**Fig. 3a and b**). Furthermore, we evaluated the crystallite size of Pt in C-R Pt/Al-PILM catalysts by XRD analysis. Four peaks, which are attributed to Pt, were observed in all Pt/Al-PILM catalysts as shown in **Fig. 4**. The intensity of these diffraction peaks has a tendency to decrease in highly active Pt/Al-PILM catalyst for the HDS of thiophene. These results imply that high activity of Pt/Al-PILM catalyst is caused by high Pt dispersion. Thus, we evaluated dispersion and particle size of Pt on Al-PILM by hydrogen adsorption in detail. In C-R Pt/Al-PILM catalysts, the significant difference in the Pt dispersion was observed by changing Pt precursors as shown in **Table 2.** The order of Pt dispersion in C-R Pt/Al-PILM catalysts was $Pt(C_5H_7O_2)_2$ > $H_2PtCl_6\cdot6H_2O$ > $[Pt(NH_3)_4](NO_3)_2$ > $[Pt(NH_3)_4]Cl_2\cdot H_2O$ > $H_2Pt(OH)_6$ and this result is in accordance with the results of TEM observation and XRD analysis. This order was the same as that of HDS activities. **Figure 5** shows the relationship between Pt dispersion on Al-PILM and HDS activities of C-R Pt/Al-PILM catalysts. The HDS activities of C-R Pt/AL-PILM catalysts were strongly correlated with Pt dispersion, suggesting that high Pt dispersion is one of the important factors to prepare highly active Pt/Al-PILM catalysts for HDS reaction. It was reported that $Pt(C_5H_7O_2)_2$ partially decompose into $Pt(C_5H_7O_2)$ on dehydrated Al_2O_3 surface and $Pt(C_5H_7O_2)$ fragment is chemically bounded to surface oxygen atom[19]. Furthermore, $[PtCl_6]^{2-}$ is electrostatically adsorbed on Al_2O_3 surface in $H_2PtCl_6\cdot6H_2O$ solution and adsorbed $[PtCl_6]^{2-}$ becomes

irreversible after drying[20]. Since these Pt precursors strongly interacts with Al atom in Al-PILM, the Pt/Al-PILM catalyst prepared by $Pt(C_5H_7O_2)_2$ and $H_2PtCl_6 \cdot 6H_2O$ shows high Pt dispersion.

Furthermore, we evaluated the HDS activities of C-R Pt/Al-PILM catalysts by turnover frequency (TOF). **Figure 6** shows the relationship between Pt dispersion and TOF of C-R Pt/Al-PILM catalysts. The TOF of Pt/Al-PILM catalyst was decreased with increasing Pt dispersion. The trend between dispersion of Pt on Al_2O_3 and TOF is negative in HDS of thiophene and this relationship was also observed in other reactions such as oxidation of carbon monooxide with oxygen and hydrogenation of ethylene [21]. At high Pt dispersion (above 0.6), Pt/Al-PILM catalysts showed the constant TOF (c.a. 8.0) for the thiophene HDS. Furthermore, we showed in our previous paper that TOF of Pt/Al_2O_3-modified SiO_2 (Pt/Al_2O_3-SiO_2) catalyst (10.4) with high Pt dispersion (0.76) was higher than that of Pt/Al_2O_3 catalyst (5.0) with the similar Pt dispersion (0.82)[22]. We concluded that high TOF of Pt/Al_2O_3-SiO_2 was caused by Brønsted acid sites, which act as one of active sites for the HDS reaction. Since the dehydration of 2-propanol (2-PA) proceeds on both Lewis and Brønsted acid sites and cumene cracking proceeds on Brønsted acid sites, the acidic properties of supports can be evaluated by 2-PA dehydration and cumene cracking. **Figure 7** shows the catalytic properties of Al-PILM for 2-PA decomposition and cumene cracking. The 2-PA decomposition activity of Al-PILM was the same as that of $SiO_2 \cdot Al_2O_3$ reference catalyst (JRC-SAH-1). However, cumene cracking activity of Al-PILM was lower than that of $SiO_2 \cdot Al_2O_3$ catalyst. This indicates that the Brønsted acidity of Al-PILM was lower than that of $SiO_2 \cdot Al_2O_3$ reference catalyst. These results indicate that the Al-PILM have both Lewis acidity and Brønsted acidity. Thus, both Pt particle and Brønsted acid sites in Pt/Al-PILM catalyst would act as active sites for the HDS

reaction. Generally, acidity of support enhances the sulfur tolerance property of noble metal catalyst, which caused by electron deficiency[12,23,24]. Accordingly, Brønsted acid sites of Al-PILM act as active sites for HDS reaction and improve the sulfur tolerance of Pt particle in Pt/Al-PILM catalyst.

3.3 Effect of Pretreatment on the HDS Activity of Pt/Al-PILM Catalyst

Since Pt dispersion was changed by kind of Pt precursor in C-R Pt/Al-PILM catalysts, HDS activity was significantly dependent on the Pt dispersion. Therefore, we studied the effect of pretreatment on the HDS activity of Pt/Al-PILM catalyst to prepare highly active supported Pt HDS catalyst. **Table 3** shows the effect of pretreatment on HDS activities of Pt/Al-PILM catalysts prepared by various Pt precursors. In calcined catalysts, HDS activity of Pt/Al-PILM catalyst was hardly changed by the pretreatment. It was reported that highly dispersed Pt particles on SiO_2 can be prepared by direct hydrogen reduction of uncalcined catalyst[25]. Thus, we evaluated the HDS activities of UC-TPR and UC-TPS Pt/Al-PILM catalysts prepared by various Pt precursors. In Pt/Al-PILM prepared by any kind of Pt precursors, the HDS activities of UC-TPR catalysts were the same as those of C-R catalysts. However, the HDS activities of UC-TPS catalysts were higher than those of other pretreated catalysts. It can be expected that Pt dispersion in UC-TPS Pt/Al-PILM catalysts were higher than those in any other pretreated catalysts. We evaluated the crystallite size and state of Pt in UC-TPR and UC-TPS Pt/Al-PILM catalysts by XRD analysis to clarify relationship Pt dispersion and the HDS activity of supported Pt catalyst. The characteristic diffraction peaks of metallic Pt were observed in XRD patterns of UC-TPR and UC-TPS Pt/Al-PILM catalysts as shown in **Fig. 8a and b**. This result indicates that the bulk phase of Pt particle was not sulfided by UC-TPS treatment. The Pt peaks was scarcely found in the UC-TPR

and UC-TPS Pt/Al-PILM catalysts prepared by $Pt(C_5H_7O_2)_2$ and $H_2PtCl_6 \cdot 6H_2O$. These results imply that Pt particles in these catalysts were highly dispersed on Al-PILM. Furthermore, TEM image of UC-TPS Pt/Al-PILM prepared by $H_2PtCl_6 \cdot 6H_2O$ (**Fig. 9)** also indicates that Pt particles were highly dispersed on Al-PILM by UC-TPS treatment. In Pt/Al-PILM prepared by $H_2PtCl_6 \cdot 6H_2O$, the UC-TPS catalyst showed higher HDS activity than UC-TPR catalyst as shown in **Table 3**. This result is hardly explained by Pt dispersion estimated by XRD patterns. It was reported that partially sulfide species on Pt particle surface in sulfided Pt catalyst was observed by XPS[26] and EXAFS[28] analysis. These results imply that Pt sulfide species could be present on a part of Pt particle surface by UC-TPS treatment. Furthermore, Yoshimura et al. reported that active sites for HDS reaction were PtS_X/PdS_X sulfide phases in Pd-Pt/Yb-USY catalyst[27]. Thus, we assumed that high HDS activity of UC-TPS catalyst was caused by partially sulfided Pt particle with high dispersion, which were also act as active sites for the HDS of thiophene. Furthermore, the reason why UC-TPS catalyst showed higher HDS activity than C-S and C-TPS catalysts can be explained by as follows; Pt sulfides species might be easily formed by UC-TPS treatment of Pt precursor than sulfidation of calcined Pt catalyst (C-S and C-TPS).

In the Pt/Al-PILM catalyst prepared by $H_2Pt(OH)_6$, the HDS activity was hardly changed by kind of pretreatment (except C-S treatment), also as shown in **Table 3**. The HDS activity of C-R catalyst was decreased by sulfidation treatment. These results can be explained by sulfur tolerance property of Pt particle. The small Pt particle showed high performance for sulfur tolerance[28]. Since particle size of Pt in Pt/Al-PILM catalyst prepared by $H_2Pt(OH)_6$ was remarkably large as shown in **Fig. 3** ~~(c)~~ and **Table 2,** sulfur tolerance of this catalyst was low. Thus, Pt/Al-PILM catalyst prepared by $H_2Pt(OH)_6$ showed a different tendency among Pt/Al-PILM

catalyst prepared by other Pt precursors. In contrast, the HDS activities of C-S Pt/Al-PILM catalysts prepared by other Pt precursors with small Pt particles were the same as those of C-R catalysts.

4. Conclusion

The effect of Pt precursor and pretreatment on the HDS activity of Pt/Al-PILM catalyst to prepare highly active supported Pt HDS catalyst was studied. The order of HDS activities of Pt/Al-PILM catalysts prepared by various Pt precursors was as follows; $Pt(C_5H_7O_2)_2$ > $H_2PtCl_6 \cdot 6H_2O$ > $[Pt(NH_3)_4](NO_3)_2$ > $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ > $H_2Pt(OH)_6$. This order was the same as that of Pt dispersion. Furthermore, the effect of pretreatment on the HDS activities of Pt/Al-PILM prepared by various Pt precursors was evaluated. The UC-TPS Pt/Al-PILM catalyst prepared by $Pt(C_5H_7O_2)_2$ showed the highest HDS activity among various pretreated Pt/Al-PILM catalysts. These results indicate that ~~the~~ high HDS activity of UC-TPS Pt/Al-PILM catalyst can be attributed to the partly sulfided Pt particles with high dispersion. It is concluded that the highly active Pt/Al-PILM catalyst for the HDS reaction could be prepared by using $Pt(C_5H_7O_2)_2$ as a precursor and UC-TPS treatment.

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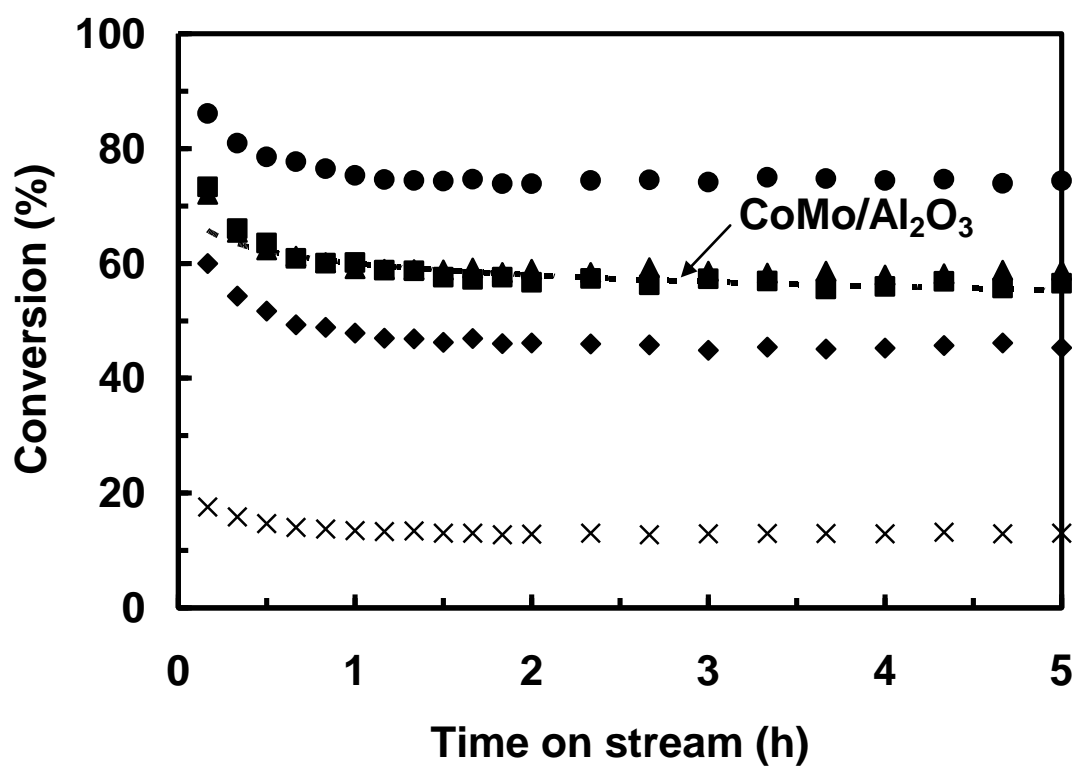
Fig. 1 Hydrodesulfurization of thiophene over C-R Pt/Al-PILM catalysts prepared by various Pt precursors at 350 °C. ● Pt(C$_5$H$_7$O$_2$)$_2$, ▲ H$_2$PtCl$_6$•6H$_2$O, ■ [Pt(NH$_3$)$_4$](NO$_3$)$_2$, ♦ [Pt(NH$_3$)$_4$]Cl$_2$•H$_2$O, × H$_2$Pt(OH)$_6$.
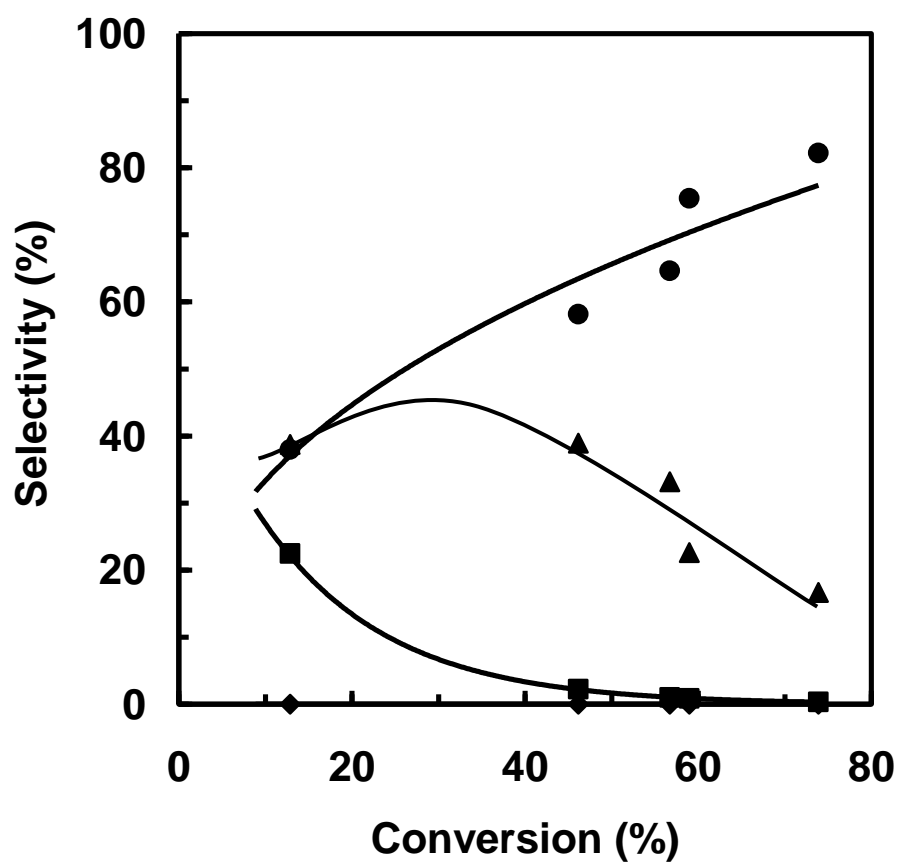
Fig. 2   Relationship between thiophene conversion over C-R Pt/Al-PILM catalyst and selectivities
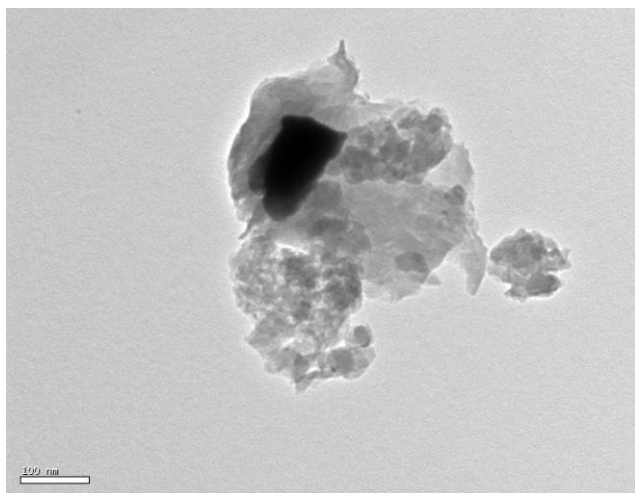of products in the thiophene HDS. ● n-butane, ▲ butenes, ■ tetrahydrothiophene, ♦
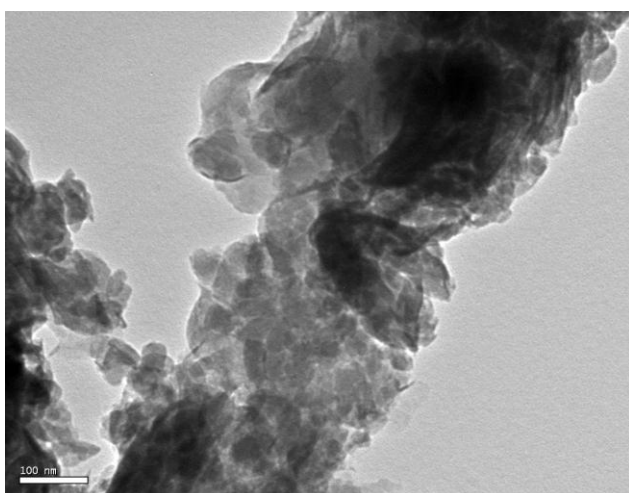1,3-butadiene.
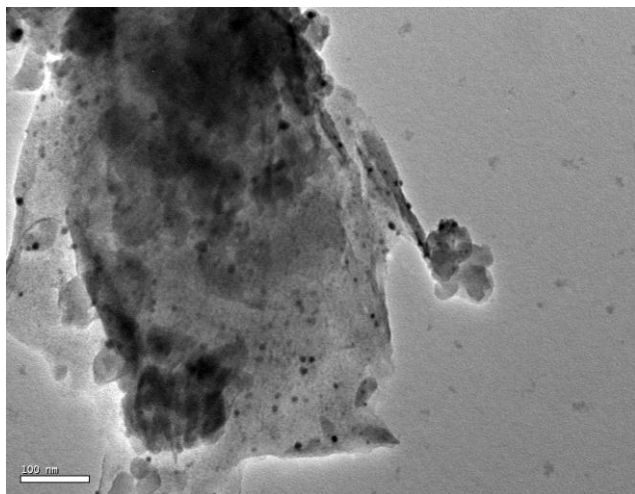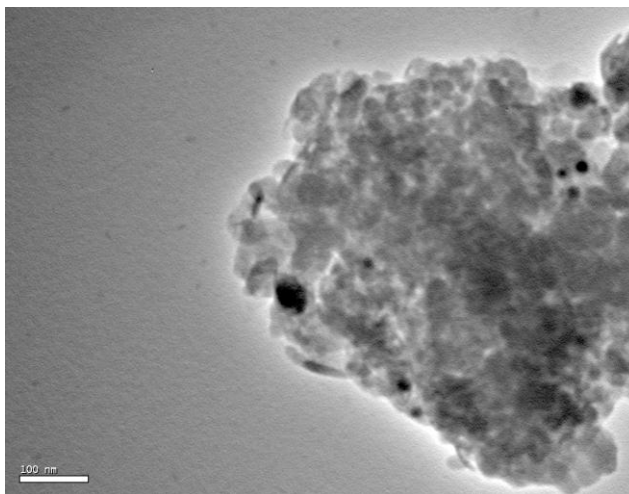
Fig. 3 TEM images of C-R Pt/Al-PILM catalysts ($\times 120000$). Pt/Al-PILM prepared by (a) Pt($C_5H_7O_2)_2$, (b) $H_2PtCl_6 \cdot 6H_2O$ (c) $H_2Pt(OH)_6$ and (d) Al-PILM.
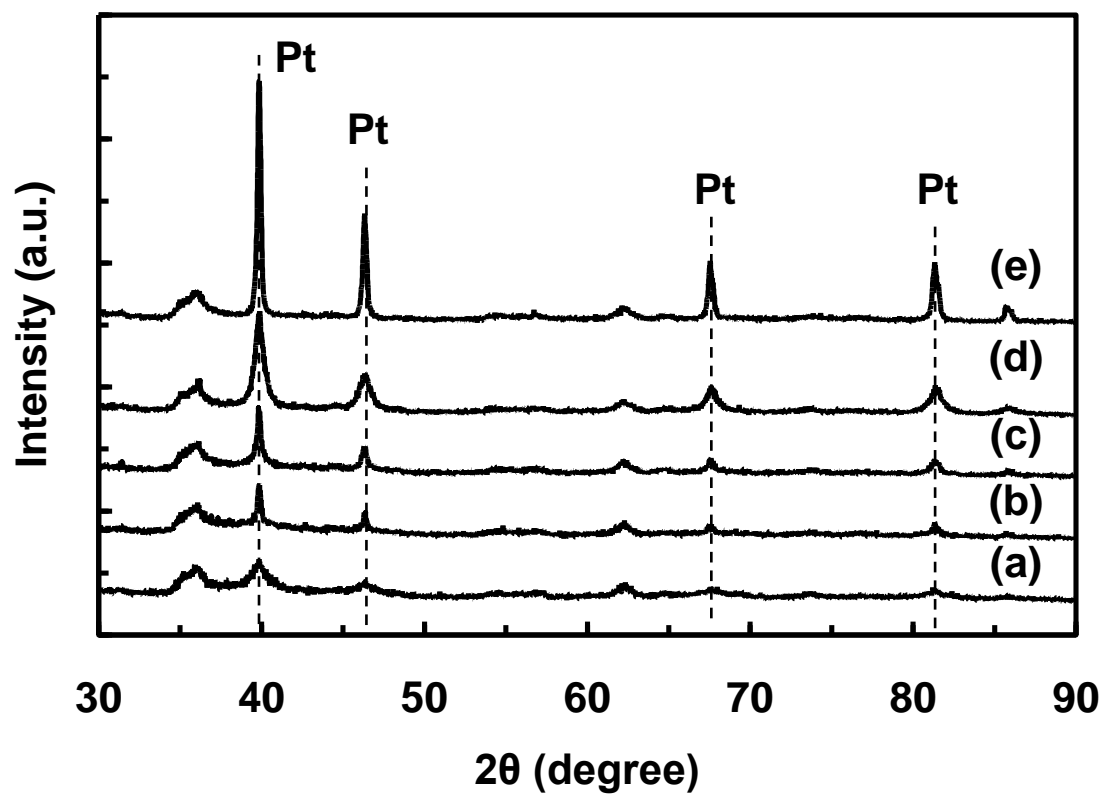
Fig. 4 XRD patterns of C-R Pt/Al-PILM catalysts prepared by various Pt precursors. (a) $Pt(C_5H_7O_2)_2$, (b) $H_2PtCl_6 \cdot 6H_2O$, (c) $[Pt(NH_3)_4](NO_3)_2$, (d) $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, (e) $H_2Pt(OH)_6$.
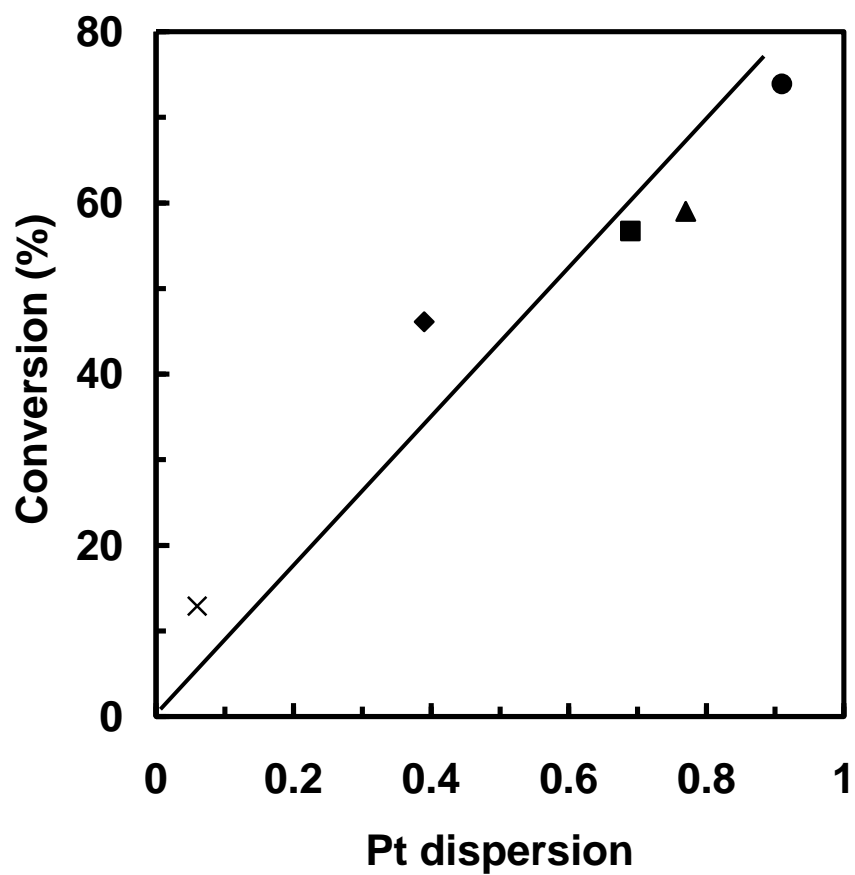
Fig. 5 Relationship between Pt dispersion on Al-PILM and HDS activity of C-R Pt/Al-PILM catalyst. ● $Pt(C_5H_7O_2)_2$, ▲ $H_2PtCl_6 \cdot 6H_2O$, ■ $[Pt(NH_3)_4](NO_3)_2$, ♦ $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, × $H_2Pt(OH)_6$.
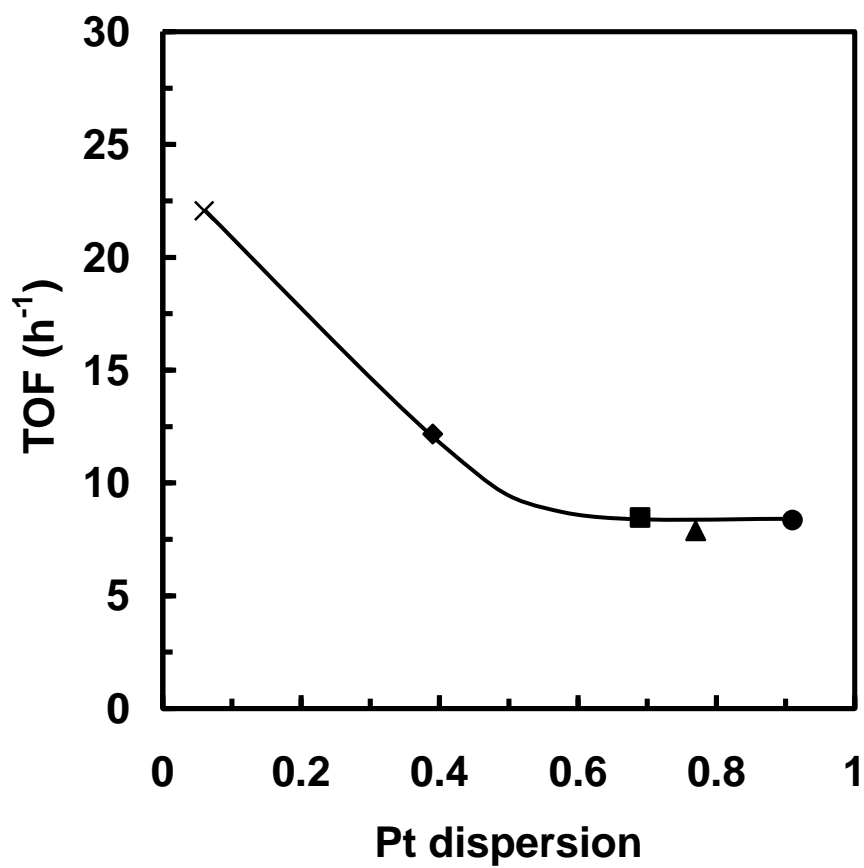
Fig. 6 Relationship between Pt dispersion on Al-PILM and TOF of C-R Pt/Al-PILM catalyst. ●
$Pt(C_5H_7O_2)_2$, ▲ $H_2PtCl_6 \cdot 6H_2O$, ■ $[Pt(NH_3)_4](NO_3)_2$, ♦ $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, ×
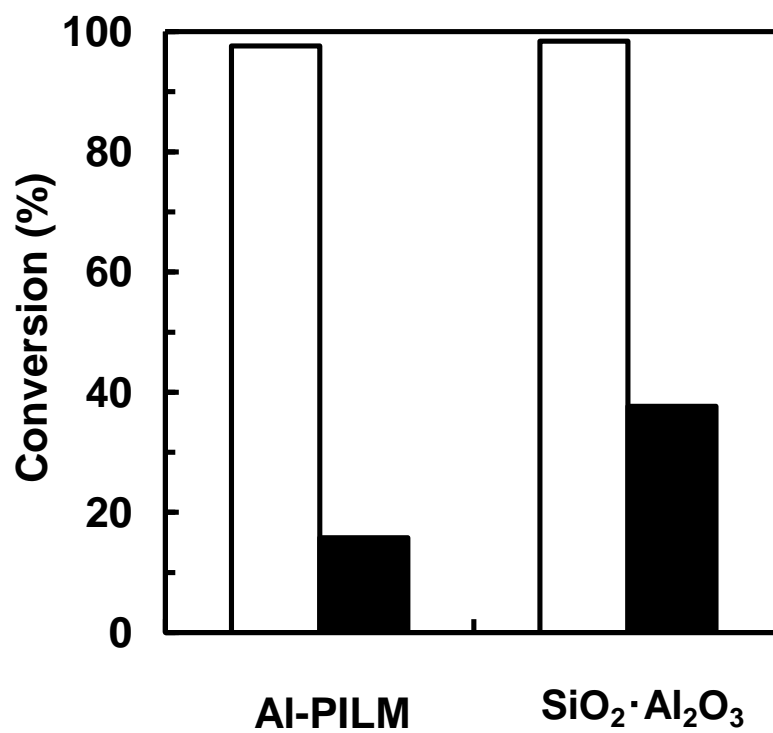$H_2Pt(OH)_6$.

Fig. 7 The catalytic activities of Al-PILM and SiO$_2$•Al$_2$O$_3$ for the (□) dehydration of 2-propanol (200 °C) and (■) cracking of cumene (400 °C).
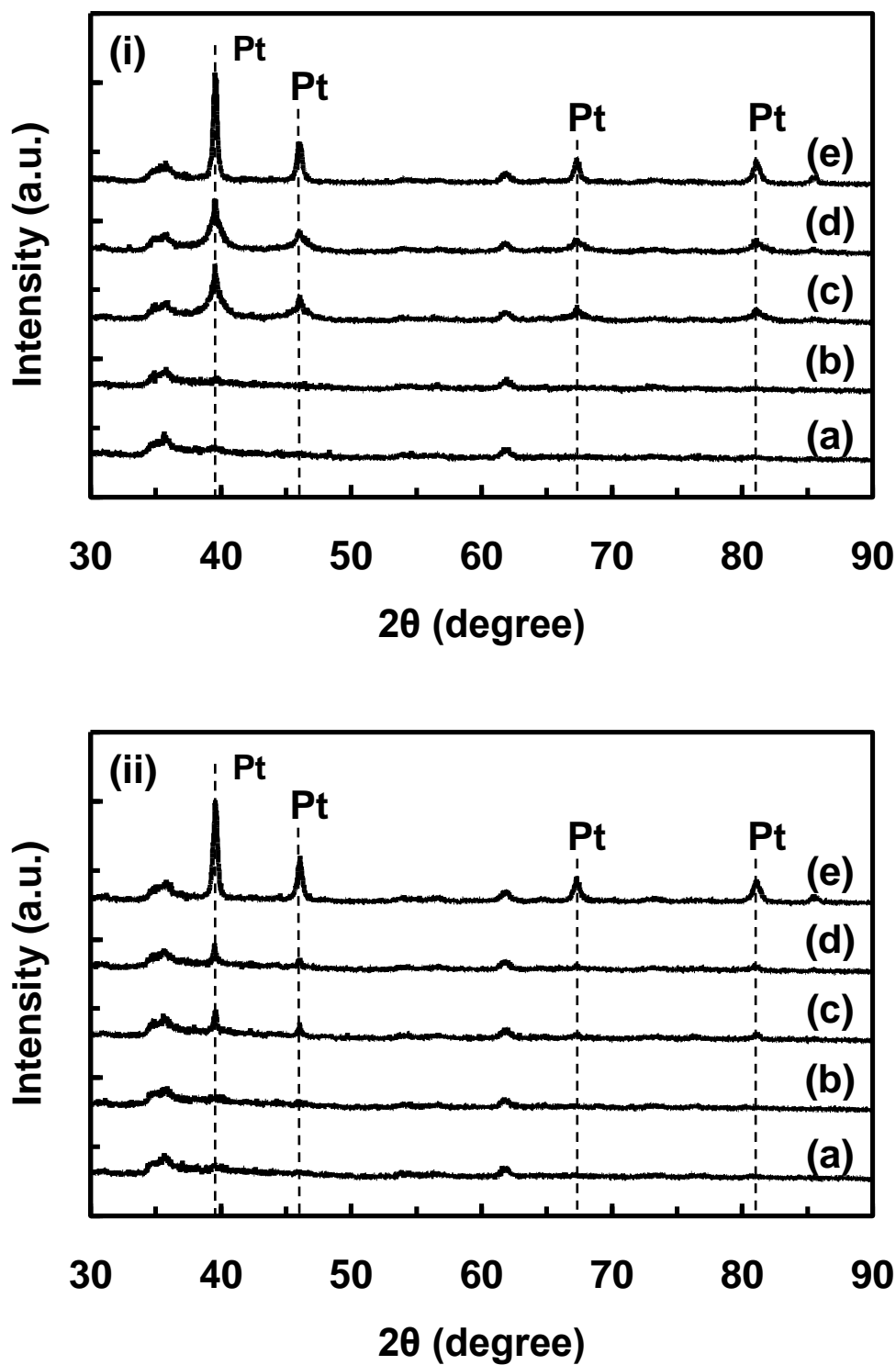
Fig. 8 XRD patterns of (i) UC-TPR and (ii) UC-TPS Pt/Al-PILM catalysts prepared by various Pt precursors. (a) $Pt(C_5H_7O_2)_2$, (b) $H_2PtCl_6 \cdot 6H_2O$, (c) $[Pt(NH_3)_4](NO_3)_2$, (d) $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, (e) $H_2Pt(OH)_6$.
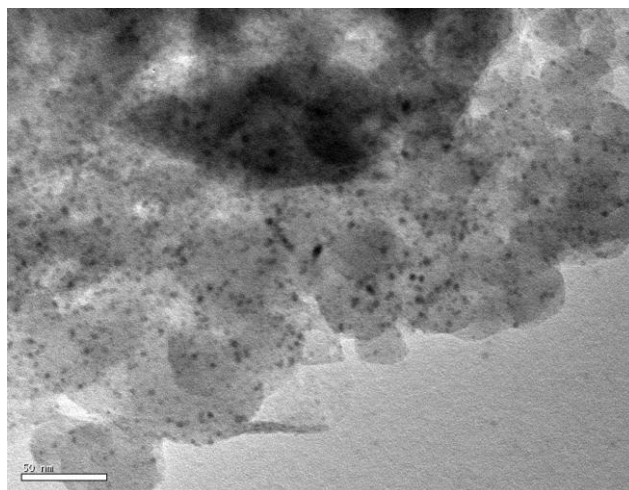
Fig. 9   TEM image of UC-TPS Pt/Al-PILM catalyst prepared by $H_2PtCl_6•6H_2O$ ($\times$300000).

Table 1

Products distribution over C-R Pt/Al-PILM prepared by various Pt precursors and CoMo/Al$_2$O$_3$ catalysts in the HDS of thiophene at 350 °C after reaction for 2 h.

Pt precursor	Thiophene conversion (%)	Selectivity of hydrocarbon (%)			
		C$_1$-C$_3$[a]	C$_4$[b]	C$_4$'[c]	C$_4$"[d]
Pt(C$_5$H$_7$O$_2$)$_2$	73.9	0.2	83.2	16.7	0.0
H$_2$PtCl$_6$·6H$_2$O	59.0	0.3	76.9	22.8	0.0
[Pt(NH$_3$)$_4$](NO$_3$)$_2$	56.7	0.2	66.3	33.5	0.0
[Pt(NH$_3$)$_4$]Cl$_2$·H$_2$O	46.1	0.5	59.7	39.8	0.0
H$_2$Pt(OH)$_6$	12.9	1.1	49.0	50.0	0.0
CoMo/Al$_2$O$_3$ catalyst	57.8	0.3	17.2	82.5	0.0

[a] C$_1$-C$_3$ hydrocarbons.

[b] Butanes.

[c] Butenes.

[d] 1,3-Butadiene.

Table 2

Dispersion and particle size of Pt in C-R Pt/Al-PILM catalysts measured by hydrogen adsorption method.

Pt precursor	Pt dispersion (H mol/Pt mol)	Particle size of Pt (nm)
$Pt(C_5H_7O_2)_2$	0.91	1.0
$H_2PtCl_6 \cdot 6H_2O$	0.77	1.2
$[Pt(NH_3)_4](NO_3)_2$	0.69	1.4
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$	0.39	2.4
$H_2Pt(OH)_6$	0.06	15.7

Table 3

Effect of pretreatment on HDS activities of Pt/Al-PILM catalysts prepared by various Pt precursors at 350 °C after reaction for 2 h.

Pt precursor	Thiophene conversion (%)				
	C-R	C-S	C-TPS	UC-TPR	UC-TPS
$Pt(C_5H_7O_2)_2$	73.9	73.9	72.3	77.7	78.3
$H_2PtCl_6 \cdot 6H_2O$	59.0	61.3	62.5	61.0	74.2
$[Pt(NH_3)_4](NO_3)_2$	56.7	58.7	59.5	50.2	72.0
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$	46.1	46.0	39.2	48.5	69.1
$H_2Pt(OH)_6$	12.9	6.4	10.2	10.9	11.8