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Hydrodesulfurization of Dibenzothiophene on Iron-Exchanged Y Zeolite

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Synopsis. An Fe(II)HY zeolite catalyst pretreated at 500 and 600 °C was highly active for the hydrodesulfurization of dibenzothiophene when the Fe(II)HY zeolite was exchanged in a solution of $FeCl_2$ and aqueous NH_3 with NaY in N_2 gas, whereas the Fe(III)NaY catalyst in a solution of $FeCl_3$ displayed a low activity.

Hydrodesulfurization (HDS) is widely performed in the hydroprocessing of heavy oils and coal-derived liquids which contain high concentrations of polynuclear aromatic sulfur compounds, such as dibenzothiophene and benzonaphthothiophenes. Commercial NiMo and CoMo catalysts are available for the HDS process due to their high dispersion and high activity per unit volume and relatively low cost. Studies on the structure and characterization of these catalysts have been made using XRD, XPS, and IR techniques. Pecoraro and Chianelli1) reported that unpromoted ruthenium and osmium sulfides possessed a significantly higher specific activity than molybdenum and tungsten sulfides toward the HDS of dibenzothiophene. However, the iron catalyst was poorly understood for HDS, although iron catalysts have been employed in coal hydroliquefaction and the Fischer-Tropsch reaction. Only recently Hidaka et al.2) reported that FeY zeolite catalysts were very active in the hydroprocessing of heavy oils for ion exchange of an HY zeolite with an $Fe(NO_3)_3$ solution at low pH. There is considerable literature concerning the preparation and characterization of iron-exchanged Y zeolites.3,4) Chao and Erf5) suggested that the Fe(III)NaY zeolite is a potentially good candidate to effectively remove pyrrole-type impurities in shale-derived fuel by pyrrole chemisorption on the zeolite.

In this present paper, we report a high activity of Fe(II)HY zeolite catalyst for the HDS of dibenzothiophene when the Fe(II)HY was exchanged in a solution of $FeCl_2$ with aqueous NH_3, while the Fe(III)NaY catalyst in a solution of $FeCl_3$ displayed low activity. The iron exchange method, the pretreatment temperature in N_2, and the presulfidation for iron-exchanged zeolites have been examined; the mechanism of dibenzothiophene HDS is also discussed.

Experimental

The starting material for the iron-exchanged zeolite was Linde sodium Y-zeolite powder (SK-40). An Fe(II)HY sample was obtained in an exchange of the parent NaY with an NH_4OH solution containing $FeCl_2$ at 60 °C under a nitrogen atmosphere to prevent Fe(II) ion oxidation to Fe(III) ion. An Fe(III)NaY sample was prepared in the exchange of an $FeCl_3$ solution at room temperature with NaY for 10 min with stirring. After the ion exchange of iron ions, these samples were washed in deionized water, and then dried in air at 100 °C overnight. The Fe and NH_4^+ contents of the samples were calculated from analytical data regarding the amount of Na^+ (EDTA titration using nickel-uranyl acetate, MX indicator)6) and Fe ($KMnO_4$ titration using $SnCl_2$, $HgCl_2$ and Zimmermann–Reinhardt solution).7) The Fe(II) and NH_4^+ ion percentages in Fe(II)HY were 80 and 14% exchanged, respectively. The Fe(III)NaY was 31% exchanged. Zeolite (0.65 g) packed into a 1 ml glass ampoule was dried in N_2 gas at 100 °C for 2 h. The temperature was raised from 100 °C to the desired temperature at a rate of 1 °C min^{-1} in N_2 gas; the sample was then heated for 5 h. After the treatment, every ampoule was immediately sealed. In order to compare the activity of the N_2-treated Fe(III)NaY with that of the sulfided Fe(III)NaY, Fe(III)NaY was presulfided before a run with either sulfur powder or CS_2 at 350 °C and 5.0 MPa initial hydrogen pressure in an autoclave for 3 h. Both the ampoule-sealed catalyst and 3.1 g of dibenzothiophene were placed without a solvent in a 300 ml autoclave equipped with a magnetic-stirring system. The glass ampoule was broken before the reaction. The reaction was carried out in 5.0 MPa initial hydrogen pressure at 350 °C for 2 h. All dibenzothiophene was made sure of vaporization at 350 °C in this study, on the basis of a calculation of the vaporized pressure of dibenzothiophene by a method of Poynting and Satoh.8) After the reaction, gaseous products were exhausted through a 10% aqueous solution of lead acetate to collect H_2S as lead sulfide. The extent of HDS was determined as a measure of the amount of lead sulfide and the sulfur content in the catalyst after the reaction. Liquid products were analyzed by G.C. packed with 1% Silicone OV-17. Powder X-ray diffraction patterns were obtained using a Rigaku Denki diffractometer with CuK radiation.

Results and Discussion

The activities of the Fe(II)HY and Fe(III)NaY catalysts pretreated at various temperatures in N_2 gas for dibenzothiophene HDS are shown in Fig. 1. The Fe(II)HY catalyst treated at 500 and 600 °C was extremely active for dibenzothiophene HDS. Although the desulfurization on the Fe(II)HY catalyst was low (350 °C), it increased with increasing pretreatment temperature up to 500 °C, and then decreased slightly at 600 °C. The Fe(III)NaY catalyst showed low activity over all ranges of the pretreatment temperature. Thus, Fe(II)HY zeolite was activated by heating in nitrogen gas, whereas the Fe(III)NaY zeolite was not promoted. A suitable pretreatment of the Fe(II)HY zeolite leads to high activity for HDS. Nagai et al.9)

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studied the HDS of dibenzothiophene on an HY catalyst and found that the activity of the HY catalyst for HDS was greatly promoted by a pretreatment of the HY catalyst at 500 °C in air. Consequently, Fe(II)HY is enhanced by cooperation of the Fe(II) ion with the H^+ ion which is produced from the NH_4^+ ion by heating at 500 and 600 °C. The iron-exchanged zeolite catalysts, however, were less active for dibenzothiophene HDS than for commercial HDS catalysts, e.g., a sulfided $CoMo/Al_2O_3$ catalyst (Ketjenfine 124) without a solvent in a batch method. The percent of sulfur removal was 83.5 mol% at 350 °C and 5 Mpa initial H_2 pressure, although it was 36.6 mol% for the Fe(II)HY catalyst treated at 500 °C in N_2.

The iron ions in the Fe(II)HY sample were mostly in the divalent state after the dehydration treatment; some Fe(III) ions on the surface can be reduced to Fe(II) ions upon a heating dehydration treatment,[4] since the color of the zeolite sample turned from yellow to ivory. Fu et al.[3] also reported a redox mechanism between the valence states of Fe(II) and Fe(III) ion in the FeY zeolite. The Fe cations are in dynamic motion in the zeolite lattice at the temperatures of the catalytic reactions.

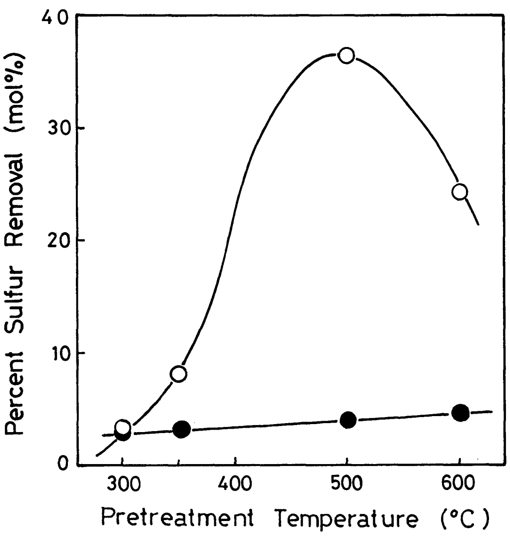

Fig. 1. The hydrodesulfurization activity of the Fe(II)HY (○) and Fe(III)NaY (●) zeolites at 350°C and 5.0 MPa initial hydrogen pressure. Catalysts were pretreated in N_2 for 4 h.

The X-ray diffraction patterns for the iron-exchanged zeolites are given in Fig. 2. Although some loss of crystallinity was detected in the X-ray diffraction pattern for the pretreated Fe(II)HY catalysts at 350, 500,

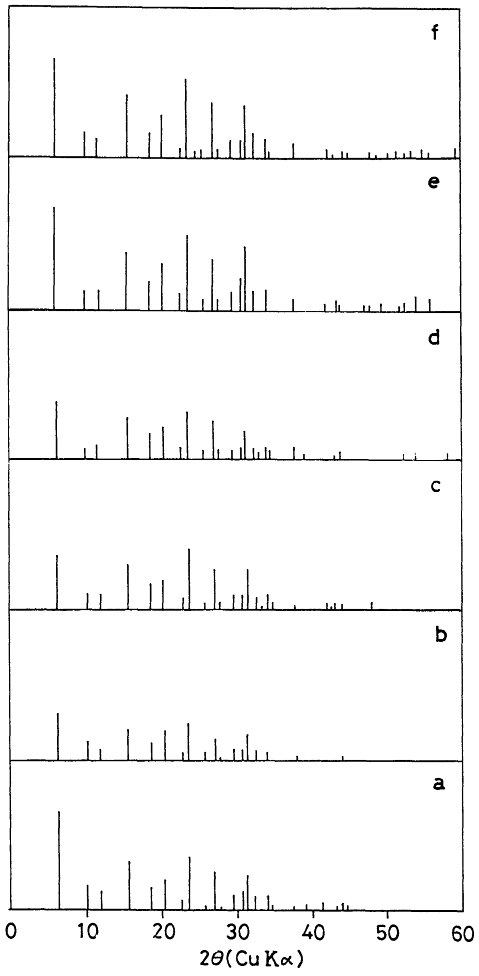

Fig. 2. X-Ray diffraction patterns of iron-exchanged zeolites. (a) Fresh Fe(II)HY; (b) Fe(II)HY pretreated in N_2 at 500°C; (c) Fe(II)HY pretreated in N_2 at 350°C; (d) after reaction sample (c) at 350°C; (e) fresh Fe(III)NaY; (f) Fe(III)NaY pretreated in N_2 at 600°C.

Table 1. Hydrodesulfurization of Dibenzothiophene on Fe(II)HY and Fe(III)NaY Zeolites[a]

Catalyst	FeNaY		FeHY		
Pretreatment temperature/°C	350	500	350	500	600
H_2S evolved/mol%	2.6	3.0	6.8	32.7	20.7
Reaction product/wt%					
Methyl, Ethyldibenzothiophene	0	0	0	4.9	9.4
Dibenzothiophene	96.0	97.0	93.3	61.8	74.1
Hydrogenated compounds	0	0	0	+	+
Biphenyl	2.4	3.0	3.4	10.7	3.7
Cyclohexylbenzene	0.1	0	+	1.8	0.6
Bicyclohexyl	0	0	0.2	2.2	0
Benzene, Toluene	0	0	0	2.0	0.3
Others	1.5	0	1.1	6.2	3.5

a) The HDS study was carried out at 350°C and 5.0 MPa initial hydrogen pressure for 2 h.

Table 2. Effect of Presulfiding on HDS Activity of Fe(III)NaY Zeolite at 350 °C and 5.0 MPa Initial H_2 Pressure for 2 h[a)]

Sulfiding agent	Desulfurization[b)] mol%
—[c)]	3.9
Sulfur[d)]	10.7
CS_2[e)]	5.0

a) Presulfiding was carried out at 350 °C and 5.0 MPa initial H_2 pressure for 3 h. b) Calculated by H_2S (mol%) evolved plus sulfur content (mol%) in catalyst. c) Pretreated in N_2 at 350 °C and for 5 h. d) 0.1 mol. e) 0.05 mol.

and 600 °C, these catalysts showed good crystallinity similar to a fresh Fe(II)HY catalyst. The 600 °C-treated Fe(III)NaY zeolite displayed the same peaks as those of the fresh zeolite. Moreover, the 350 °C-treated Fe(II)HY catalyst possessed good crystallinity, even after the reaction.

The distribution of the reaction products in the dibenzothiophene HDS is shown in Table 1. The main product was biphenyl in the reaction overall the catalysts. Many other products, methyl- and ethyldibenzothiophenes, were found in large quantity with the Fe(II)HY catalysts pretreated at 500 and 600 °C, while they were not observed with the 350 °C-treated Fe(II)HY and all the Fe(III)NaY catalysts. A greater amount of alkyldibenzothiophene was formed with the 600 °C-treated Fe(II)HY catalyst than with the 500- and 350 °C-treated Fe(II)HY catalysts. The 600 °C-treated Fe(II)HY catalyst showed a lower activity than the 500 °C-treated catalyst due to the production of high molecular weight compounds, not to a loss of crystallinity.

Iron ions of the catalyst are converted to iron sulfides during the reaction. In order to determine whether the iron ions or sulfides are active for dibenzothiophene HDS, the effect of presulfidation on the activity of Fe(III)NaY catalyst is shown in Table 2. The desulfurization activity of the presulfided Fe(III)NaY catalyst with CS_2 or sulfur powder was greater than that of the N_2-treated Fe(III)NaY catalyst. The addition of sulfur powder produced twice as much activity as that with CS_2. Sugioka et al.[10)] also reported that the presence of H_2S produced Brønsted acid sites on the cation-exchanged zeolites and enhanced the activity of the zeolites for cumene cracking and toluene disproportionation. Therefore, presulfidation promotes the activity for HDS due to the formation of Brønsted acid sites on iron sulfide when hydrogen molecules are adsorbed on the zeolite at high hydrogen pressure. Since dibenzothiophene is a Lewis base, the dibenzothiophene is easily adsorbed on the Brønsted acid sites of the sulfide catalyst as well as iron ions (Lewis acid). The HDS of dibenzothiophene proceeds with Fe(II)HY zeolite as follows: First dibenzothiophene is adsorbed on a Fe(II) ion through the sulfur atom of dibenzothiophene, which leads to a weakening of the C-S bonds in dibenzothiophene. The C–S bond is attacked by a proton on Fe(II)HY zeolite and cleavaged to form biphenyl. Iron atoms are finally sulfided and are improved much more than an unsulfided iron-exchanged catalyst. Sulfidation increases the number of Brønsted acid sites by activating hydrogen molecules on the sulfur atoms of the sulfided zeolite catalyst.

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