Catalytic Activities of Platinum Supported on Silica-modified Alumina for Hydrodesulfurization of Thiophene

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Hydrodesulfurization (HDS) of thiophene over silica-modified alumina-supported platinum (Pt/SiO$_2$-Al$_2$O$_3$) catalysts was examined. The HDS activity of a Pt/Al$_2$O$_3$ catalyst was enhanced by silica modification. However, the optimal silica loading for HDS activity could not be identified. The dispersion of platinum on alumina, as measured by the hydrogen adsorption method, was enhanced by silica modification and the optimal silica loading for platinum dispersion was 10 to 40 wt%. The acidity of SiO$_2$ Al$_2$O$_3$ was evaluated by 2-propanol dehydration (200°C) and cumene cracking (400°C). The optimal silica loading for the acidity of SiO$_2$ Al$_2$O$_3$ was 90 wt%. Furthermore, the presence of Brønsted acid sites on SiO$_2$-Al$_2$O$_3$ was confirmed by a pyridine adsorption method with FT-IR spectroscopy. The high HDS activity of the Pt/SiO$_2$ Al$_2$O$_3$ catalyst is caused by both high Pt dispersion and formation of Brønsted acid sites.

Keywords
Hydrodesulfurization, Thiophene, Platinum catalyst, Silica modification, Bifunctional catalysis

1. Introduction

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the important processes in the petroleum industry to produce clean fuel. Highly active HDS catalysts, which exhibit higher activity than commercial CoMo/Al$_2$O$_3$ HDS catalyst, have been developed to produce lower sulfur content fuel.

We previously investigated the development of highly active supported noble metal HDS catalysts.

Supported noble metal catalysts, especially platinum supported on zeolites and mesoporous silicates had higher HDS activities than commercial CoMo/Al$_2$O$_3$ HDS catalyst. We also reported that the HDS activities of Pt supported on silica gel (SiO$_2$) and mesoporous silica MCM-41 were enhanced by alumina modification of the siliceous support. We concluded that the high activities of these catalysts were caused by the formation of both highly dispersed Pt particles and Brønsted acid sites on the supported Pt catalyst, which act as the active sites for the HDS of thiophene. Therefore, we expected that the HDS activity of Pt/Al$_2$O$_3$ could also be enhanced by the modification of alumina with silica.

In the present study, we examined the catalytic performance of platinum supported on silica-modified aluminas (SiO$_2$-Al$_2$O$_3$) for the HDS of thiophene. The catalytic properties of Pt/SiO$_2$-Al$_2$O$_3$ were characterized to clarify the essential factors involved in the HDS activity of supported Pt catalyst.

2. Experimental

Alumina (Al$_2$O$_3$, JRC-ALO-8) was obtained from the Catalysis Society of Japan, and silica (SiO$_2$) from Nippon Aerosil Co. Silica-modified alumina (SiO$_2$-Al$_2$O$_3$) was prepared by an impregnation method using tetraethoxysilane (TEOS, Si(OC$_2$H$_5$)$_4$, Kanto Chemical Co.) ethanol solution. After TEOS impregnation, supports were dried at 120°C and then calcined at 500°C (10°C/min) for 4 h in air. Supported Pt catalysts were prepared by an impregnation method using hydrogen hexachloroplatinate (H$_2$PtCl$_6$:6H$_2$O, Kanto Chemical Co.) aqueous solution and the Pt loading was 5 wt%. 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. HDS of thiophene was carried out at 350°C under 0.1 MPa using a conventional fixed bed flow reactor. Thiophene was introduced into the reactor by passing the hydrogen stream (30 ml/min) through a saturator containing liquid thiophene 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.

The dispersion of platinum on SiO₂-Al₂O₃ was measured by hydrogen adsorption. Adsorption of hydrogen on the supported Pt catalyst was carried out in a Pyrex glass vacuum system at 25°C. The supported Pt catalysts were stood under a vacuum at 500°C for 1 h followed by reduction with hydrogen (26.7 kPa) at 450°C for 1 h and stood under a vacuum at the same temperature for 1 h before hydrogen adsorption. The acidity of SiO₂-Al₂O₃ was evaluated by 2-propanol (2-PA) dehydra-tion (200°C) and cumene cracking (400°C) using a pulse reactor with helium carrier gas. For both reactions, the catalyst (0.03 g) was charged into the reactor and pretreated at 500°C for 1 h before the reaction. Fourier transform infrared spectroscopy (FT-IR) spectra of pyridine adsorbed on Al₂O₃ and SiO₂-Al₂O₃ were observed using a Jasco FT-IR spectrometer. The catalysts were stood under a vacuum at 500°C for 2 h prior to the measurement.

3. Results and Discussion

The effect of silica modification on the catalytic activity of Pt supported on Al₂O₃ for the HDS of thiophene was examined at 350°C. The catalytic activity of Pt/Al₂O₃ was enhanced by silica modification of Al₂O₃ as shown in Fig. 1. Figure 2 shows the relationship between the amount of SiO₂ loading and HDS activity of Pt/SiO₂-Al₂O₃ after reaction for 2 h. The HDS activities of Pt/SiO₂-Al₂O₃ catalysts were higher than those of Pt/Al₂O₃ and Pt/SiO₂ catalysts. The optimal SiO₂ loading for the HDS activity of Pt/SiO₂-Al₂O₃ could not be identified. However, the enhanced activities of Pt/SiO₂-Al₂O₃ catalysts in the range of SiO₂ loading from 10 to 90 wt% were comparable to that of sulfided commercial CoMo/Al₂O₃ catalyst. The relationship between the amount of Al₂O₃ loading and HDS activity of Pt supported on alumina-modified SiO₂ (Al₂O₃-SiO₂) after reaction for 2 h is presented in Fig. 2. The optimal Al₂O₃ loading for the HDS activity of Pt/Al₂O₃-SiO₂ was clearly observed as 8 wt%. The effect of silica modification on catalytic activity of Pt/Al₂O₃ was remarkably different from the effect of alumina modification on catalytic activity of Pt/SiO₂. We previously reported that the dispersion of Pt on SiO₂ was enhanced to about 0.8 with Al₂O₃ loading from 8 to 24 wt%[13]. Therefore, we performed detailed characterizations of Pt/SiO₂-Al₂O₃ catalysts to clarify why the optimal amount of SiO₂ loading for the HDS of thiophene was not observed.

Dispersion of Pt on Al₂O₃ and SiO₂-Al₂O₃ was measured by the hydrogen adsorption method. Figure 3 shows the effect of silica modification of Al₂O₃ on the dispersion of Pt in Pt/SiO₂-Al₂O₃ catalysts. The dispersion of Pt on Al₂O₃ was higher than that on SiO₂. The Pt precursor such as [PtCl₆]³⁻ reacts with the hydroxyl groups on the Al₂O₃ surface (Al-OH)[16,17]. Furthermore, [PtCl₆]³⁻ is adsorbed irreversibly on the Al₂O₃ surface by drying at 90°C[17]. In contrast, the hydroxyl group on the SiO₂ surface (Si OH) also acts as a ligand of the Pt complex, but the Si OH ligand in the Pt complex is reversibly exchanged with H₂O even
after drying at 90°C[18]. These results indicate that the interaction between Pt particles and the Al₂O₃ surface is stronger than that with the SiO₂ surface. Thus, the dispersion of Pt in Pt/Al₂O₃ was higher than that in Pt/SiO₂. However, the dispersion of Pt in Pt/Al₂O₃ was enhanced by silica modification as discussed below.

The acidic properties of supports can be evaluated by measuring the dehydration of 2-propanol (2-PA), which proceeds on both Lewis and Brønsted acid sites, and the cracking of cumene, which proceeds only on Brønsted acid sites. The acidic properties of Al₂O₃ and SiO₂-Al₂O₃ were evaluated with 2-PA dehydration (200 °C) and cumene cracking (400°C) using a pulse reactor. The 2-PA dehydration activity decreased, whereas the cumene cracking activity increased with increasing SiO₂ loading. These results are also shown in Fig. 3, indicating that the Lewis acid sites on Al₂O₃ were covered by SiO₂ addition, resulting in formation of Brønsted acid sites. The highest activities for both acid-catalyzed reactions were found in 90 wt% SiO₂-Al₂O₃. Furthermore, the presence of Brønsted acid sites on SiO₂-Al₂O₃ was confirmed by the FT-IR spectra of pyridine adsorbed on SiO₂-Al₂O₃ (at 1547 cm⁻¹) as shown in Fig. 4. The dispersion of Pt on ZSM-5 zeolite increases with increasing proton content[19]. The anionic Pt precursor such as [PtCl₆]²⁻ interacts electrostatically with the Brønsted acid sites on the SiO₂-Al₂O₃ surface. Therefore, the dispersion of Pt on SiO₂-Al₂O₃ was slightly enhanced by increasing the SiO₂ loading from 10 to 40 wt%.

Previously, we proposed two reaction routes for HDS of thiophene over highly active Pt/Al₂O₃-SiO₂ catalyst: (i) a monofunctional route in which HDS reactions proceed only on Pt particles, and (ii) a bifunctional route in which both Pt particles and Brønsted acid sites are involved in the HDS reaction[13]. In reaction route (ii), thiophene is activated on the Brønsted acid sites of Al₂O₃-SiO₂ and hydrogen is activated on the Pt particles to form spillover hydrogen. In the present study, we observed that the Brønsted acid sites were generated by silica modification of Al₂O₃ as shown in Figs. 3 and 4. Therefore, both the Pt particles and Brønsted acid sites in the Pt/SiO₂-Al₂O₃ catalyst can act as active sites in the HDS of thiophene, as in the Pt/Al₂O₃-SiO₂ catalyst. However, Pt dispersion and Brønsted acidity were low but HDS activity of Pt/SiO₂-Al₂O₃ catalyst was not low in the range of SiO₂ loading from 60 to 80 wt%. Previously, we reported that the high activity of Pt/alumina-modified MCM-41 catalyst for HDS reaction is due to the good balance of high dispersion of Pt particles and Brønsted acidity of the support[15]. This indicates that both high Pt dispersion and Brønsted acidity of the support are important in the preparation of highly active supported Pt HDS catalyst.

4. Conclusions

The optimal SiO₂ loading for the activity of Pt/SiO₂-Al₂O₃ in HDS reaction could not be identified, in contrast to Pt/Al₂O₃-SiO₂. The characterization re-

![Dispersion of Pt, ▲ 2-propanol dehydration, ■ Cumene cracking.](image)

**Fig. 3** Effect of SiO₂ Modification of Al₂O₃ Support on the Dispersion of Pt on SiO₂-Al₂O₃ and Catalytic Activities of SiO₂-Al₂O₃ for Acid-catalyzed Reactions

Pyridine was adsorbed at 150°C followed by standing in a vacuum at 150°C for 0.5 h.

**Fig. 4** FT-IR Spectra of Pyridine Adsorbed on (a) Al₂O₃, (b) 11 wt% SiO₂-Al₂O₃, (c) 39 wt% SiO₂-Al₂O₃, (d) 60 wt% SiO₂-Al₂O₃, and (c) 90 wt% SiO₂-Al₂O₃.
sults of the catalysts revealed that the optimal SiO₂ loading for dispersion of Pt on SiO₂-Al₂O₃ was 10 to 40 wt%, and that for Brønsted acidity was ca. 90 wt%. We conclude that the high HDS activity of the Pt/SiO₂-Al₂O₃ catalyst results from both high Pt dispersion and formation of Brønsted acid sites.

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References