

[Research Note]

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

Yasuharu KANDA*, Yasunobu OOKA, Takao KOBAYASHI, Yoshio UEMICHI, and Masatoshi SUGIOKA

Dept. of Applied Chemistry, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, JAPAN

(Received May 17, 2006)

Hydrodesulfurization (HDS) of thiophene over silica-modified alumina-supported platinum (Pt/SiO₂-Al₂O₃) catalysts was examined. The HDS activity of a Pt/Al₂O₃ 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 SiO₂-Al₂O₃ was evaluated by 2-propanol dehydration (200°C) and cumene cracking (400°C). The optimal silica loading for the acidity of SiO₂-Al₂O₃ was 90 wt%. Furthermore, the presence of Brønsted acid sites on SiO₂-Al₂O₃ was confirmed by a pyridine adsorption method with FT-IR spectroscopy. The high HDS activity of the Pt/SiO₂-Al₂O₃ 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 fuels^{1)~4)}. Highly active HDS catalysts, which exhibit higher activity than commercial CoMo/Al₂O₃ HDS catalyst, have been developed to produce lower sulfur content fuels^{5),6)}.

We previously investigated the development of highly active supported noble metal HDS catalysts^{7)~15)}. Supported noble metal catalysts, especially platinum supported on zeolites^{7),8),12)} and mesoporous silicates^{9)~12)}, had higher HDS activities than commercial CoMo/Al₂O₃ HDS catalyst. We also reported that the HDS activities of Pt supported on silica gel (SiO₂)¹³⁾ and mesoporous silica MCM-41^{14),15)} 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/Al₂O₃ 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 alu-

mina (SiO₂-Al₂O₃) for the HDS of thiophene. The catalytic properties of Pt/SiO₂-Al₂O₃ were characterized to clarify the essential factors involved in the HDS activity of supported Pt catalyst.

2. Experimental

Alumina (Al₂O₃, JRC-ALO-8) was obtained from the Catalysis Society of Japan, and silica (SiO₂) from Nippon Aerosil Co. Silica-modified alumina (SiO₂-Al₂O₃) was prepared by an impregnation method using tetraethoxysilane (TEOS, Si(OC₂H₅)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 (H₂PtCl₆·6H₂O, 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, H₂/thiophene = 30 mol/mol, W/F = 37.9 g·h/mol. The

* To whom correspondence should be addressed.

* E-mail: kanda@mmm.muroran-it.ac.jp

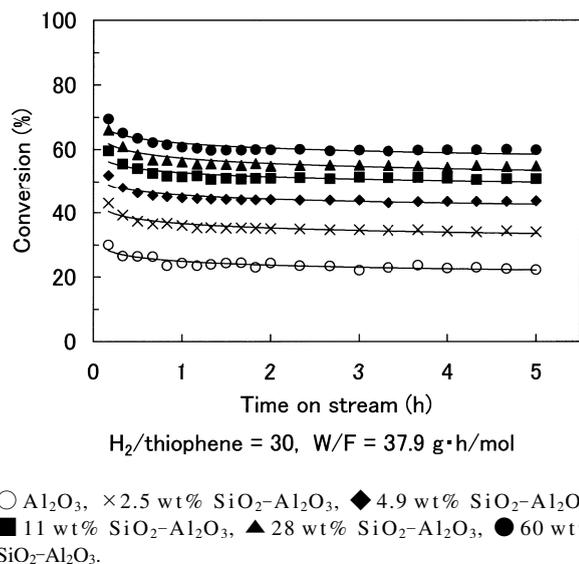


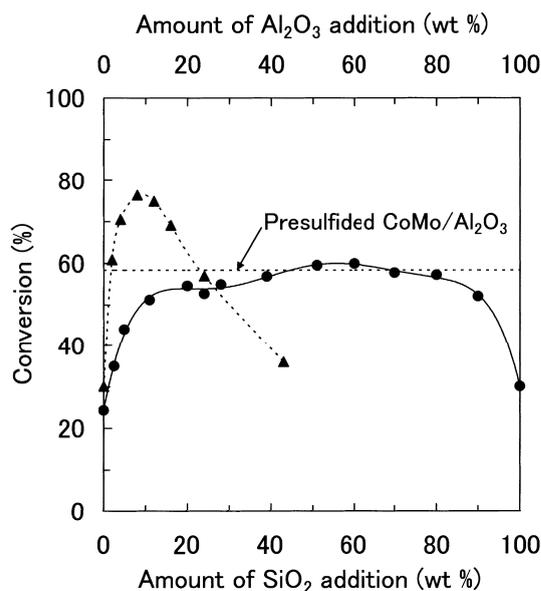
Fig. 1 Hydrodesulfurization of Thiophene over Pt/SiO₂-Al₂O₃ Catalysts at 350°C

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) dehydration (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/

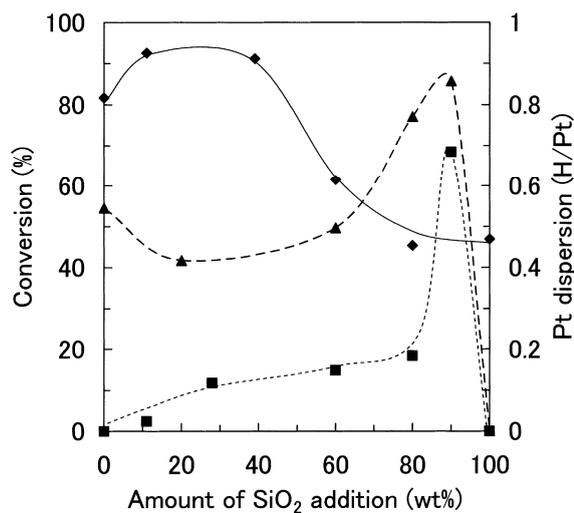


● Effect of SiO₂ modification on HDS activity of Pt/SiO₂-Al₂O₃, ▲ Effect of Al₂O₃ modification on HDS activity of Pt/Al₂O₃-SiO₂ catalyst¹³.

Fig. 2 Effect of Surface Modification on the HDS Activities of Pt/SiO₂-Al₂O₃ and Pt/Al₂O₃-SiO₂ Catalysts

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 h¹³ 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]²⁻ reacts with the hydroxyl groups on the Al₂O₃ surface (Al-OH)^{16,17}. Furthermore, [PtCl₆]²⁻ is adsorbed irreversibly on the Al₂O₃ surface by drying at 90°C¹⁷. 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



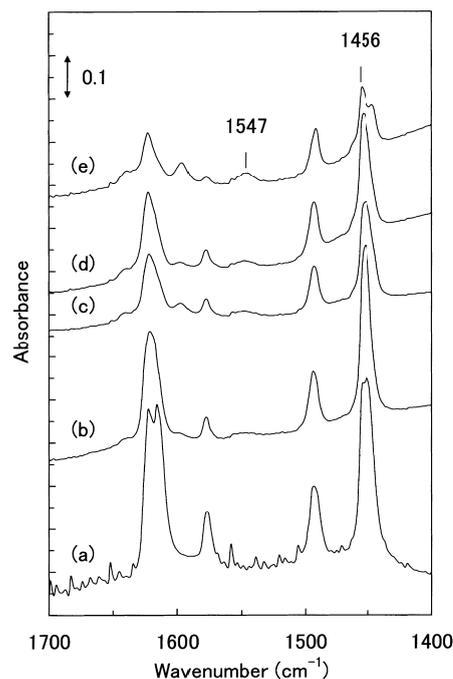
◆ Dispersion of Pt, ▲ 2-propanol dehydration, ■ Cumene cracking.

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

after drying at 90°C¹⁸). 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 content⁸). 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 pro-



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 (e) 90 wt% SiO₂-Al₂O₃

ceed only on Pt particles, and (ii) a bifunctional route in which both Pt particles and Brønsted acid sites are involved in the HDS reaction¹³). 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 support¹⁵). 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-

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.

Acknowledgment

We would like to thank Nippon Aerosil Co., for supplying the silica gel.

References

- 1) Prins, R., de Beer, V. H. J., Somorjai, G. A., *Catal. Rev.-Sci. Eng.*, **31**, 1 (1989).
- 2) Chianelli, R. R., Daage, M., Ledoux, M. J., *Adv. Catal.*, **40**, 177 (1994).
- 3) Topsøe, H., Clausen, B. S., Massoth, F. E., *Catal.-Sci. Tech.*, **11**, 1 (1996).
- 4) Whitehurst, D. D., Isoda, T., Mochida, I., *Adv. Catal.*, **4**, 345 (1998).
- 5) Sugioka, M., *PETROTECH*, **19**, (6), 458 (1996).
- 6) Kabe, T., Ishihara, A., Qian, W., "Hydrodesulfurization and Hydrodenitrogenation," Kodansha Scientific, Wiley-VCH, Tokyo, New York, Berlin (1999), p. 266.
- 7) Sugioka, M., Sado, F., Kurosaka, T., Wang, X., *Catal. Today*, **45**, 327 (1998).
- 8) Kurosaka, T., Sugioka, M., Matsushashi, H., *Bull. Chem. Soc. Jpn.*, **74**, 757 (2001).
- 9) Sugioka, M., Andalaluna, L., Morishita, S., Kurosaka, T., *Catal. Today*, **39**, 61 (1997).
- 10) Sugioka, M., Morishita, S., Kurosaka, T., Seino, A., Nakagawa, M., Namba, S., *Stud. Surf. Sci. Catal.*, **125**, 531 (1999).
- 11) Sugioka, M., Aizawa, T., Kanda, Y., Kurosaka, T., Uemichi, Y., Namba, S., *Stud. Surf. Sci. Catal.*, **142**, 739 (2002).
- 12) Sugioka, M., Kurosaka, T., *J. Jpn. Petrol. Inst.*, **45**, (6), 342 (2002).
- 13) Kanda, Y., Kobayashi, T., Uemichi, Y., Sugioka, M., *J. Jpn. Petrol. Inst.*, **49**, (2), 49 (2006).
- 14) Kanda, Y., Uemichi, Y., Kobayashi, T., Andalaluna, L., Sugioka, M., *Stud. Surf. Sci. Catal.*, **156**, 747 (2005).
- 15) Kanda, Y., Kobayashi, T., Uemichi, Y., Namba, S., Sugioka, M., *Appl. Catal. A: General*, **308**, 111 (2006).
- 16) Martens, J. H. A., Prins, R., *Appl. Catal.*, **46**, 31 (1989).
- 17) Shelimov, B., Lambert, J. F., Che, M., Didillon, B., *J. Catal.*, **185**, 462 (1999).
- 18) Boujday, S., Lehman, J., Lambert, J. F., Che, M., *Catal. Lett.*, **88**, 23 (2003).

要 旨

チオフェンの水素化脱硫反応に対するシリカ修飾アルミナ担持白金の触媒活性

神田 康晴, 大岡 康伸, 小林 隆夫, 上道 芳夫, 杉岡 正敏

室蘭工業大学応用化学科, 050-8585 北海道室蘭市水元町27-1

シリカ修飾アルミナ担持白金 (Pt/SiO₂-Al₂O₃) のチオフェンの水素化脱硫 (HDS) 活性および特性について検討した。アルミナ担持白金 (Pt/Al₂O₃) の HDS 活性はシリカ修飾を施すことによって向上するが, Pt/SiO₂-Al₂O₃ の HDS 活性に対する最適シリカ添加量は確認されなかった。Pt/SiO₂-Al₂O₃ における白金の分散度は水素吸着法によって測定した。その結果, 白金の分散度はアルミナにシリカ修飾を施すことによって向上し, 白金の分散度に対するシリカの最適添加量は 10 から 40 wt% である

ことを明らかにした。SiO₂-Al₂O₃ の酸性質は 2-プロパノールの脱水反応 (200°C) およびクメンの分解反応 (400°C) より評価した。これより, SiO₂-Al₂O₃ の酸性質に対する最適シリカ添加量は 90 wt% であることを明らかにした。さらに, 吸着ピリジン FT-IR スペクトルより SiO₂-Al₂O₃ には Brønsted 酸点が存在することを確認した。以上の結果から, Pt/Al₂O₃ 触媒の HDS 活性がシリカ修飾により向上したのは, Pt の分散度および担体の Brønsted 酸性が高められたためであると結論した。