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New hydrodesulfurization catalysts: noble metals supported on USY zeolite

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Abstract

It was revealed that Pt–Pd bimetal supported on USY zeolite showed high and stable catalytic activity for the hydrodesulfurization of thiophene at 400°C and this activity was higher than that of commercial Co–Mo/Al_2O_3 catalyst. It was concluded that the strong Brønsted acid site of USY and spillover hydrogen formed on Pt–Pd bimetal particle in Pt–Pd/USY catalyst play an important role for the hydrodesulfurization of thiophene.

Keywords: Hydrodesulfurization; Pt–Pd catalysts

1. Introduction

Hydrodesulfurization of petroleum feedstocks is one of the important process in the petroleum industry to produce clean fuels. Co–Mo/Al_2O_3 catalyst has been widely used in the hydrodesulfurization process of petroleum. However, recently, the development of highly active hydrodesulfurization catalysts, which are higher than commercial Co–Mo/Al_2O_3 hydrodesulfurization catalyst, have been claimed in the petroleum industry to produce lower sulfur content fuels because of serious problems of global scale air pollution by SO_x which is produced by petroleum feedstocks combustion. It has been accepted that metal-zeolite catalysts have high possibility as a new hydrodesulfurization catalyst for petroleum [1–3]. We have also investigated the hydrodesulfurization of thiophene over reduced Me-Y zeolites[4–7]. In our studies of the hydrodesulfurization of thiophene over reduced Me-Y zeolites, a general rule was derived that the combination of strong Brønsted acid site of zeolites and metal particles with high hydrogenating ability on zeolites provide high catalytic activity for the hydrodesulfurization of organic sulfur compounds and the adjustment of the Brønsted acidity of zeolites and hydrogenating ability of metals is important for highly active zeolite-based hydrodesulfurization catalysts.

In the present work, we examined the catalytic activities of various noble metals supported on USY zeolite for the hydrodesulfurization of thiophene in order to develop highly active zeolite-based hydrodesulfurization catalysts.

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2. Experimental

Hydrodesulfurization of thiophene over noble metal/USY catalysts was carried out at 400°C under 1 atm by using a conventional fixed bed flow reactor. Thiophene was introduced into the reactor by passing hydrogen through thiophene trap cooled at 0°C. The reaction products were analyzed by gaschromatography.

Zeolite-supported noble metal catalysts were prepared by impregnation method using noble metal chloride aqueous solutions and the amount of metal loading was 5 wt.-%. All catalysts were calcined at 500°C for 4 h in air and were reduced at 450°C for 1 h prior to the reaction. XRD analysis of the catalysts was carried out by using Rigaku diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Catalytic activities of noble metals supported on USY

In the previous paper [6], it was revealed that USY showed the highest activity in the cracking of thiophene over H-zeolites such as USY, H-Y, H-mordenite and H-ZSM-5, in which the strong Brønsted acid site of USY acts as active site for the cleavage of C–S bond in thiophene molecule and USY is the most suitable support for metal/zeolite catalysts in the hydrodesulfurization of thiophene. The catalytic activities of various noble metals supported on USY for the hydrodesulfurization of thiophene were, thus, examined at 400°C by using a fixed bed flow reactor.

Fig. 1 shows the hydrodesulfurization of thiophene over various noble metal/USY catalysts at 400°C. It was found that the catalytic activities of noble metal/USY were remarkably changed by the kind of noble metals and the order of the activities of these catalysts for the hydrodesulfurization of thiophene was as follows; Pt/USY > Rh/USY > Pd/USY ≫ Ru/USY.

The initial activities of Pt/USY, Rh/USY and Pd/USY were higher than that of Co-Mo/Al_2O_3 catalyst. It was revealed that Pt/USY showed the highest activity and relatively long catalyst life among these noble metal/USY catalysts. These results indicate that Pt/USY catalyst has both high hydrogenating ability and Brønsted acidity, which are necessary for the hydrodesulfurization of thiophene to

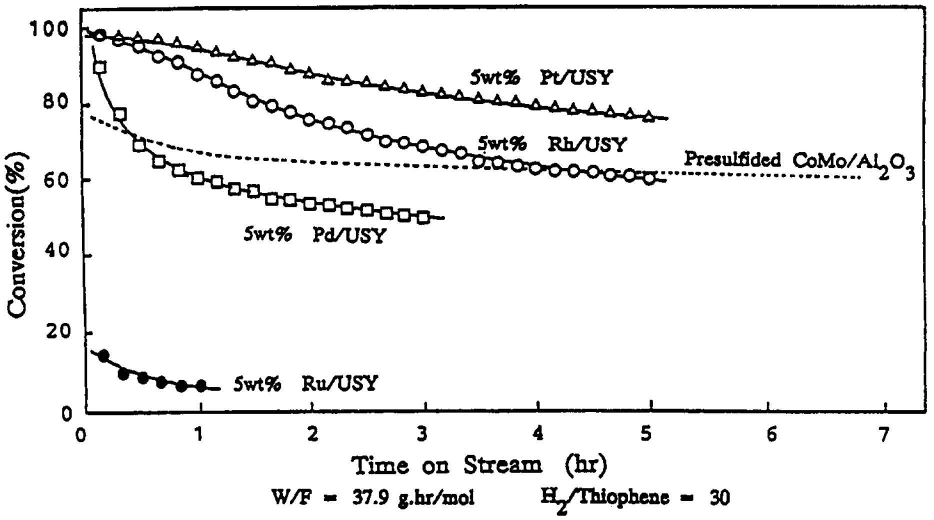


Fig. 1. Hydrodesulfurization of thiophene over noble metal/USY catalysts at 400°C.

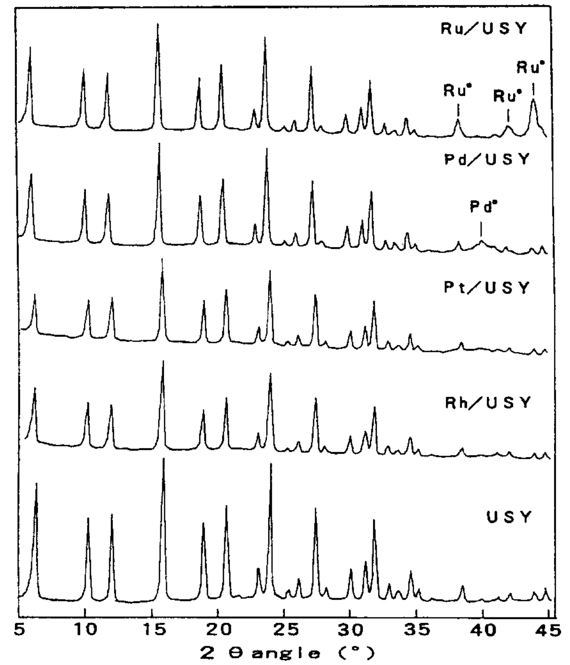


Fig. 2. XRD patterns for various noble metal/USY catalysts reduced at 450°C for 1 h.

proceed smoothly. On the other hand, it was found that the catalytic activities of transition metals supported on USY such as Ni/USY, Co/USY, Fe/USY, Mo/USY (5 wt.-% loading), 15 wt.-% Mo/USY, 5 wt.-% Ni–15 wt.-% Mo/USY and 5 wt.-% Co–15 wt.-% Mo/USY were lower than that of Co–Mo/Al_2O_3 catalyst. These results indicate that the hydrogenating abilities of these transition metals and their mixtures are insufficient.

On the other hand, no peaks of Pt and Rh metals were observed but large peaks of Ru metal and small peak of Pd metal were observed in the XRD analysis of reduced noble metal/USY catalysts as shown in Fig. 2. These results indicate that Ru/USY has the lowest dispersion and the order of the dispersion of noble metals on USY is assumed to be Pt/USY = Rh/USY > Pd/USY ≫ Ru/USY. This order is consistent with that of the initial activity and catalyst stability of noble metal/USY catalysts in the hydrodesulfurization of thiophene. Thus, it is very important to prepare noble metal/USY catalysts with high dispersion noble metal in order to maintain high and stable activity for the hydrodesulfurization reaction.

3.2. *Catalytic activities of bimetallic noble metal / USY*

It was revealed that Pt/USY showed high catalytic activity for the hydrodesulfurization of thiophene but the catalytic activity of Pt/USY in the hydrodesulfurization of thiophene de-

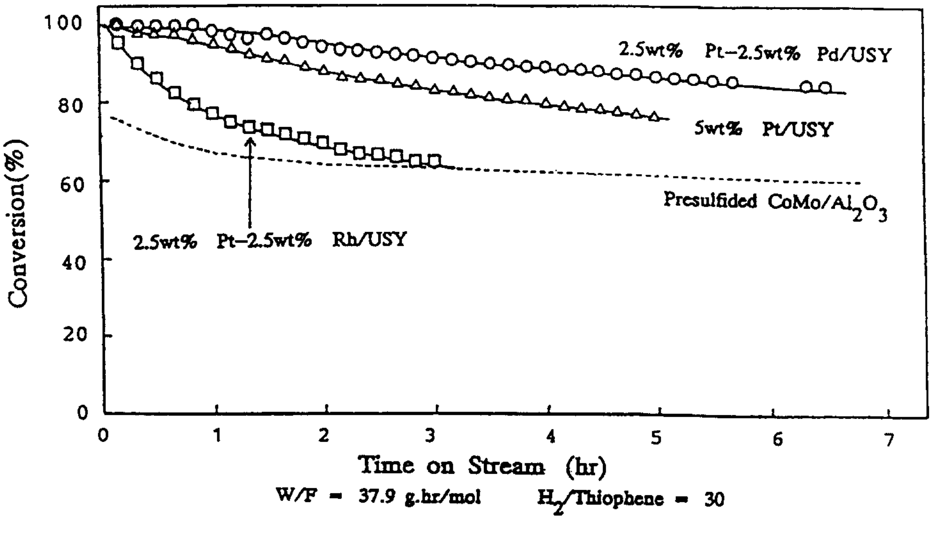


Fig. 3. Hydrodesulfurization of thiophene over bimetallic noble metal/USY catalysts at 400°C.

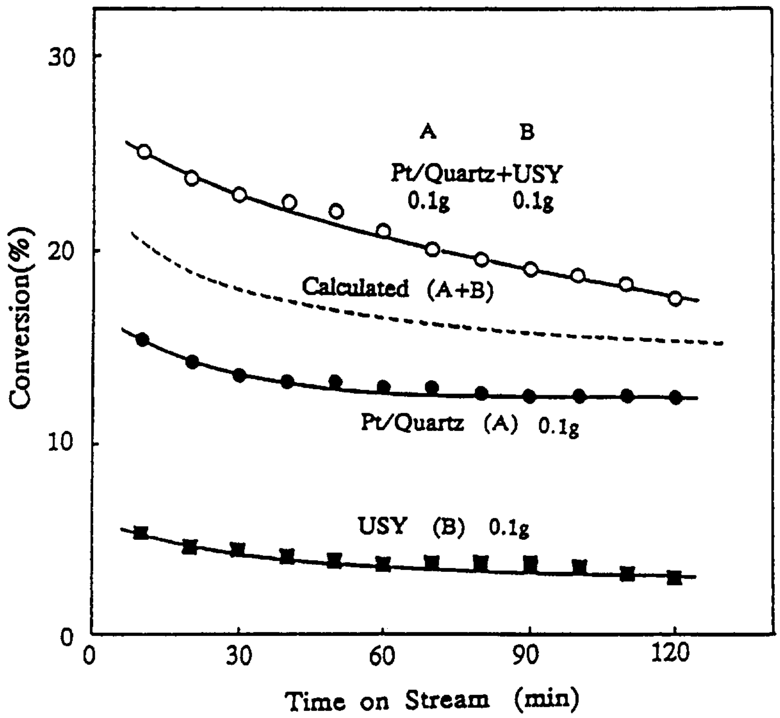
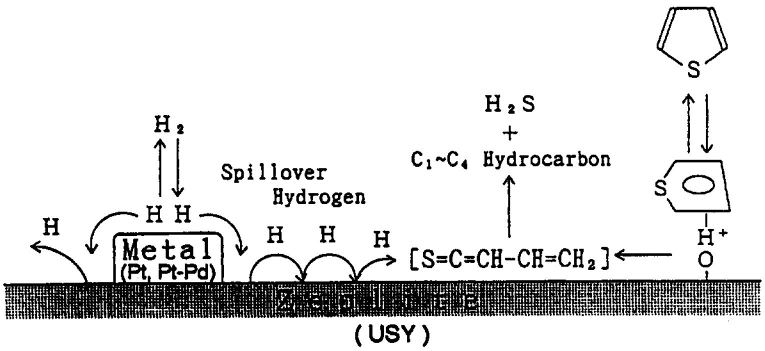


Fig. 4. Hydrodesulfurization of thiophene over Pt/quartz (A), USY (B) and mechanically mixed (Pt/quartz (A) + USY (B)) catalysts at 400°C.

creased gradually with the reaction time as shown in Fig. 1. We tried to enhance the hydrogenating ability of Pt on USY by combinating Pt with Pd and Rh in order to improve the catalyst deactivation of Pt/USY. It was found that the combination of Pt with Pd on USY was effective and Pt–Pd/USY catalyst showed higher and more stable activity than Pt/USY and Co–Mo/Al_2O_3 catalysts in the hydrodesulfurization of thiophene as shown in Fig. 3. This may be attributed to the increase of the hydrogenating ability of Pt by the combination with Pd. However, it was not evident from the XRD analysis of reduced Pt–Pd/USY catalyst whether Pt and Pd on USY form alloys or not.

3.3. Mechanism of hydrodesulfurization of thiophene on Pt / USY and Pt–Pd / USY catalysts

It was revealed that Pt/USY and Pt–Pd/USY showed higher catalytic activity than commercial Co–Mo/Al_2O_3 catalyst in the hy-



Scheme 1. A possible mechanism for the hydrodesulfurization of thiophene over Pt/USY and Pt–Pd/USY catalysts.

drodesulfurization of thiophene. We also studied the mechanism of hydrodesulfurization of thiophene over Pt/USY and Pt–Pd/USY catalysts. As mentioned above, the strong Brønsted acid site of USY in Pt/USY and Pt–Pd/USY catalysts plays an important role for the hydrodesulfurization of thiophene. That is to say, it is assumed that the Brønsted acid site of USY in Pt/USY and Pt–Pd/USY catalyst acts as active site for the activation of thiophene, whereas Pt or Pt–Pd bimetal particles on USY act as active site for the activation of hydrogen in the hydrodesulfurization of thiophene. In other words, Pt/USY and Pt–Pd/USY catalysts behave as bifunctional catalyst in the hydrodesulfurization of thiophene. Furthermore, it was supposed the existence of spillover hydrogen in the hydrodesulfurization of thiophene over Pt/USY and Pt–Pd/USY catalysts. Hence, we tried to confirm the existence of spillover hydrogen in the hydrodesulfurization of thiophene over Pt/USY catalyst. The catalytic activity of Pt/SiO_2 (quartz) mechanically mixed with USY in the hydrodesulfurization of thiophene was examined. It was found that the activity of mixed catalyst obtained experimentally was higher than that of the calculated one as shown in Fig. 4.

This implies that there exists spillover hydrogen on Pt/USY in the hydrodesulfurization of thiophene. Therefore, we propose a possible mechanism for the hydrodesulfurization of thiophene over Pt/USY and Pt–Pd/USY catalysts as shown in Scheme 1. In the proposed mechanism, thiophene is adsorbed on the Brønsted acid site of USY and hydrogen is activated on Pt or Pt–Pd bimetals to form spillover hydrogen. The spillover hydrogen formed on Pt or Pt–Pd particles attacks the reaction intermediate like $S=C=CH-CH=CH_2$, which is formed on the strong Brønsted acid site of the zeolite [4].

On the basis of the proposed mechanism, it would be possible to develop much more highly active zeolite-based hydrodesulfurization catalysts for petroleum feedstocks.

4. Conclusion

It was found that the Pt–Pd/USY catalyst showed high and stable activity for the hydrodesulfurization of thiophene. Therefore, it is concluded that there is a possibility of using Pt–Pd/USY as a new hydrodesulfurization catalyst for the petroleum feedstocks.

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