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Hydrodesulfurization over noble metals supported on ZSM-5 zeolites

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Abstract

Pt/HZSM-5 showed high and stable catalytic activity for the hydrodesulfurization of thiophene at 400°C and its catalytic activity was higher than that of commercial CoMo/Al₂O₃ catalyst. Pt/HZSM-5 zeolite was not poisoned by hydrogen sulfide in the hydrodesulfurization of thiophene and hydrocracking of hydrocarbons. The catalytic activity of Pt/HZSM-5 decreased with increase of SiO₂/Al₂O₃ ratio in HZSM-5. The Brønsted acid site of HZSM-5 and spillover hydrogen formed on Pt particle in Pt/HZSM-5 catalyst play an important role for the hydrodesulfurization of thiophene. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulfurization; Noble metals; ZSM-5 zeolite; Pt/HZSM-5 catalyst

1. Introduction

Hydrodesulfurization of petroleum feedstocks is one of the important processes in the petroleum industry to produce clean fuels. The CoMo/Al₂O₃ catalyst has been widely used. Recently, the need for fuels of lower sulfur content due to the serious problems of global-scale air pollution by burning petroleum feedstocks initiated the development of new hydrodesulfurization catalysts, which are of higher activity than commercial CoMo/Al₂O₃ [1–3].

It has been accepted that metal-zeolite catalysts have high possibility as new hydrodesulfurization catalysts for petroleum [4–8]. We have studied the catalytic activities of metal-zeolites and related materials such as MeY [9], MoS₂/MeY [10], Rh–Na/USY

[11,12], Pt–Pd/USY [13], Pt/HZSM-5 [14], Pt/Mesoporous silicate (FSM-16) [15] and Rh/Pillared clay (PIL-C) [16]. These metal-zeolites and related materials, especially noble metals supported on zeolites, mesoporous silicate and pillared clay, showed higher catalytic activity for the hydrodesulfurization of thiophene than commercial CoMo/Al₂O₃ catalyst and they have some possibilities for application as second generation highly active hydrodesulfurization catalysts for petroleum feedstocks. However, there are many unclarified issues concerning the catalytic properties and performances of metal-zeolites and related materials in the hydrodesulfurization of organic sulfur compounds.

In the present work, we studied in detail the catalytic performance of noble metals (Pt, Rh, Pd, Ru) supported on ZSM-5 zeolites for the hydrodesulfurization of thiophene in order to develop more highly active zeolite-based hydrodesulfurization catalysts.

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2. Experimental

Hydrosulfurization of thiophene over various noble metal/ZSM-5 catalyst (cat. wt.=0.1 g) was carried out at 400°C at 1 atm using conventional fixed-bed flow reactor. Thiophene was introduced into the reactor with flowing hydrogen (30 ml/min) saturated by thiophene at 0°C. The reaction products were analyzed by gas-chromatography. The hydrocracking of hexanes and benzene over noble metal/HZSM-5 catalysts (cat. wt.=0.05 g) was performed at 400°C with similar method to thiophene hydrosulfurization. The infrared spectra of thiophene adsorbed on HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3=22$) were observed at room temperature by using an in situ IR cell. Twenty Torr of thiophene was introduced into the cell at room temperature followed by evacuation at the same temperature for 30 min.

ZSM-5($\text{SiO}_2/\text{Al}_2\text{O}_3=22$ 100 and 1200)-supported noble metal catalysts were prepared by the impregnation method using aqueous noble metal chloride solutions. 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 under hydrogen stream (30 ml/min) for 1 h prior to use. HZSM-5 zeolites

were prepared by ion-exchange of NaZSM-5 with 1 N HCl aqueous solution. NaZSM-5 zeolites used in this work were provided by Tosoh ($\text{SiO}_2/\text{Al}_2\text{O}_3=22$) and Mizusawa Industrial ($\text{SiO}_2/\text{Al}_2\text{O}_3=100$ and 1200). Commercially available CoMo/ Al_2O_3 catalyst was used to obtain the standard activity of industrial hydrosulfurization catalyst. Presulfiding of the catalysts was carried out at 400°C for 1 h with 5 vol% $\text{H}_2\text{S}-\text{H}_2$ mixture after reduction at 450°C.

3. Results and discussion

3.1. Activities of noble metal/ZSM-5 zeolite catalysts

The catalytic activity of various noble metals supported on NaZSM-5 and HZSM-5 zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3=22$) in the hydrosulfurization of thiophene was examined at 400°C. Fig. 1 shows the hydrosulfurization of thiophene over various noble metals supported on NaZSM-5 catalysts. The activities of noble metal/NaZSM-5 catalysts were markedly changed by the kind of noble metals and the order of the

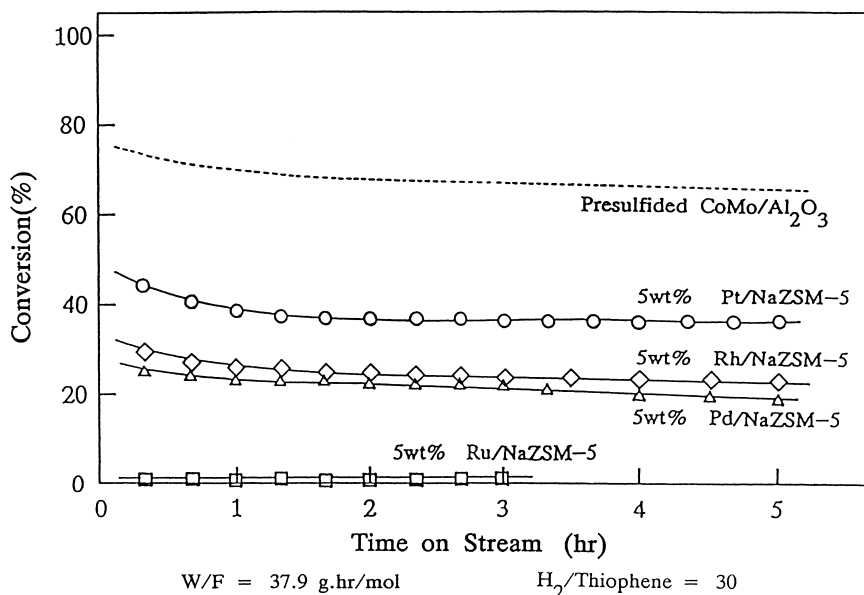


Fig. 1. Hydrosulfurization of thiophene over noble metal/NaZSM-5 catalysts at 400°C.

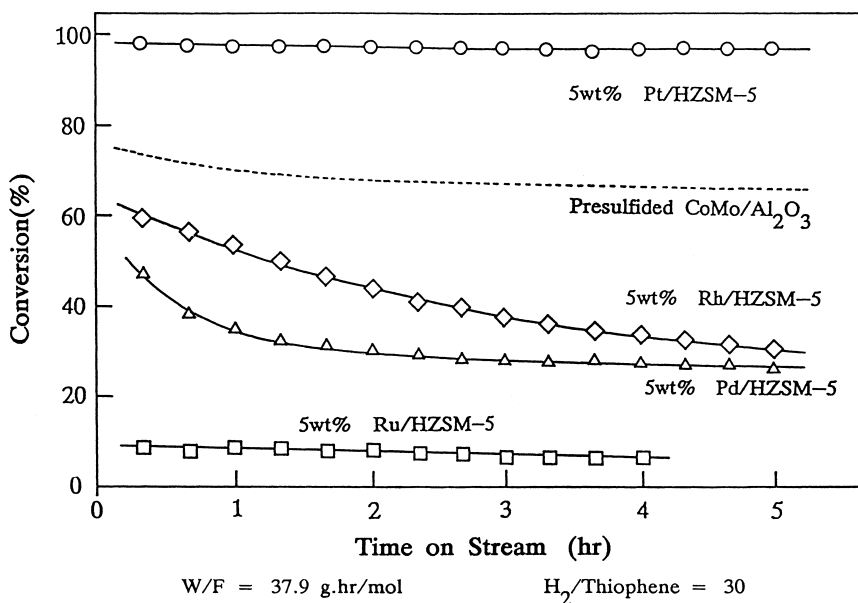


Fig. 2. Hydrodesulfurization of thiophene over noble metal/HZSM-5 catalysts at 400°C.

catalytic activities of noble metal/NaZSM-5 catalysts was as follows:

Pt/NaZSM-5 > Rh/NaZSM-5 > Pd/NaZSM-5
> Ru/NaZSM-5

Pt/NaZSM-5 showed the highest activity but it was lower than that of commercial CoMo/Al₂O₃ catalyst (dotted line).

In the hydrodesulfurization of thiophene over various noble metal/HZSM-5 catalysts, it was found that the order of the catalytic activities of noble metal/HZSM-5 corresponded to that found with NaZSM-5. Pt/HZSM-5 catalyst showed high and stable activity as shown in Fig. 2. The high and stable activity of Pt/HZSM-5 catalyst in the hydrodesulfurization of thiophene was kept even after it had reacted for 20 h. The activity of Pt/HZSM-5 catalyst was higher than that of CoMo/Al₂O₃ catalyst as shown in Fig. 2. The high and stable activity (conversion=ca.95%) of Pt/HZSM-5 catalyst in the hydrodesulfurization of thiophene was obtained even in the half contact time (W/F=19.0 g h/mol) (see Fig. 5).

The reaction products in the hydrodesulfurization of thiophene over Pt/HZSM-5 catalyst were hydrogen sulfide, C₂–C₄ hydrocarbons (C₂ 10%, C₃ 40% and C₄

50%) and small amount of C₁ and C₅⁺ hydrocarbons. These results indicate that Pt/HZSM-5 catalyst have both high activities for the hydrodesulfurization of organic sulfur compounds and hydrocracking of hydrocarbons.

Furthermore, the effect of SiO₂/Al₂O₃ ratios of HZSM-5 on the catalytic activity of Pt/HZSM-5 in the hydrodesulfurization of thiophene was examined in order to develop much more highly active Pt/HZSM-5 catalysts. Fig. 3 shows the conversions of thiophene after 2 h over Pt/HZSM-5 with different SiO₂/Al₂O₃ ratios. Activities of Pt/NaZSM-5 catalyst were also shown. It was found that the catalytic activity of Pt/NaZSM-5 was almost independent of SiO₂/Al₂O₃ ratios but the activity of Pt/HZSM-5 decreased with increasing SiO₂/Al₂O₃ ratio in HZSM-5 as shown in Fig. 3, suggesting that the number of acid sites of HZSM-5 decreases with increase of the SiO₂/Al₂O₃ ratio. Pt/HZSM-5 catalysts with low SiO₂/Al₂O₃ ratio (22) showed stable activity in the hydrodesulfurization of thiophene as shown in Fig. 2. However, the activity of Pt/HZSM-5 catalyst with high SiO₂/Al₂O₃ ratios (100 and 1200) decreased gradually with reaction time and then attained the constant activity as shown in Fig. 4, probably due to the coke formation by higher acid strength of these

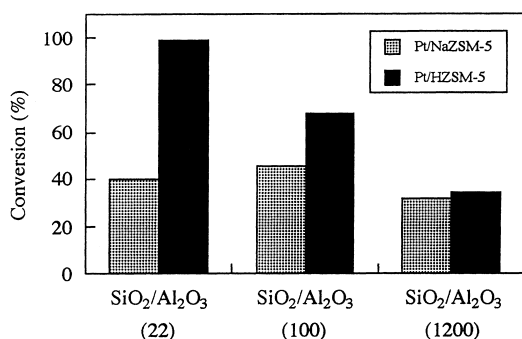


Fig. 3. Effect of SiO₂/Al₂O₃ ratio of ZSM-5 on the catalytic activities of Pt/ZSM-5 in the hydrodesulfurization of thiophene at 400°C.

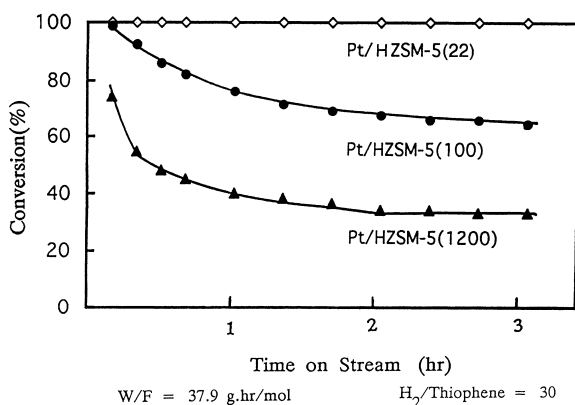


Fig. 4. Hydrodesulfurization of thiophene over Pt/HZSM-5 catalyst with different SiO₂/Al₂O₃ ratio.

catalysts with high SiO₂/Al₂O₃ ratio than the catalyst with low SiO₂/Al₂O₃ ratio.

3.2. Catalytic properties of Pt/HZSM-5

It was found that Pt/HZSM-5 (SiO₂/Al₂O₃=22) catalyst showed remarkable high and stable activity for the hydrodesulfurization of thiophene in comparison with other noble metal/HZSM-5 catalysts. The effect of sulfiding with H₂S on the catalytic activity of noble metal/HZSM-5 in the hydrodesulfurization of thiophene and hydrocracking of benzene and cyclohexane was examined in order to learn more about the origin of high and stable catalytic activity of Pt/HZSM-5.

Fig. 5 shows the effect of presulfiding of Pt/HZSM-5 on the catalytic activity in the hydrodesulfurization of thiophene over Pt/HZSM-5 catalysts. Presulfiding of Pt/HZSM-5 catalyst was performed by the same method as for CoMo/Al₂O₃ catalyst. In Fig. 5, effect of presulfiding of Pd/HZSM-5 and Ru/HZSM-5 was also indicated. It was revealed that high and stable activity of the Pt/HZSM-5 catalyst was hardly affected even by the presulfiding with hydrogen sulfide but the activities of Pd/HZSM-5 and Ru/HZSM-5 catalysts decreased. The activity of Rh/HZSM-5 catalyst was enhanced by presulfiding but the enhanced activity of Rh/HZSM-5 catalyst decreased with time on stream as shown in Fig. 6. This suggests that Rh on HZSM-5 is changed into active rhodium sulfide species like Rh₂S₃ [17] for hydrodesulfurization by presulfiding with H₂S and the initial activity of Rh/HZSM-5 catalyst increased by presulfiding treatment. However, the hydrogenating activity of rhodium sulfide species formed on HZSM-5 for the precursor of carbonaceous deposit, which is formed on the strong Brønsted acid site of HZSM-5 and it causes the catalyst deactivation, is not sufficient.

Fig. 7 shows the effect of introduction of H₂S (10 ml) on the hydrocracking of benzene over various noble metal/HZSM-5 catalysts. It was found 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 regained almost its original activity with time on stream as shown in Fig. 7. Before introduction of H₂S, various low molecular weight hydrocarbons were formed in the hydrocracking of benzene on noble metal/HZSM-5 catalysts. However, the reaction product in benzene hydrocracking on Pt/HZSM-5 after introduction of H₂S was mainly cyclohexane. These results suggest that the metallic state of platinum is present on HZSM-5 before sulfiding and the catalyst has high hydrocracking ability for benzene molecule. However, hydrocracking activity of Pt/HZSM-5 catalyst is weakened by the introduction of H₂S but Pt/HZSM-5 catalyst does not lose the hydrogenating ability, i.e., ability of dissociation of hydrogen, even after the introduction of H₂S. For other noble metal/HZSM-5 catalysts, both hydrocracking and hydrogenating activities of noble metals on HZSM-5 are strongly depressed by the introduction of H₂S. Furthermore,

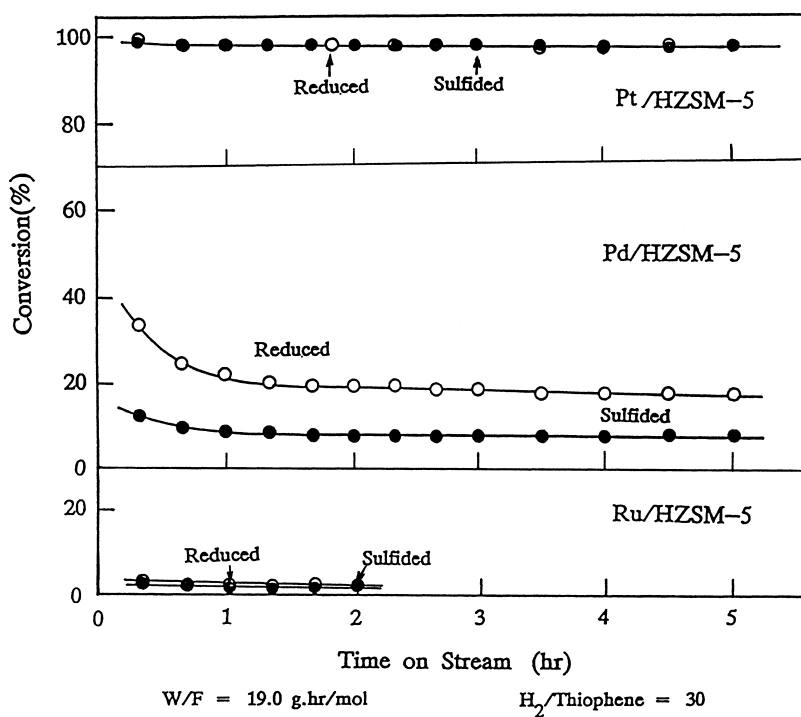


Fig. 5. Effect of presulfiding by hydrogen sulfide on the hydrodesulfurization of thiophene over Pt/HZSM-5, Pd/HZSM-5 and Ru/HZSM-5 catalysts at 400°C.

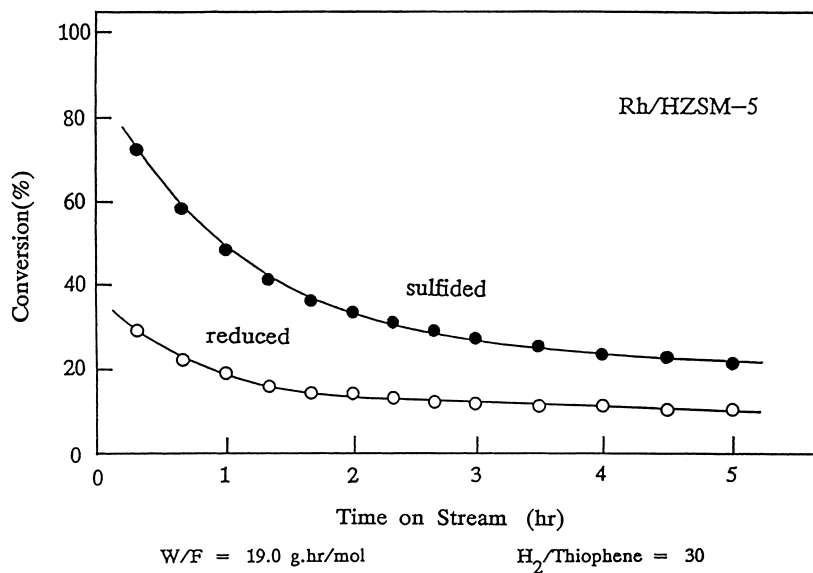


Fig. 6. Effect of presulfiding by hydrogen sulfide on the hydrodesulfurization of thiophene over Rh/HZSM-5 catalyst at 400°C.

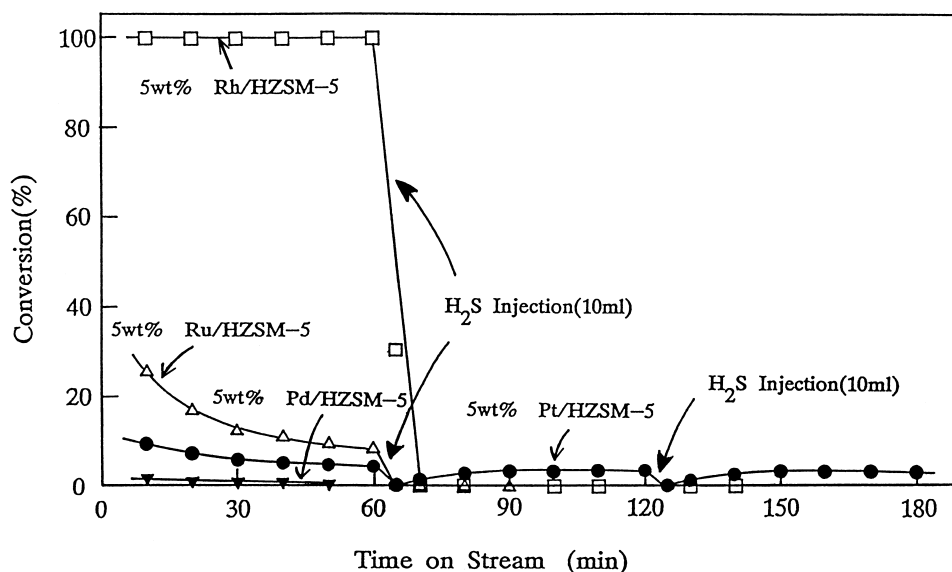


Fig. 7. Effect of introduction of hydrogen sulfide on the hydrocracking of benzene over noble metal/HZSM-5 catalysts at 400°C.

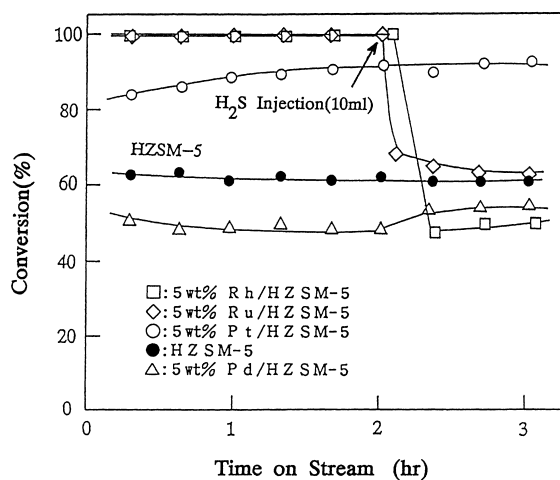


Fig. 8. Effect of introduction of hydrogen sulfide on the hydrocracking of cyclohexane over noble metal/HZSM-5 catalysts at 400°C.

the hydrocracking of cyclohexane over Pt/HZSM-5 catalyst at 400°C was not poisoned by the introduction of H₂S but that over Rh/HZSM-5 and Ru/HZSM-5 catalysts were remarkably poisoned by H₂S and their activities after introduction of H₂S decreased to similar activity level of HZSM-5 as shown in Fig. 8. Almost the same results as the hydrocracking of

cyclohexane were obtained in the hydrocracking of *n*-hexane over noble metal/HZSM-5 catalysts at 400°C [18].

These results indicate that the interaction of hydrogen sulfide and platinum on the HZSM-5 is not so strong. Thus, the ability of dissociation of hydrogen of platinum is easily regenerated by the hydrogen stream during the hydrodesulfurization reaction. By these reasons, Pt/HZSM-5 catalyst shows high and stable activity for the hydrodesulfurization of thiophene and Pt/HZSM-5 catalyst has high sulfur tolerant property in the hydrocracking of hydrocarbons.

3.3. Mechanism of hydrodesulfurization of thiophene on Pt/HZSM-5 catalyst

Pt/HZSM-5 showed higher catalytic activity than commercial CoMo/Al₂O₃ catalyst in the hydrodesulfurization. We also studied the mechanism of hydrodesulfurization of thiophene over Pt/HZSM-5 catalyst.

As mentioned above, Pt/HZSM-5 showed higher activity than Pt/NaZSM-5 in the hydrodesulfurization of thiophene. This indicates that the Brønsted acid sites of HZSM-5 in Pt/HZSM-5 catalyst play an important role for the hydrodesulfurization of thiophene. In the infrared spectra of thiophene adsorbed on HZSM-5 (SiO₂/Al₂O₃=22), it was revealed that the

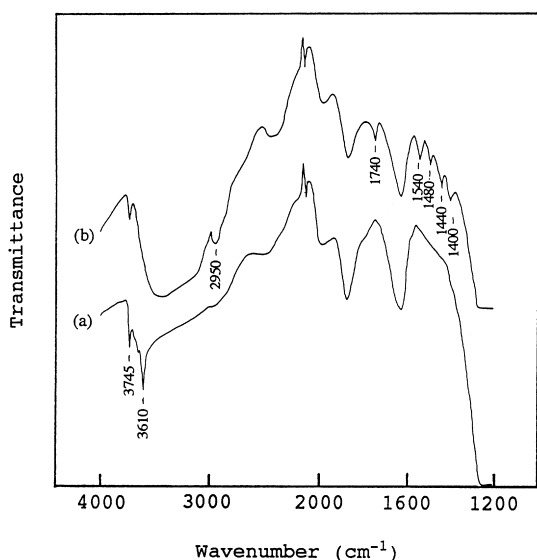


Fig. 9. Infrared spectra of thiophene adsorbed on HZSM-5 zeolite: (a) background of HZSM-5 evacuated at 500°C for 2 h; (b) thiophene adsorption (20 Torr) at room temperature followed by evacuation at room temperature.

thiophene molecule is adsorbed on HZSM-5 with strong interaction to acidic hydroxyl groups at 3610 cm^{-1} , i.e., the Brønsted acid site, as shown in Fig. 9. It can be, thus, assumed that the Brønsted acid site in the Pt/HZSM-5 catalyst is one active site for the activation of thiophene, whereas Pt is an active site for the activation of hydrogen. In other words, Pt/HZSM-5 catalyst is a bifunctional catalyst for the hydrodesulfurization of thiophene, in which both Brønsted acid and platinum metal sites are active sites.

Further, participation of spillover hydrogen in the hydrodesulfurization of thiophene over Pt/HZSM-5 catalyst was also assumed. It was found that catalytic activity of Pt/SiO₂ (quartz) mixed mechanically with HZSM-5 was higher than that obtained by simple addition of the results for pure components as shown in Fig. 10. This implies that spillover hydrogen on Pt/HZSM-5 mainly participates in the hydrodesulfurization of thiophene.

On the basis of these results, we propose a possible mechanism for the hydrodesulfurization of thiophene over Pt/HZSM-5 catalyst as shown in Scheme 1.

In this mechanism, thiophene is adsorbed on Brønsted acid site of Pt/HZSM-5 and hydrogen is activated on Pt to form spillover hydrogen. The spil-

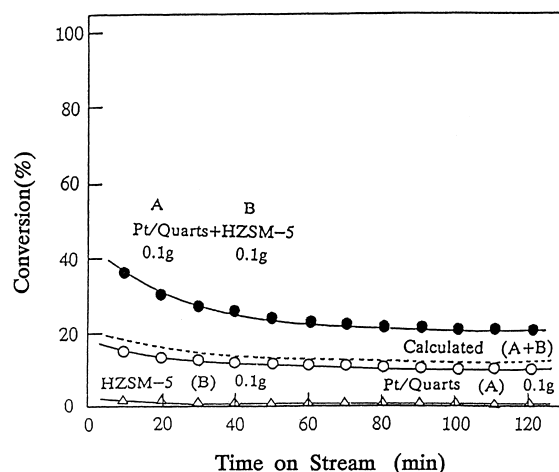
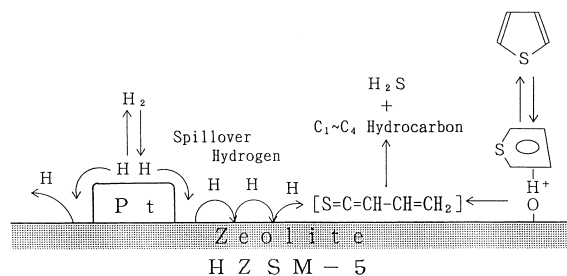


Fig. 10. Hydrodesulfurization of thiophene over Pt/quartz(A), HZSM-5(B) and mechanically mixed (Pt/quartz(A)+HZSM-5(B)) catalysts at 400°C.



Scheme 1. The possible mechanism of thiophene hydrodesulfurization over Pt/HZSM-5 catalyst.

lover hydrogen formed on Pt attacks the reaction intermediate such as $[S=C-CH-CH=CH_2]$, which is formed by the decomposition of thiophene adsorbed on the strong Brønsted acid site of H-zeolites [9].

4. Conclusion

It was revealed that Pt/HZSM-5 showed higher catalytic activity than commercial CoMo/Al₂O₃ in the hydrodesulfurization of thiophene. Therefore, there is a possibility for using Pt/HZSM-5 as highly active second generation hydrodesulfurization catalyst for petroleum feedstocks. The pore diameter (5.6 Å) of HZSM-5 is not sufficient for the hydro-

desulfurization of organic sulfur compounds with large molecular diameter. However, on the basis of the proposed mechanism, there are some possibilities to develop much more highly active zeolite-based hydrodesulfurization catalysts for large organic sulfur compounds using some other zeolites and related materials which have much more larger pore diameter and cages like mesoporous silicates and pillared clays.

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