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Enhancement in Cracking Activity of USY Zeolites Treated with Ammonium Nitrate Solution

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USY zeolites prepared by steam treatment of NH_4-Y zeolites were treated with ammonium nitrate solutions. Treatment with ammonium nitrate solutions resulted in a remarkable enhancement in the octane-cracking activity of the USY zeolites. This enhancement in the octane-cracking activity was attributed to the increase in the amount of acid sites and the enhancement of the acid strength, as observed in the ammonia IRMS–TPD method.

Ultrastable Y (USY) zeolites are widely used in petroleum refineries as catalysts in fluid catalytic cracking. USY zeolites are conventionally prepared by high-temperature steam treatment of NH_4-Y zeolites[1] or by chemically treating NH_4-Y zeolites with hexafluorosilicate.[2] High-temperature steam treatment of NH_4-Y zeolite causes dealumination of the faujasite framework, thereby generating strong Brønsted acid sites.[3] The catalytic activity of USY zeolites depends on the steam-treatment conditions, i.e., the temperature, time, and steam concentration. After steam treatment, the acidic properties of USY zeolites are modified by treating them with citric acid, oxalic acid, nitric acid, hydrochloric acid, EDTA,[4] and aqueous solutions of CH_3COONH_4 and $C_6H_5COONH_4$.[5] Such treatment leads to realumination of the USY zeolite, thereby modifying its acidic properties. Treatment with H_2Na_2-EDTA results in the generation of strong Brønsted acid sites at the O_1H sites. This generation of strong Brønsted acid sites can be attributed to the induction effect caused by the extraframework $Al(OH)^{2+}$ species.[6] In this paper, we report the remarkable enhancement in the octane-cracking activity of crude USY zeolites treated with ammonium nitrate solution. Zeolites have typically been treated with ammonium nitrate solution simply to obtain an NH_4-type zeolite through the exchange of Na^+ or H^+ cations with $NH_4{}^+$ cations; therefore, the enhancement in the octane-cracking activity of the zeolites, which was observed in this study, is a rather unexpected finding.

Na-Y zeolite (320NAA, $Si/Al_2 = 5.5$) supplied by Tosoh Corp., Tokyo, Japan, was used as the starting material for the preparation of the USY zeolite. The Na-Y zeolite was ion-exchanged three times with a solution of NH_4NO_3 ($0.5\,mol\,L^{-1}$) at 353 K to afford NH_4-Y zeolite. USY zeolite was prepared from NH_4-Y zeolites by steam treatment diluted by a N_2 flow. The concentration of steam was 18 vol %. The NH_4-Y (5 g) zeolite was placed in a quartz tube and treated with steam at 823 K for 10 h. The net flow rate was $50\,mL\,min^{-1}$. The USY zeolite obtained was treated with ammonium nitrate solution (0.5–$7.5\,mol\,L^{-1}$) three times to give NH_4-USY. Each treatment was carried out for 4 h at 353 K. The obtained USY zeolite will henceforth be abbreviated as USY-*x*M, where *x* denotes the concentration of the ammonium nitrate solution. NH_3 gas was adsorbed on the USY zeolite to give NH_4-USY zeolite (denoted as USY-NH_3), which was used for comparison. The octane cracking activity of the USY zeolites was measured by a continuous flow method. The octane vapor was mixed with nitrogen carrier gas (partial pressure of octane: 1.9 kPa), and the gas mixture was allowed to flow into a Pyrex glass reactor heated at 773 K. Prior to the reaction taking place in the reactor, a zeolite sample (5 mg) was activated in situ at 773 K in a dried N_2 flow for 1 h. The products and reactant were fed into a gas chromatograph (Shimadzu, GC-2014) directly through a six-way valve and analyzed using a silicone capillary column and flame-ionization detector.

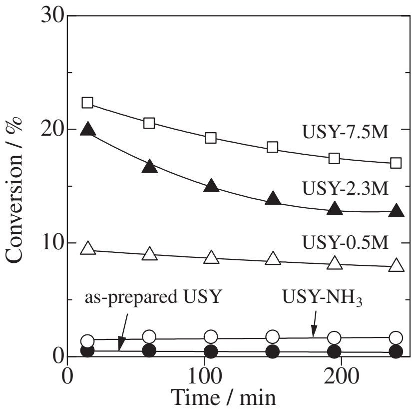

Figure 1. Time-course change in the conversion of octane catalyzed by USY zeolites.

Figure 1 shows the time-course change in the conversion of octane over as-prepared USY and USY-NH_3 zeolites. The conversion of octane over as-prepared USY and USY-NH_3 were 0.5% and 1.5%, respectively. The initial conversion rates of octane over USY zeolite treated with 0.5, 2.3, and 7.5 M ammonium nitrate solution were 9.4, 19.9, and 23.3%, respectively. Thus, USY zeolites treated with aqueous ammonium nitrate solution exhibited considerably high activity. Although the rate of octane conversion gradually decreased with time, it was still considerably higher than the octane conversion over as-prepared USY or NH_3-adsorbed USY zeolite four hours from the start of the reaction. The reason for decrease in activity was ascribed to the deposition of coke during reactions because the activity was completely recovered after calcination of the catalyst with O_2 at 773 K. A comparison made 15 min from the start of the reaction revealed that the conversion rate of USY-7.5 M zeolite was considerably higher than that for Na_2–H_2–EDTA-treated USY zeolite (19%) and oxalate-treated USY zeolite at pH 4.5 (9.3%).

The Si/Al_2 ratio of the as-prepared USY zeolites was 5.5, and those for the USY zeolites treated 1, 2, and 3 times with 7.5 M ammonium nitrate solution were 7.3, 7.7, and 7.9, respectively. Approximately 25% of Al was removed from the USY zeolites after treating the zeolites three times with a 7.5 M ammonium nitrate solution. XRD patterns of the USY zeolites

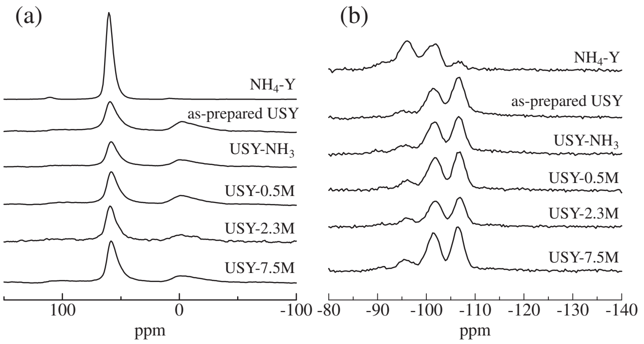

Figure 2. ^{27}Al (a) and ^{29}Si (b) MAS NMR spectra of NH_4-Y, as-prepared USY, and USY zeolites treated with NH_3 and ammonium nitrate solution.

remained unchanged even after treatment with ammonium nitrate solutions.

Figure 2a shows the ^{27}Al MAS NMR spectra of both the as-prepared and treated samples. A single peak corresponding to the four-coordinated Al species can be seen at 60 ppm in the spectrum of the NH_4-Y zeolite. Steam treatment of the NH_4-Y zeolite yielded a new peak at 0 ppm. Treatment with ammonium nitrate solution slightly reduced the intensity of the peak at 0 ppm, which suggests that the extraframework Al species were partially removed by the treatment. Figure 2b shows the ^{29}Si MAS NMR spectra of the NH_4-Y and USY zeolite samples. Four peaks corresponding to the $Si(OSi)_4$, $Si(OSi)_3(OAl)_1$, $Si(OSi)_2(OAl)_2$, and $Si(OSi)_1(OAl)_3$ appeared at −106, −102, −96, and −89 ppm, respectively.[7] In addition to these, two peaks assignable to the $Si(OSi)_3(OH)_1$ and $Si(OSi)_2(OAl)_1(OH)_1$ overlapped at −98 and −91 ppm.[8] The intensity of the peak at −96 ppm decreased after steam treatment; in contrast, the intensity of the peak at −106 ppm increased considerably, owing to the dealumination that occurred during steam treatment. However, the ^{27}Al MAS NMR spectra of the USY zeolites treated with ammonium nitrate solutions were almost identical to those of the as-prepared USY zeolites. The ICP and NMR observations suggested that the extraframework Al species were partially removed while the original framework structure of USY zeolites was retained. The sample USY zeolites used in the study did not exhibit mesopore formation, as indicated by N_2 adsorption isotherms, which rules out the possibility of mesopores participating in the catalytic reaction in our study.

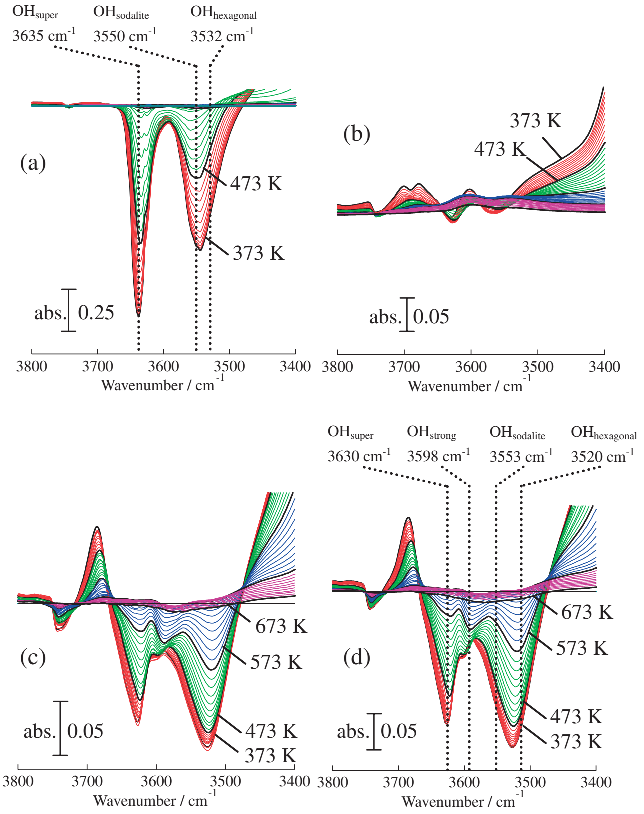

Figure 3. IR spectra of (a) H-Y zeolite, (b) as-prepared USY, (c) USY-0.5M, and (d) USY-7.5M zeolites with adsorbed ammonia, as the temperature was increased from 373 to 773 K.

Table 1. Amount of Brønsted acid sites in USY determined by NH_3 IRMS–TPD methods

Sample	OH_{super} /mol kg^{-1}	OH_{strong} /mol kg^{-1}	$OH_{sodalite}$ /mol kg^{-1}	$OH_{hexagonal}$ /mol kg^{-1}
H-Y	1.20	—	0.38	0.31
USY-0.5M	0.16	0.15	0.05	0.07
USY-2.3M	0.22	0.22	0.07	0.09
USY-7.5M	0.27	0.25	0.09	0.10

The acidic properties of the USY zeolites were determined using IRMS–TPD (infrared mass spectrometry–temperature-programmed desorption). In this method, IR and MS follow the thermal behavior of adsorbed and desorbed NH_3, respectively.[9] Figure 3a shows the IR–TPD spectra of the H-Y zeolites, as the temperature was increased from 373 to 773 K. The OH stretching region consisted of three types of OH groups: OH groups in the supercage (OH_{super}, 3635 cm^{-1}), sodalite cage ($OH_{sodalite}$, 3550 cm^{-1}), and hexagonal prism ($OH_{hexagonal}$, 3532 cm^{-1}).[10] These OH groups were not obviously seen in the IR spectra of as-prepared USY zeolite (Figure 3b). However, they appeared after the treatment with ammonium nitrate solution, probably due to the removal of the extraframework Al species that covered the acid sites of USY zeolite. In addition to the OH groups present in the H-Y zeolite, the spectra of USY-0.5M and -7.5M zeolites (Figures 3c and 3d) showed the emergence of strong Brønsted acid sides characteristic to USY zeolites at 3598 cm^{-1} (OH_{strong}), which were not observed in the spectra of the H-Y zeolites. The IR–TPD profiles of the USY zeolites prepared under different conditions were then obtained for OH bands and adsorbed ammonia species. The amount and strength of the acid sites determined by curve-fitting analysis are summarized in Tables 1 and 2, respectively. The amount of each acid site increased with an increase in the concentration of the ammonium nitrate solution. At the same time, the acid strength of each site was considerably higher than the site in the H-Y zeolite. The OH_{strong} group, in particular, seems to have the strongest influence on the cracking because it has a high acid strength and it is located in the supercage group. The observed enhancement of the cracking activity of the USY zeolites when treated with ammonium nitrate solution is thereby attributed to the OH_{strong} group located in the supercage.

Table 2. Strength of Brønsted acid sites in USY determined by NH_3 IRMS–TPD methods

Sample	OH_{super} /kJ mol^{-1}	OH_{strong} /kJ mol^{-1}	$OH_{sodalite}$ /kJ mol^{-1}	$OH_{hexagonal}$ /kJ mol^{-1}
H-Y	112	—	117	107
USY-0.5M	136	157	152	151
USY-2.3M	135	153	148	147
USY-7.5M	130	146	142	141

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