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Effects of the Proton Content of ZSM-5 and the Amount of Pt on the Hydrodesulfurization Activity of Pt/ZSM-5

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The effects of the proton content of ZSM-5 and the amount of Pt on the hydrodesulfurization (HDS) activity of Pt/ZSM-5 were studied. The extent of proton exchange was shown to affect the reaction selectivity, the formation of aromatics, the cracking of hydrocarbons, and the dispersion of Pt. The HDS activity depended on the surface area of loaded Pt. A catalyst consisting of 5 wt% Pt supported on a 50% cation exchanged ZSM-5 gave a higher HDS activity than other tested catalysts and a small amount of cracking products.

In recent years, the problem of global environmental pollution has become a serious matter of concern. This has resulted in stringent regulations aimed at reducing the sulfur content of diesel oil, which is a major source of SO_x in the atmosphere in many countries. The concentration of sulfur in diesel oil would be further decreased in European countries. In view of these situations, the development of new highly active HDS catalysts would be required. Sulfur is contained in oils in the form of organosulfur compounds, which are converted into H_2S and hydrocarbons in the HDS process. Many papers concerning conventional HDS catalysts, such as $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, and NiW/Al_2O_3, have been published.[1–6]

On the other hand, new HDS catalysts which have a possibility to replace the conventional catalysts have also been studied.[7–10] We have reported that some metals supported on zeolites, mesoporous silicas, and pillared clays, such as MY (M = Co, Ni), Rh-Na/USY, Pt-Pd/USY, Pt/HZSM-5, Pt/FSM-16, and Rh/pillared montmorillonite,[11–18] have shown higher HDS activity than the conventional catalysts. In particular, Pt/HZSM-5 showed the highest and most stable activity for the HDS of thiophene.[15,18] In general, noble metals show higher HDS activity than transition metals when they are supported on zeolites and mesoporous silicas.

As mentioned above, Pt/HZSM-5 is one of the candidates for new HDS catalysts. However, the high cracking activity of Pt/HZSM-5 gives a large amount of short alkanes, mainly propane, in the HDS of thiophene.[18] It is undesirable that the gas component increases during the HDS process. The high cracking activity of Pt/HZSM-5 can be ascribed to the strong acidity of HZSM-5, because Pt supported on NaZSM-5, which has virtually no acid sites, fundamentally, showed higher C4 selectivity for the HDS of thiophene. On the other hand, the HDS activity depends on the dispersion of Pt, which are active sites for hydrogen. It has been pointed out that Pt is highly dispersed on acidic media. Indeed, low HDS activity was observed on Pt/NaZSM-5 due to a lower dispersion of Pt.[18] These results suggest that the support for Pt must have a necessary and sufficient number of acid sites in order to obtain high activity and selectivity.

In this study, the number of acid sites of ZSM-5 used as the support material of Pt was controlled by varying the extent of ion-exchange from the Na form to the proton form to obtain a HDS catalyst having low cracking activity and high C4 selectivity for the HDS of thiophene.

Usually, 4,6-Dimethyl-dibenzothiophene is used as a model compound for HDS and is well known to be difficult to desulfurize. It can, however, be desulfurized after hydrogenation of the benzene ring.[1,2] In the HDS step, it is converted into alkylthiophenes. The difference in the reactivities between alkylthiophene and thiophene without any alkyl substituent is attributed, basically, to a steric effect. Therefore, thiophene can be used as a model compound to evaluate the HDS activities of catalysts.[11–18]

Expermiental

The ion-exchange of NaZSM-5, provided by Tosoh Co. (SiO_2/Al_2O_3 = 22), was carried out using a specified concentration (0.001–1.0 mol dm^{-3}) of HCl solution. NaZSM-5 powder (1 g) was added to 200 cm^3 of a HCl solution and allowed to stand for 5 min, or 1 day, at room temperature. The solution was filtered by suction, washed with distilled water until a chloride test with $AgNO_3$ became negative, and then dried at room temperature for two or three days. Finally, the dried sample was calcined in air at 773 K for 4 hours.

The extent of ion-exchange from the Na form of ZSM-5 to the proton form, which is indicated as the proton-exchange ratio, was determined by atomic absorption spectrometry (AAS). For the AAS analysis, a calcined sample (0.1 g) was completely digested with a mixture of concentrated HCl (1 cm^3) and HF (3 cm^3), and then made up to volume in a 100 cm^3 Teflon volumetric flask.

Pt/ZSM-5 was prepared by a conventional impregnation method using an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$. Calcined ZSM-5 was added to a solution containing the desired amount of platinum, followed by evaporation of water by heating on a hot plate. After drying, the catalyst was calcined at 773 K for 4 hours in air using a glass ampoule; the sample was kept in a sealed glass ampoule until use.

The hydrodesulfurization of thiophene was carried out at 623 K under atmospheric pressure in a conventional fixed-bed reactor. A catalyst (0.1 g) was pretreated in a stream of helium at 773 K for 1 hour, followed by reduction with hydrogen at 723 K for 1 hour. Flowing hydrogen saturated by thiophene (purity 98%, Tokyo Kasei Kogyo Co., Ltd) at 273 K was introduced into the reactor. The flow rates of He and H_2 were 30 cm^3 min^{-1}. The purity of the feed gases was more than 99.9 vol%. Thiophene and the gases were used without further purification. Under these conditions, the H_2/thiophene molar ratio was 34.55 and W/F was 44.25 g h mol^{-1}.

The HDS of thiophene was also carried out over presulfided $CoMo/Al_2O_3$ (Japan Cyanamid Co.). $CoMo/Al_2O_3$ (0.1 g) was pretreated in a stream of helium at 773 K for 1 hour, followed by reduction with hydrogen at 723 K for 1 hour. The sulfiding of $CoMo/Al_2O_3$ was carried out at 673 K for 1 hour with a mixture of hydrogen sulfide and hydrogen (5 vol% of H_2S). The reaction products were analyzed by a gas chromatograph (GC) equipped with a 1 m column packed with Silicone DC-550 operated at 343 K. Since small hydrocarbons (C1–C4) gave a single peak in the analysis by Silicone DC-550, C1–C4 products were separated by GC using a 4 m column of Propylene carbonate operated at 273 K. The HDS activities were compared based on the catalysts' weight, as described later.

The temperature-programed desorption (TPD) spectra of ammonia adsorbed on the catalyst were observed by measuring the pressure of NH_3 with a pirani gauge in a vacuum line. Each sample (0.1 g) was evacuated at 773 K for 1 hour. In the case of Pt/ZSM-5, the sample was pretreated in a stream of helium at 773 K for 1 hour, followed by reduction with hydrogen at 723 K for 1 hour, and sulfiding at 623 K for 1 hour with a mixture of hydrogen sulfide and hydrogen (5 vol% of H_2S). The adsorption of NH_3 was carried out at 373 K for 45 min under 40 torr of NH_3 followed by sufficient evacuation at the same temperature. The TPD spectra were measured from 373 K to 823 K under the condition that the rate of heating was 10 K min^{-1}. The acid amount was measured from the peak area of the TPD spectra above 543 K.

The X-ray diffraction (XRD) of pretreated Pt/ZSM-5 was measured. The sample was pretreated in the same manner as that for the HDS of thiophene, described above. The pretreated sample was sealed and kept in a glass ampoule until the measurement. The measurement was performed using an X-ray diffractometer (Rigaku Co., Cu $K\alpha$, 40 kV, 20 mA).

The dispersion of platinum on the catalysts was determined by CO chemisorption using a conventional pulse flow method[19] (flow rate of He carrier gas, 25 cm^3 min^{-1}; pulse size, 0.53 cm^3 STP). The adsorption of CO was carried out at 298 K. The pretreatment of the catalyst was the same as that for the HDS of thiophene. Carbon monoxide (purity 99.9%) was injected repeatedly until CO chemisorption could not be observed. The effluent CO gas was detected by a thermal-conductivity detector. The amount of adsorbed CO was calculated from the difference between the amounts of CO injected and that of the effluent CO.

Results and Discussion

The HDS of thiophene was carried out over Pt/ZSM-5 (0–5 wt% Pt). The proton-exchange ratio of the support, ZSM-5, was 93%. The results are shown in Fig. 1. In HDS on Pt catalysts supported on acidic oxides, acid sites play an important role because thiophene is activated there and attacked by hydrogen activated on platinum.[13–16] It is assumed that the acid sites on catalysts act as active sites for the activation of thiophene. Furthermore, the existence of spillover hydrogen is supposed on the catalysts. It was found that hybrid catalysts prepared by the mechanical mixing of Pt/SiO_2 with the solid acid of FSM-16 showed higher activity for the HDS of thiophene than each catalyst.[16] It can be said that the HDS activity depends on both of the acidity and the hydrogen-activation ability. For this reason, the activities of catalysts are indicated by the unit of the amount of converted thiophene per weight of catalyst. Pt/ZSM-5, having platinum loading greater than 1 wt%, showed a higher HDS activity than presulfided $CoMo/Al_2O_3$. The HDS activity increased along with the increase in the amount of platinum until 5 wt%.

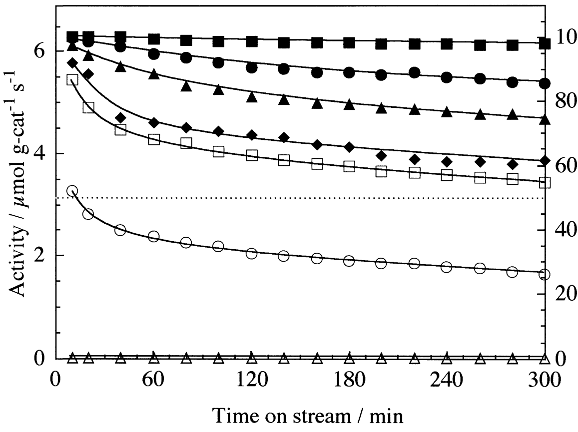

Fig. 1. Hydrodesulfurization of thiophene over Pt/ZSM-5 at 623 K, effect of the amount of loaded platinum. The proton-exchange ratio of ZSM-5 were 93% in all samples. Dotted line shows HDS activity of presulfided $CoMo/Al_2O_3$ in steady state. W/F = 44.25 g h mol^{-1}, H_2/thiophene = 34.55. ■ : 5 wt%, ●: 4 wt%, ▲ : 3 wt%, ◆ : 2 wt%, □ : 1 wt%, ○ : 0.5 wt%, △ : ZSM-5.

As shown in Table 1, the selectivities of toluene and xylenes, which were products of aromatization, decreased with increasing the amount of loading platinum. This suggests that the aromatization, which eventually achieves the formation of a carbon deposit,[20] was inhibited by loaded platinum. The activity for HDS in the steady state was higher when a larger amount of platinum was loaded. However, there was no significant effect on the inhibition of cracking.

Figure 2 shows the HDS of thiophene over some 5 wt% Pt/ZSM-5 based on a ZSM-5 support having various proton-exchange ratios. Pt/ZSM-5 having a high proton-exchange ratio (43% and 93%) showed a higher HDS activity.

Table 2 shows the effect of the proton-exchange ratio on the selectivity of the products in the HDS of thiophene. Catalysts having a low proton-exchange ratio (0% and 15%) showed high *n*-butane selectivity. In addition, the selectivities for cracking products and aromatics were lower on these catalysts, indicating that HDS progressed selectively on them. In contrast, the selectivity of propane was high on catalysts having a high proton-exchange ratio. In the actual HDS process, apart

Table 1. Product Disribution in HDS of Thiophene over Pt/ZSM-5, Effect of the Amount of Pt

Amount of Pt/wt%	0	0.5	1	2	3	4	5
Conversion/%	1.4	32.6	63.4	69.4	81.5	90.6	98.5
Activity/μmol g-cat^{-1} s^{-1}	0.09	2.05	3.95	4.36	5.12	5.69	6.18
TOF/s^{-1}	—	0.36	0.60	0.15	0.24	0.12	0.11
Selectivity/wt%							
Methane	0.0	0.2	0.3	0.3	0.3	0.3	0.3
Ethane	0.0	5.4	5.5	5.3	5.0	3.9	3.5
Ethene	6.8	0.0	0.0	0.0	0.0	0.0	0.0
Propane	1.2	18.8	25.1	25.3	28.2	30.4	28.4
Propene, isobutane	22.3	7.5	4.6	5.3	4.2	3.7	3.9
n-Butane	0.4	15.6	17.8	19.6	24.1	36.3	39.5
1-Butene	0.6	0.5	0.4	0.4	0.3	0.2	0.1
Isobutene	8.4	3.2	2.3	2.6	2.1	2.0	1.9
trans-2-Butene	2.6	1.3	0.8	0.5	1.6	0.4	0.1
cis-2-Butene	0.6	0.9	0.4	0.5	0.3	0.2	0.0
Pentanes	0.0	1.7	4.9	5.3	5.8	8.8	9.8
n-Hexane	0.0	0.7	0.9	1.0	1.0	1.4	1.3
Cyclohexane	0.0	0.5	0.1	0.0	0.1	0.0	0.0
n-Decane	0.0	1.4	1.7	1.6	1.3	0.0	0.0
Benzene	0.0	0.0	3.0	3.1	2.6	1.6	1.4
Toluene	8.1	12.0	15.2	13.5	10.8	5.2	4.8
m,p-Xylene	10.3	13.4	11.4	10.3	8.4	4.1	3.8
o-Xylene	0.0	2.9	2.4	2.2	1.9	0.7	0.7
Tetrahydrothiophene	0.0	1.9	0.8	1.2	0.5	0.0	0.0
Others	37.6	12.1	2.4	2.0	1.5	0.8	0.5

All data were obtained at 2h. Proton-exchange ratio of ZSM-5 were 93% in all samples. TOF was based on surface platinum (amount of CO absorbed).

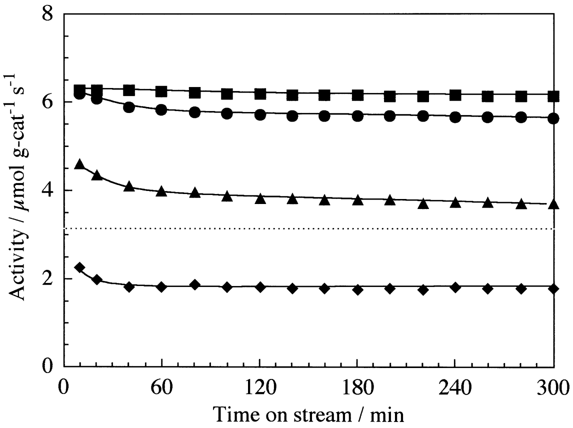

Fig. 2. Effect of proton-exchange ratio of ZSM-5 on HDS activity of thiophene over 5 wt% Pt/ZSM-5 at 623 K. Dotted line shows HDS activity of presulfided CoMo/Al_2O_3 in steady state. W/F = 44.25 g h mol^{-1}, H_2/thiophene = 34.55. ■ : 93 %, ● : 43 %, ▲ : 15 %, ◆ : 0 %.

from the organosulfur components, many other hydrocarbons come into contact with the HDS catalyst. Therefore, catalysts with a low cracking ability are preferred as HDS catalysts for diesel oil. From this point of view, ZSM-5 with a low proton-exchange ratio is favorable as the support for platinum in the Pt/ZSM-5 HDS catalyst system.

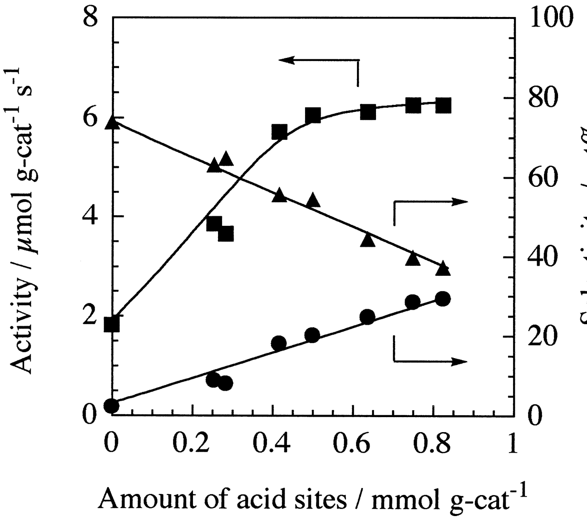

Fig. 3. Effect of acid amount of the support ZSM-5 on HDS activity and selectivity of 5 wt% Pt/ZSM-5. All data were obtained at 2 h. Amounts of acid sites were measured based on NH_3–TPD spectra. ■ : Activity, ● : Selectivity of propane, ▲ : Selectivity of *n*-butane.

Figure 3 shows the effect of acid amount on the HDS activity and the product selectivity. High HDS activity over 6.00 μmol g-cat^{-1} s^{-1}, close to 100% conversion, was maintained when the number of acid sites was 0.5 mmol g-cat^{-1} (about

Table 2. Product Distribution in HDS of Thiophene over 5 wt% Pt/ZSM-5, Effect of the Proton-Exchange Ratio of ZSM-5

Proton-exchange ratio of ZSM-5/%	0	15	43	93
Conversion/%	28.9	58.1	91.0	98.5
Activity/μmol g-cat^{-1} s^{-1}	1.82	3.84	5.71	6.18
TOF/s^{-1}	0.18	0.21	0.10	0.11
Selectivity/wt%				
Methane	0.1	0.1	0.1	0.3
Ethane	0.1	0.4	1.2	3.5
Ethene	0.0	0.0	0.0	0.0
Propane	2.3	8.0	18.1	28.4
Propene, isobutane	1.1	2.1	3.3	3.9
n-Butane	73.9	64.7	55.5	39.5
1-Butene	3.5	1.8	0.3	0.1
Isobutene	1.1	3.1	2.3	1.9
trans-2-Butene	8.0	4.2	0.7	0.1
cis-2-Butene	5.3	2.4	0.2	0.0
Pentanes	0.0	5.9	11.3	9.8
n-Hexane	0.1	1.0	0.1	1.3
Cyclohexane	0.0	0.0	0.0	0.0
n-Decane	0.0	0.5	0.6	0.0
Benzene	0.0	0.0	0.2	1.4
Toluene	0.0	0.7	2.1	4.8
m,p-Xylene	0.0	1.2	2.1	3.8
o-Xylene	0.0	0.1	0.4	0.7
Tetrahydrothiophene	3.1	1.8	0.2	0.0
Others	1.4	2.0	1.3	0.5

All data were obtained at 2h. TOF was based on surface platinum (amount of CO absorbed).

50% of the proton-exchange ratio) or above. However, a rapid decrease of the activity was observed when the number of acid sites was below 0.5 mmol g-cat^{-1}. There was a tendency that the catalyst having a lower proton-exchange ratio provided a higher selectivity of *n*-butane in the hydrocarbon products. A linear relation was observed between the number of acid sites and the selectivity of propane, which is a typical cracking product. With a decrease in the number of acid sites, cracking after the formation of *n*-butane and butenes became more difficult to proceed. This result shows that the selectivity can be varied by controlling the proton-exchange ratio.

The variation in the number of acid sites had little effect on the thiophene HDS activity of Pt/HZSM-5 for 0.5 mmol g-cat^{-1} (about 50% of the proton-exchange ratio) or above. This indicates that strong acid sites corresponding to a proton-exchange above 50% were not necessary for the HDS of thiophene.

The number of acidic hydroxyl groups increased with increasing the proton-exchange ratio. It is known that the hydrogenation activity of platinum in close contact with strong acid sites is tolerant to sulfur poisoning.[21] Thus, it is desirable that the support material of platinum possess some acid sites. However, deactivation caused by the carbon deposit formed from aromatics takes place on strong acid sites. It can therefore be concluded that the presence of excess acid sites was undesirable.

The HDS proceeds on platinum supported on a weak solid acid, like FSM-16.[16] This indicates that the acid amount is an important property of the support. TPD using ammonia was performed to clarify the change in the acid amount of Pt/ZSM-5 by ion-exchange and platinum loading. The results are shown in Fig. 4 and 5. Two peaks were observed in the TPD

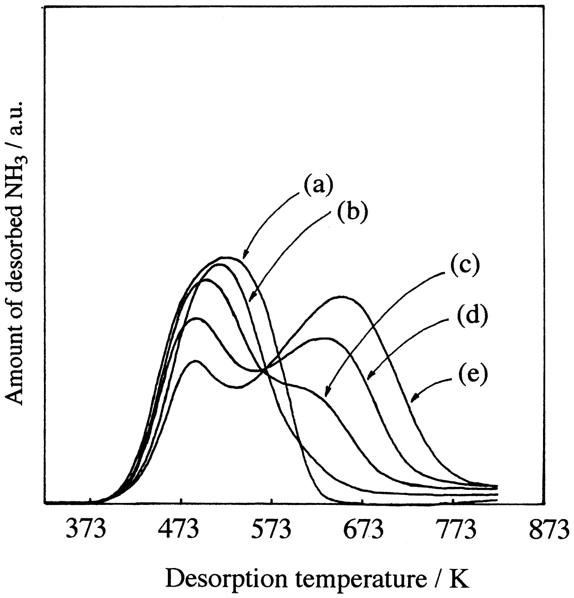

Fig. 4. Effect of proton-exchange ratio on NH$_3$–TPD spectra of ZSM-5. (a) 0%, (b) 15%, (c) 43%, (d) 61%, (e) 91%.

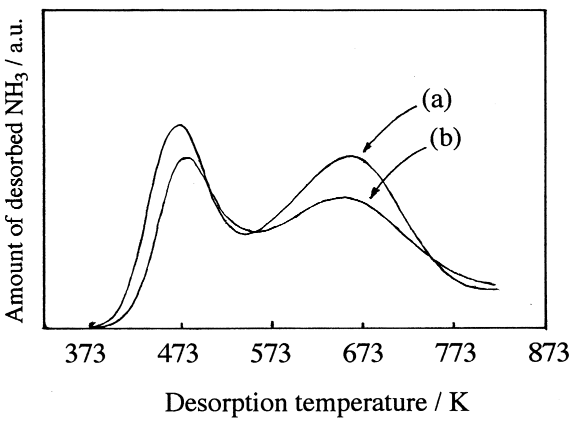

Fig. 5. Effect of platinum loading on NH_3–TPD spectra. (a) ZSM-5, (b) 5 wt% Pt/ZSM-5. Proton-exchange ratio of ZSM-5 was 93% each other. 5 wt% Pt/ZSM-5 was sulfided at 623 K for 1 hour.

spectra. The peak at around 460–560 K would be due to NH_3 adsorbed on NH_4^+ or Na^+ by hydrogen bonding. Earl et al. observed NH_3 adsorbed on NH_4^+ or Na^+ by a NMR study.[22] It has also been reported that such a peak disappeared upon a treatment with water.[23] The desorption of these NH_3 species does not have any relation to the acid sites. The peak at around 650–660 K corresponds to the desorption of ammonia from acid sites. The peak area increased along with an increase in the proton-exchange ratio. The loading of platinum provided a small decrease in the TPD peak area. Therefore, the acid amount remaining on Pt/ZSM-5, 5 wt% Pt supported on 50% proton-exchanged ZSM-5 is assumed to be less than 50% of the H-type ZSM-5. As previously stated, the HDS activity is determined by the amount of activated thiophene on acid sites and activated hydrogen. The amount of activated hydrogen is determined by the number of active sites of platinum. The acid amount remaining on Pt/ZSM-5, less than 50% of the H-type ZSM-5, would correspond to that of supplied activated hydrogen.

The HDS activity of Pt/ZSM-5 varied with the proton-exchange ratio. It is expected that the dispersion of loaded metal would be influenced by the state of the support. In order to clarify this, the effect of the proton-exchange ratio of the ZSM-5 on the platinum dispersion was investigated by means of the XRD technique and the chemisorption of carbon monoxide.

Figure 6 shows the XRD profiles of Pt/ZSM-5 having a proton-exchange ratio of 7%. It can be observed that the peak for the platinum of Pt/ZSM-5 after reduction as well as that after a reaction were larger than that of the calcined Pt/ZSM-5.

The platinum peaks of the reduced and used samples were much larger when the proton-exchange ratio of ZSM-5 was lower. In the case of a catalyst based on ZSM-5 with a higher exchange ratio, the peak intensity of platinum remained almost the same for all calcined, reduced and used samples (Fig. 7). This result indicates that the acidic hydroxyl groups on ZSM-5 played an important role to maintain the dispersion of platinum.

Figure 8 shows the effect of the acid amount of ZSM-5 on the amount of CO adsorbed on reduced Pt/ZSM-5. The platinum contents of all samples were 5 wt%. The Pt particle size, estimated by the amount of adsorbed CO, was larger than the pore diameter of ZSM-5 in all Pt/ZSM-5. Therefore, the Pt particles should be located mainly on the external surface of ZSM-5. The amount of CO adsorbed on the surface of Pt/ZSM-5 catalysts was almost equal when the number of acid sites was above 0.5 mmol g-cat^{-1} (about 50% of proton-ex-

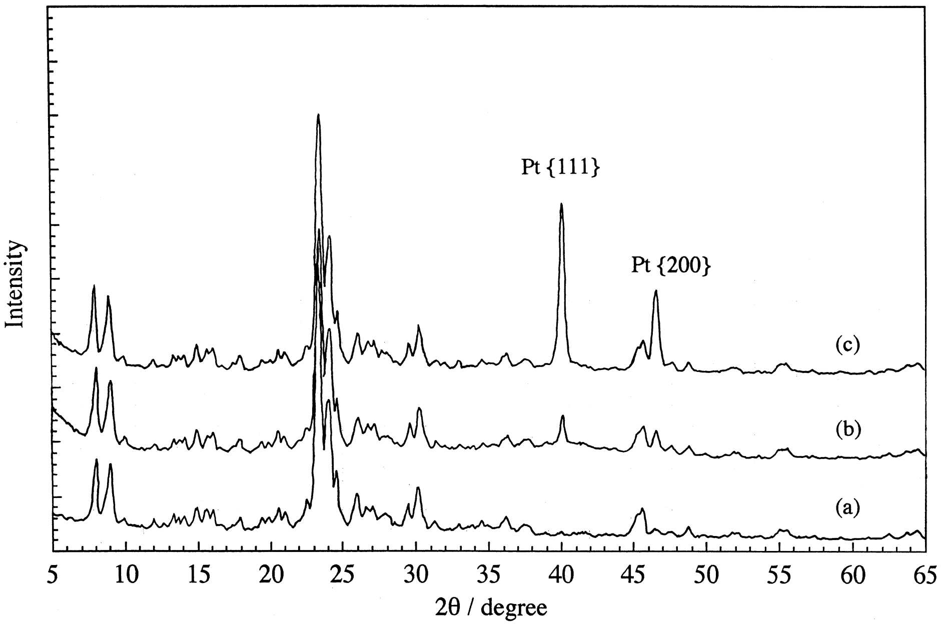

Fig. 6. XRD profiles of 5 wt% Pt/ZSM-5. Proton-exchange ratio of ZSM-5 was 7%. a) After calcination. b) After reduction. c) After reaction.

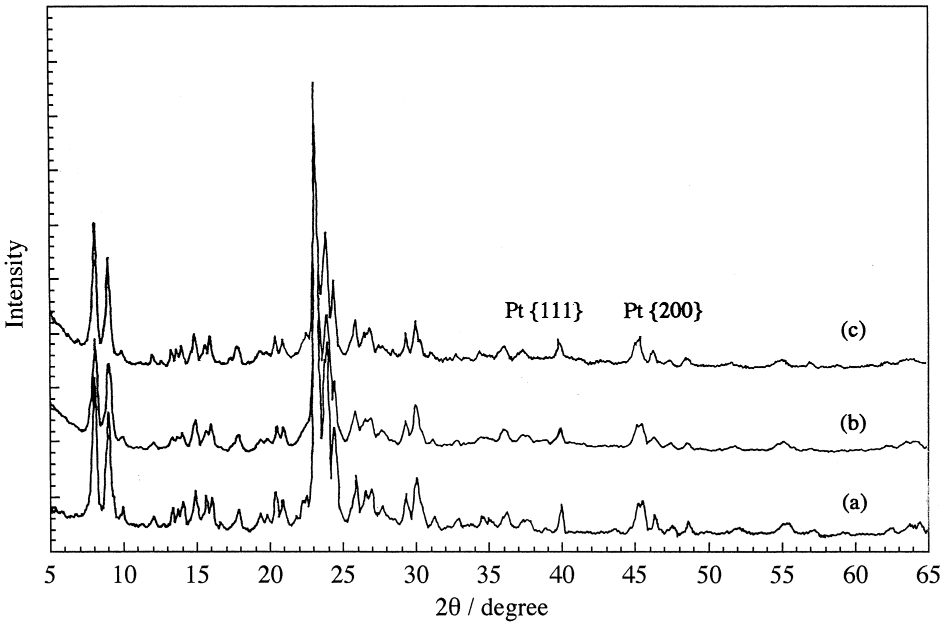

Fig. 7. XRD profiles of 5 wt% Pt/ZSM-5. Proton-exchange ratio of ZSM-5 was 93%. a) After calcination. b) After reduction. c) After reaction.

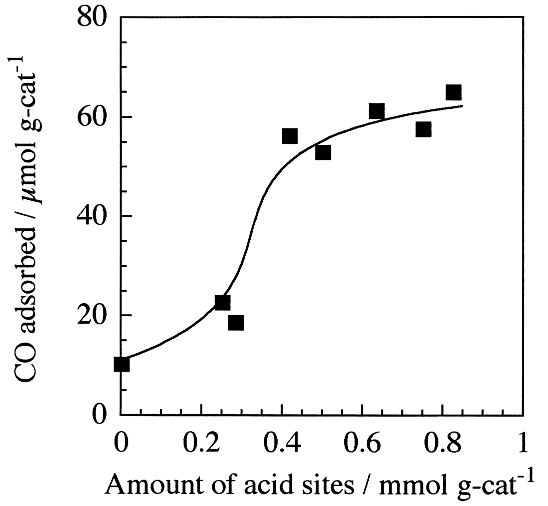

Fig. 8. Effect of acid amount of ZSM-5 on the amount of CO adsorbed on 5 wt% Pt/ZSM-5. Amounts of acid sites were measured based on NH_3-TPD spectra.

change). On the other hand, the dispersion in Pt/ZSM-5 having a lower acid amount was low. This observation is consistent with the result of the XRD measurement. These results suggest that more than 50% of the cations in ZSM-5 should be exchanged in order to obtain a highly dispersed platinum catalyst.

Figure 9 shows a comparison between the HDS activity and the amount of adsorbed CO. There was a linear relationship between them when the amount of adsorbed CO was more than 20 μmol g-cat^{-1}. This relationship was essentially independent on the proton-exchange ratio and the amount of supporting platinum. Accordingly, the surface area of platinum in the catalyst is an important factor concerning its activity for thiophene HDS. It was noted that higher C4 product selectivity was obtained on catalysts with a higher platinum dispersion. Moreover, when the platinum dispersion was the same for Pt/ZSM-5 catalysts, cracking and aromatization were more inhibited on those catalysts having a lower proton-exchange ratio.

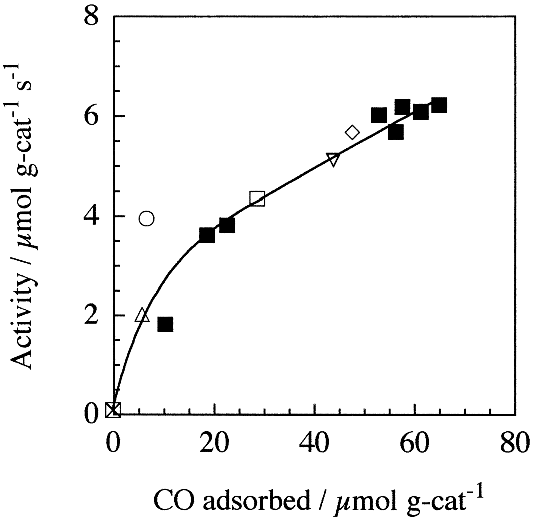

Fig. 9. Relationship between the amount of CO adsorbed and the HDS activity of thiophene on Pt/ZSM-5. All data were obtained at 2 h. proton-exchange ratio of the support, ZSM-5, was 93% in 0.5–4 wt% Pt/ZSM-5. 5 wt% Pt/ZSM-5 have various proton-exchange ratio (0–93%). ■ : 5 wt% Pt/ZSM-5, ◇ : 4 wt% Pt/ZSM-5, ▽ : 3 wt% Pt/ZSM-5, □ : 2 wt% Pt/ZSM-5, ○ : 1 wt% Pt/ZSM-5, △ : 0.5 wt% Pt/ZSM-5, ⊠ :ZSM-5.

This implies that cracking and aromatization addition to thiophene HDS proceed on those catalyst supports which have strong acid sites, such as HZSM-5, and products such as hydrocarbons lower than C4 are formed. This result agrees with the suggestion of Garcia and Lercher,[20] that a secondary reaction proceeds over strong acid sites, causing the formation of carbon deposits.

In the reaction of thiophene over Pt/ZSM-5, gas-phase hydrogen is supposed to be activated on the platinum, and moves to the active sites as a spillover hydrogen. It would then react with the thiophene, which is activated by acidic hydroxyl groups.[16] As shown in Fig. 9, the HDS activity of Pt/ZSM-5 rapidly decreased when the amount of adsorbed CO was less than 20 μmol g-cat^{-1}. This implies that the supply of activated hydrogen was insufficient for thiophene conversion in this region.

In the first step of HDS of thiophene, thiophene would be hydrogenated into tetrahydrothiophene (THT). Cleavage of the C–S bond of THT, which transforms into thiol-like intermediates, would be the next step. However, in the case that the supply of spillover hydrogen is insufficient, this step would be limited. This corresponds to the tendency that catalysts giving lower HDS activity showed higher selectivity for THT. This phenomenon may be related to the activity and mobility of spillover hydrogen.

Our results show that those catalysts with low acidity display low selectivity for cracking due to a small number of acid sites. Aromatization and subsequent coke formation were inhibited on these catalysts. Therefore, a support possessing fewer acid sites is desirable to prepare HDS catalysts. However, platinum supported on HZSM-5 with a large number of acid sites was highly dispersed and exhibited a high tolerance against poisoning by sulfur. Additionally, thiophene would be activated on the acid sites of ZSM-5. This means that ZSM-5 should have an appropriate number of acid sites. Under the conditions used in this study, the appropriate proton-exchange ratio is expected to be 50%.

Conclusion

The HDS activity increased with increasing the amount of platinum loading. The formation of aromatics was inhibited as the platinum loading increased. However, the cracking of products was not inhibited by platinum loading.

The proton-exchange ratio of ZSM-5 affects the HDS activity of thiophene over Pt/ZSM-5. High HDS activity over 6.00 μmol g-cat^{-1} s^{-1} was obtained by 5 wt% Pt/ZSM-5, whose ZSM-5 had a high proton-exchange ratio of more than 50%. In the high proton-exchange ratio region, Pt/ZSM-5 showed the same HDS activity. However, the selectivity of the cracking products depended on the proton-exchange ratio. This indicates that the selectivity of the products in HDS can be controlled by the extent of the proton exchange of the support.

The dispersion of platinum depended on the proton-exchange ratio of ZSM-5. The HDS activity was related to the amount of CO adsorbed over Pt/ZSM-5. This indicates that the surface area of platinum was an important factor for the HDS activity of Pt/ZSM-5.

In order to prepare Pt/ZSM-5 which showed high HDS activity and low selectivity of cracking products, using ZSM-5 having a 50% proton-exchange ratio as the support and loading the platinum about 5 wt% were desirable.

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