

Acidic property of modified ultra stable Y zeolite: increase in catalytic activity for alkane cracking by treatment with ethylenediaminetetraacetic acid salt

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Abstract

Temperature-programmed desorption (TPD) of ammonia with improved techniques was applied to quantitative determination of the strength and number of acid sites of a series of modified Y zeolites. A weak acid site was generated by the isomorphous substitution of aluminum for silicon, and the strength was independent of the aluminum concentration. This type of acid site showed almost no activity for cracking of octane at 573 K. Multiple types of extra-framework aluminum were formed on the ultra stable Y (USY) zeolite by steaming to create the cracking activity. Strong Brønsted acid sites were increased by the treatment of USY with a sodium salt of ethylenediaminetetraacetic acid (EDTA). The catalytic activity for alkane cracking showed a positive relationship with the number of this type of acid site, suggesting that the active site of USY for the catalytic cracking is this strong Brønsted acid site.

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1. Introduction

Cracking of alkane (paraffin) is one of the largest chemical processes. It is catalyzed by a modified ultra stable Y (USY, dealuminated Y) zeolite [1,2], and therefore the USY is the zeolite most widely used as a catalyst and one of the most widely used solid catalysts. In spite of the importance of USY, its acidic property has been unclear, because it has been difficult to determine the acidic property of solids. A number of attempts have been made to analyze the acidic property of USY zeolite by advanced techniques [3–14].

Temperature-programmed desorption (TPD) of ammonia is a simple and convenient method for analyzing the solid acidity [15]. Principally the area of desorption peak shows the acid amount, and the peak position reflects the acid strength. However, the ammonia TPD under usual conditions

has two problems. First, ammonia molecules weakly-held by non-acidic sites form a large desorption peak at ca. 400 K to disturb the analysis of such a weakly acidic zeolite as Y. This type of ammonia is considered to be hydrogen-bonded to the NH_4^+ cation which has been adsorbed on Brønsted acid site [3,16]. It should give no information about the property of acid site. Second, the temperature of desorption peak from the acid site does not directly show the acid strength but is affected by the readsorption of ammonia, and hence affected by the measurement conditions and acid amount [17]. The low temperature peak in TPD was diminished by feed of water vapor [18,19], and we have established a method of water vapor treatment for the ammonia TPD to remove the irrelevant peak from the TPD spectrum [20]. Moreover, we have derived a theory [21,22] to precisely determine the heat of ammonia adsorption. The number and strength of acid site on a solid can be precisely measured by the thus improved ammonia TPD.

It has been applied to Y zeolite, which is the precursor of the USY with almost no extra-framework aluminum [23].

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The number of acid site approximately agreed with the number of framework aluminum atom, and the adsorption heat of ammonia was ca. 110 kJ mol^{-1} , which was lower than those on β [24], ZSM-5 and mordenite [21] (125, 135 and 145 kJ mol^{-1} , respectively).

However, the acidic property of USY zeolite is complex, and this is another reason why understanding the catalysis of USY is difficult. The USY has strong acid sites, both Lewis and Brønsted [7], with a wide distribution of strength presumably due to various extra-framework aluminum species. Because the activity for alkane cracking is observed on the USY but not on the Y, some possibilities are considered as origin of the activity. The enhancement of Brønsted acidity due to the extra-framework species [25–28], or change in the aluminum concentration of the framework [4,29–31] is speculated. Generation of the meso-porosity accompanying the dealumination [7,32] and enrichment of alkane adsorbed in the micropore [33] are also supposed.

In order to investigate the origin of activity on USY, both a new technique for characterization of the acidity and a simple model of zeolite are required. Among various dealumination techniques, the ethylenediaminetetraacetic acid (EDTA) treatment [34] after steaming the Y zeolite has been reported to result in a simple structure [35] and a high activity for the alkane cracking [36]. The conventional ammonia TPD method has been applied to the $\text{Na}_2\text{H}_2\text{-EDTA}$ -treated USY [37] but the analysis of spectrum has not been enough. In the present paper, the improved ammonia TPD was applied to the examination of the strong Brønsted acidity on the EDTA salt-treated USY zeolite. We also exhibit that the high activity for the alkane cracking is owing to this type of acidity on the basis of the systematic experiments using the USY zeolites modified with various treatments. In addition, the quantitative analysis of acid site will contribute to the clarification of the structure of active site in the USY, on which there is a serious controversy [38].

2. Experimental

An ammonium Y zeolite was prepared from a sodium Y ($\text{Si}/\text{Al}_2 = 5.1$, kindly supplied by Catalysts and Chemicals Ind., Co. Ltd.) as described in our paper [23] and steamed at 573 to 973 K for 1 h in a mixture of 40 mol% of water vapor and nitrogen. As shown in Table 1, the steamed samples are shown as U_t where t is the steaming temperature in K. Thus obtained U823 (3 g) was stirred in an aqueous solution of $\text{Na}_2\text{H}_2\text{-EDTA}$, $\text{Na}_3\text{H-EDTA}$, $\text{Na}_4\text{-EDTA}$ and $\text{K}_4\text{-EDTA}$ under refluxing (the conditions are shown in Table 1), followed by cooling, filtration, washing with 1 dm^3 of water, ion-exchange in an ammonium nitrate solution, filtration, washing again with 1 dm^3 of water and drying at 373 K for 10 h in atmosphere. The USY treated with $\text{Na}_2\text{H}_2\text{-}$, $\text{Na}_3\text{H-}$ and $\text{Na}_4\text{-EDTA}$ solutions are termed 2E-, 3E- and 4E-U823, respectively. The $\text{K}_4\text{-EDTA}$ -treated sample is called K4E-U823. The NH_4Y zeolite was also treated

with the $\text{Na}_2\text{H}_2\text{-EDTA}$ solution (2E-Y). The treatments with ammonia and nitric acid solutions were also carried out. The ammonia-treated USY is termed B-U823 and the nitric acid-treated one is A-U823, because these treatments are considered to be base and acid treatments. As a control, commercially available USY supplied by Catalysts and Chemicals Industries Co. Ltd. [U(CCIC)], was also used.

All the samples were exposed to atmosphere with ca. 80% of the relative humidity by co-presence of an aqueous solution saturated with NH_4Cl for more than 2 days, in order to stabilize the weight, and the content of adsorbed water was measured by heating up to 1273 K with a Rigaku Thermoflex TAS-200 thermogravimeter. The chemical composition was measured by a Shimadzu ICPS-5000 inductively coupled plasma emission spectrometer (ICP-ES) after dissolving the sample into fluoric acid. All the compositions will be shown by the value per unit weight of the dry solid hereafter. The total content of silicon was determined as follows:

$$w_{\text{SiO}_2} = 1 - w_{\text{Al}_2\text{O}_3} - w_{\text{Na}_2\text{O}} \quad (1)$$

$$[\text{Si}] = \frac{w_{\text{SiO}_2}}{\text{formula weight of SiO}_2, 60.08 \times 10^{-3} \text{ kg mol}^{-1}} \quad (2)$$

where w_i was the content expressed by weight of the component i in 1 kg of dry zeolite sample.

The crystal structure was analyzed by a Rigaku Miniflex plus X-ray diffractometer (XRD). The magic angle spinning nuclear magnetic resonance (MAS-NMR) was measured by a JEOL JNM-ECP300 spectrometer at 78.3 and 59.7 MHz resonance frequency for ^{27}Al and ^{29}Si , respectively. The chemical shift is shown with an aqueous solution saturated with $\text{Al}_2(\text{SO}_4)_3$ as a standard material for ^{27}Al and with $\text{Si}(\text{CH}_3)_4$ liquid for ^{29}Si .

An ammonia TPD spectrum was collected after evacuation at 773 K followed by the adsorption of ammonia and the water vapor treatment at 373 K as described [15]. An infrared (IR) spectrum was measured by a JASCO FT-IR/5300 spectrometer on a self-supporting disk molded from 10 mg of the zeolite in an in situ cell after evacuation at 773 K for 1 h, followed by the adsorption of pyridine vapor at 373 K and evacuation at 573 K for 1 h.

The catalytic activity for the cracking of octane was evaluated by a pulse method. After pretreatment at 773 K for 1 h in $2.04 \times 10^{-5} \text{ mol s}^{-1}$ of helium, a pulse of octane vapor (1 mm^3 as liquid) was admitted onto the sample (10 mg) at 573 K, and the products were analyzed by an FID-GC (flame ionization detector-gas chromatography) with a column of silicone SE-30. The cracking of 2,2,4-trimethylpentane (isooctane) was carried out under the same conditions. The cracking of 1,3,5-triisopropylbenzene into benzene, propene, cumene (isopropylbenzene) and diisopropylbenzene was carried out by a pulse of 1 mm^3 of the reactant at 523 K in a nitrogen flow ($4.08 \times 10^{-5} \text{ mol s}^{-1}$) on 2 mg of the zeolite.

Table 1
List of zeolite samples

Nomenclature	Raw material	Treating reagent (concentration/mol dm ⁻³)	Treatment temperature (K)	Treatment time (h)	Post-treatment	
NaY	Supplied by Catalysts and Chemicals Industries Co. Ltd.					
NH ₄ Y	NaY	NaY ion-exchanged in NH ₄ NO ₃ aqueous solution at 343 K for 4 h with (NH ₄ in solution)/(Al in zeolite) molar ratio = 100 and weight ratio water/zeolite = 100. The ion exchange was repeated 3 times with drying the solid at 373 K for 10 h after each exchange [23]				
2E-Y	NH ₄ Y	Na ₂ H ₂ –EDTA (0.1)	371	24	Ion-exchange in 300 cm ³ of 1 mol dm ⁻³ NH ₄ NO ₃ aqueous solution at 353 K for 4 h and drying at 373 K for 10 h	
U573	NH ₄ Y	Steaming in a flow of water vapor and nitrogen (4:6 molar ratio)	573	1		
U673			673	1		
U823			823	1		
U873			873	1		
U973			923	1		
2E-U823	U823	Na ₂ H ₂ –EDTA (0.1)	371	24	Ion-exchange in 300 cm ³ of 1 mol dm ⁻³ NH ₄ NO ₃ aqueous solution at 353 K for 4 h and drying at 373 K for 10 h	
3E-U823	U823	Na ₃ H–EDTA (0.1)	353	4		
4E-U823		Na ₄ –EDTA (0.1)				
K4E-U823		K ₄ –EDTA (0.1)				
A-U823	U823	HNO ₃ (0.1)	353	4	Drying at 373 K for 10 h	
B-U823		NH ₃ (0.1)				
U(CCIC)	Ultra stable Y zeolite supplied by Catalyst and Chemicals Industries Co. Ltd.					

3. Results

3.1. Structure

All the obtained samples had the FAU structure. The crystallinity was evaluated from the intensity of (5 5 5) diffraction. The Na₂H₂-EDTA treatment of NH₄Y did not affect the crystallinity (data not shown). Steaming the NH₄Y above 673 K slightly weakened the diffraction. The treatments of U823 with the sodium salts of EDTA did not change the intensity (2E-U823, 3E-U823 and 4E-U823 in Fig. 1), while the treatments in acidic and strongly basic conditions decreased the crystallinity (A-U823, K4E-U823 and B-U823 in Fig. 1).

The nitrogen adsorption showed that the micropore volume of NH₄Y was decreased by steaming at 573 to 673 K, whereas steaming at 823 K kept the high micropore volume. The NaY and NH₄Y zeolites are stable, but the proton form of Y zeolite with high framework aluminum concentration is readily decomposed under humid atmosphere [23,39]. Steaming the NH₄Y zeolite at a high temperature stabilizes the structure by removal of a fraction of framework aluminum atom [40]. The micropore volume kept at the high temperatures indicates the high crystallinity kept by the high temperature steaming. The micropore volume gradually decreased with increasing steaming temperature

from 823 to 973 K, while the mesopore volume increased by the high temperature steaming (▲ and ▼ in Fig. 2). The Na₂H₂-EDTA treatment of U823 did not affect the micropore volume, and increased the mesopore volume (△ and ▽ in Fig. 2).

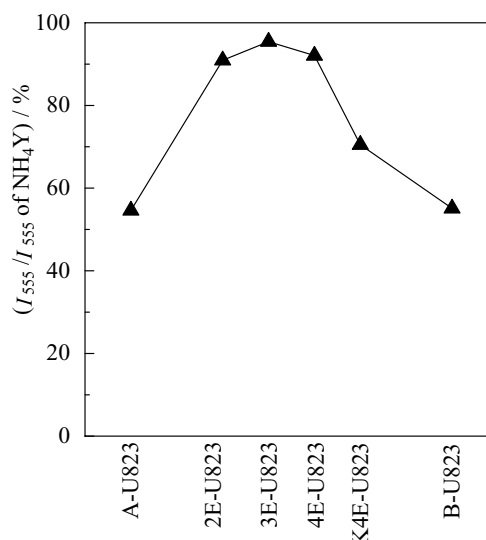


Fig. 1. Change in intensity of (555) diffraction of USY steamed at 823 K followed by treatment with acid (A), base (B), Na₂H₂-EDTA (2E), Na₃H-EDTA (3E), Na₄-EDTA (4E) and K₄-EDTA (K4E).

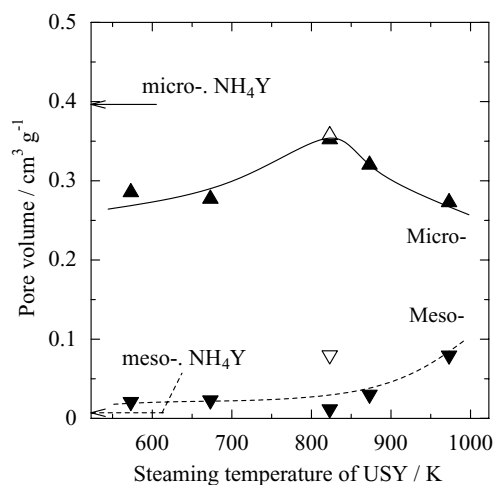


Fig. 2. Micro- (▲ and △) and mesopore volume (▼ and ▽) of USY steamed at various temperatures (▲ and ▼) followed by treatment with Na₂H₂-EDTA (△ and ▽).

3.2. NMR

Fig. 3 shows the ²⁹Si NMR spectra. The Si(OSi)₄ species appeared at −106 to −108 ppm, and the Si(OSi)_{4−n}(OAl)_n (*n* = 1, 2 and 3) species were observed at ca. −101, −95, and −90 ppm, respectively, as known well [40]. The framework Si/Al ratio was estimated from the deconvolution as shown in Fig. 4. The concentration of framework aluminum [Al_F] was calculated on the assumption that all the silicon atoms were located at the framework position as follows (Table 2).

$$\frac{[\text{Si}]}{[\text{Al}_F]} = \frac{\text{Total peak area in } ^{29}\text{Si NMR}}{0.25I_{\text{Si}(\text{OSi})_3(\text{OAl})_1} + 0.25I_{\text{Si}(\text{OSi})_2(\text{OH})_1(\text{OAl})_1} + 0.5I_{\text{Si}(\text{OSi})_2(\text{OAl})_2} + 0.75I_{\text{Si}(\text{OSi})_1(\text{OAl})_3} + I_{\text{Si}(\text{OAl})_4}} \quad (3)$$

where *I_x* was the peak intensity of species *x* in the ²⁹Si NMR.

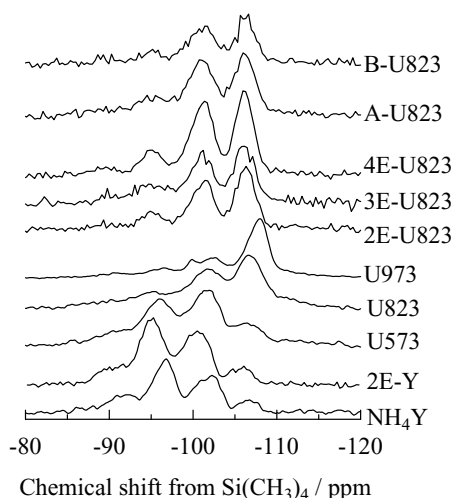


Fig. 3. ²⁹Si NMR spectra of zeolite samples.

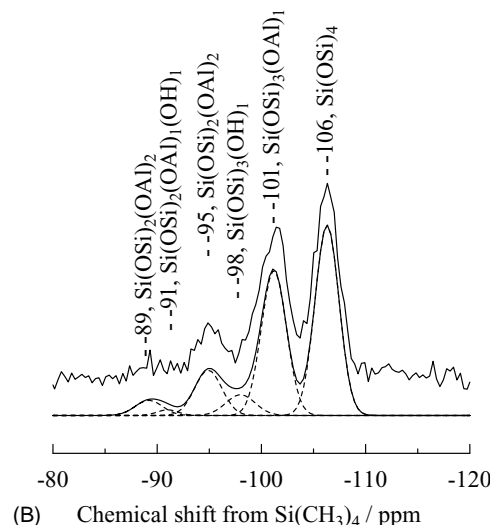
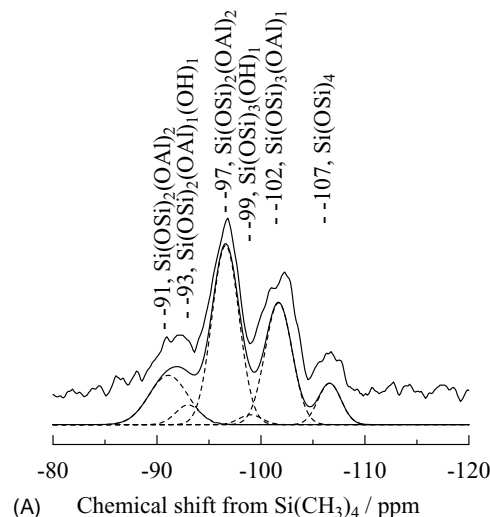


Fig. 4. Deconvolution of ²⁹Si NMR spectra of NH₄Y (A) and 2E-U823 (B).

On the other hand, the framework aluminum content was also calculated from the unit cell constant (*a*₀) from the XRD based on the Eq. (1) [7,41], although there is a controversy [42].

$$\frac{[\text{Al}_F]}{\text{uc}} = 115.2(a_0 - 24.191) \quad (4)$$

Fig. 5 shows the correlation between the framework aluminum contents determined by the ²⁹Si NMR and XRD. Almost 1:1 relationship supports the validity of these measurements and the deconvolution of NMR spectra.

The ²⁷Al NMR was measured as shown in Fig. 6. One sharp line at ca. 60 ppm, ascribed to the tetra-coordinated aluminum Al_{IV} [40], was observed on a flat baseline in the spectra of NH₄Y and Na₂H₂-EDTA treated NH₄Y (2E-Y). Steaming the NH₄Y (U573) generated an additional peak at ca. 0 ppm, attributed to the hexa-coordinated aluminum Al_{VI} [40]. Increasing the steaming temperature increased the

Table 2

Total, framework and extra-framework aluminum concentrations determined by ICP and ^{29}Si NMR (mol kg^{-1})^a

Sample	[Na] from ICP	[Al] from ICP	[Al]–[Na]	[Al _F] from ^{29}Si NMR	[Al _F]–[Na]
NaY	4.51	5.24	0.73		
NH ₄ Y	0.11	5.50	5.39	4.9	4.8
2E-Y	0.68	4.45	3.77	3.8	3.1
U573	0.26	5.02	4.76	4.1	3.8
U673	0.17	5.24	5.07	3.5	3.3
U823	0.07	5.08–5.92	5.01–5.85	2.0	1.9
U873	0.13	5.17	5.04	2.5	2.4
U973	0.16	5.38	5.22	2.1	1.9
2E-U823	0.26	5.01	4.75	2.2	2.1
3E-U823	0.24	4.63	4.39	2.3	2.1
4E-U823	0.47	3.90	3.43	2.4	1.9
K4E-U823	0.15	3.09	2.94	2.6	2.5
A-U823	0.42	3.92	3.50	2.1	1.7
B-U823	0.75	3.66	2.91	2.2	1.5
U (CCIC)	0.09	3.46	3.37		

^a Could not be determined because of broad peak shape.

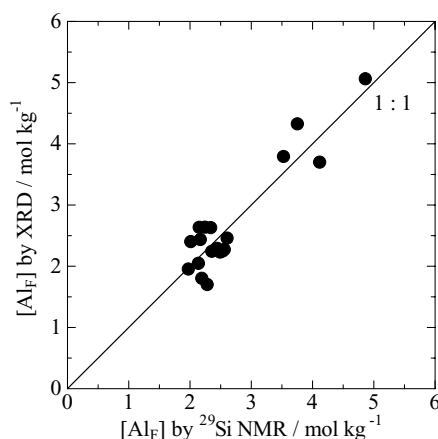
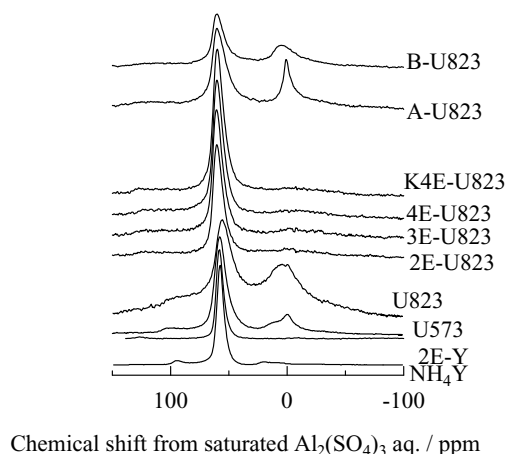
Al_{VI} species and simultaneously broadened the both peaks (U823). The treatments of USY with the EDTA salts obviously suppressed the peak at 0 ppm. The sharp peak of Al_{IV} was regenerated at 60 ppm (2E-U823, 3E-U823, 4E-U823 and K4E-U823). This change in the ^{27}Al NMR by the EDTA treatment has been reported [35].

The parent NH_4Y zeolite had almost no extra-framework aluminum, as revealed by both ^{27}Al (Fig. 6) and ^{29}Si NMR spectra (Table 2). The $\text{Na}_2\text{H}_2\text{-EDTA}$ treatment of NH_4Y decreased the total aluminum content with keeping the low content of the extra-framework aluminum, which was estimated to be 0.7 mol kg^{-1} from $[\text{Al}]-[\text{Al}_\text{F}]$ (2E-Y in Table 2). The ^{27}Al NMR supports this, because almost no Al_{VI} peak was observed on the 2E-Y sample (Fig. 6). In other words, the $\text{Na}_2\text{H}_2\text{-EDTA}$ treatment of NH_4Y resulted in dealumination. The dealumination ability of $\text{Na}_2\text{H}_2\text{-EDTA}$ has been described [43].

The total aluminum content $[\text{Al}]$ was 4.7 to 6 mol kg^{-1} , but the framework aluminum content $[\text{Al}_\text{F}]$ was decreased

by steaming as shown in Table 2. Increasing the steaming temperature up to 823 K decreased $[\text{Al}_\text{F}]$ to 1/2–1/3 of the parent zeolite. Further increase of the steaming temperature did not change the framework composition.

As shown in Table 2, the $\text{Na}_2\text{H}_2\text{-EDTA}$ treatment of U823 (2E-U823) kept the total aluminum amount at ca. 5 mol kg^{-1} , while the framework aluminum slightly increased. This may be due to reinsertion of the extra-framework aluminum into the FAU framework. The reinsertion in a basic medium has been reported [44]. On the other hand, a considerable amount of the extraframework aluminum $[\text{Al}_\text{EF}]$ is estimated from the difference $[\text{Al}]-[\text{Al}_\text{F}]$. However, in the ^{27}Al NMR spectra, no clear peak of Al_{VI} was observed on the 2E-U823 sample, in agreement with Gola et al. [35]. Enhancing the basicity of the EDTA salt from 2E-U823 ($\text{Na}_2\text{H}_2\text{-EDTA}$) to K4E-U823 ($\text{K}_4\text{-EDTA}$) predominantly decreased the total aluminum content, while the framework aluminum slightly increased. Acid and base treatments also decreased $[\text{Al}]$, whereas the Al_{VI} species was found (A-U823 and B-U823).

Fig. 5. Comparison of $[\text{Al}_\text{F}]$ determined by ^{29}Si NMR and XRD.Fig. 6. ^{27}Al NMR spectra of zeolite samples.

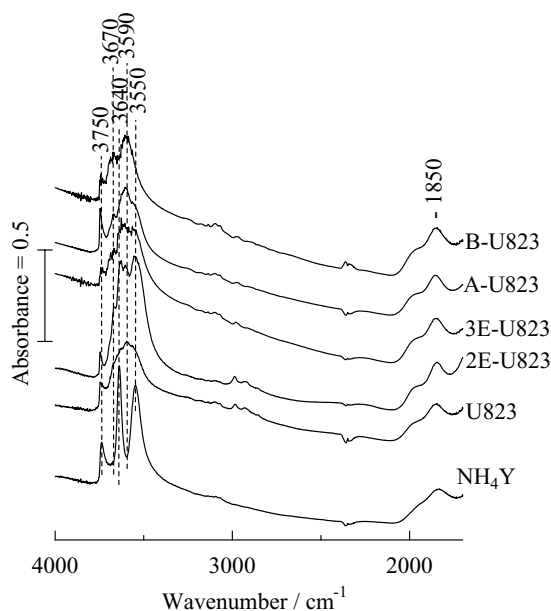


Fig. 7. IR spectra in hydroxyl region collected after in-situ evacuation at 773 K.

3.3. IR

Terminal silanol (3750 cm^{-1}), bridged Si–OH–Al (3640 cm^{-1}) and bridged Si–OH–Al in sodalite cage (3550 cm^{-1}) were observed in IR spectrum of the evacuated NH_4Y , namely the in situ prepared HY (Fig. 7). Steaming weakened the intensities of bridged Si–OH–Al bands and generated the peaks ascribed to the extra-framework Al–OH species at 3670 and 3590 cm^{-1} [45]; there is an opinion that the latter peak is attributed to silanols in defects [46]. The $\text{Na}_2\text{H}_2\text{–EDTA}$ treatment regenerated the bridged Si–OH–Al, while the acid treatment generated relatively large amount of the terminal silanols.

The IR spectrum of adsorbed pyridine indicates that the evacuated NH_4Y , i.e. the in situ prepared HY, has both Brønsted and Lewis acidity, since the bands attributed to the pyridinium cation bound to the Brønsted acid site and the pyridine molecule coordinated to the Lewis acid site were observed at 1544 and 1457 cm^{-1} , respectively (Fig. 8). On the other hand, the number of acid site was close to the $[\text{Al}_\text{F}]\text{–}[\text{Na}]$ composition, as shown by the ammonia TPD (vide infra), indicating the stoichiometric generation of one acid site by one framework aluminum atom. The following equilibrium can be assumed [47]. The Brønsted acid site must be the proton H_a in this model, as well established. In contrast, origin of the Lewis acid site is unclear. A possible model is the vacant orbital of the tricoordinated aluminum Al_a .

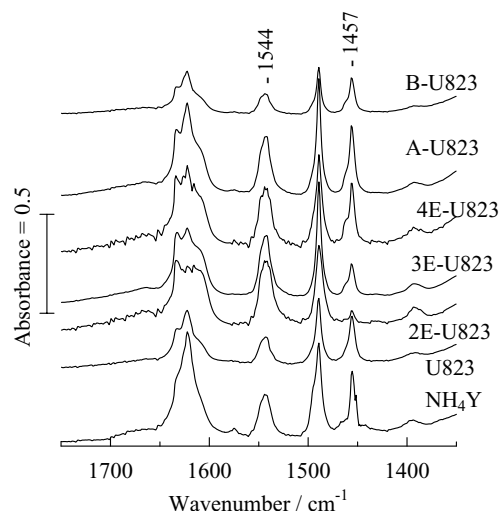
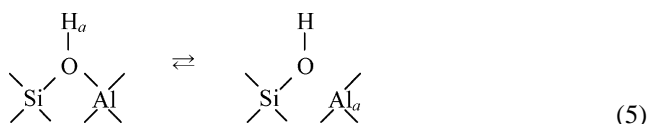


Fig. 8. IR spectra collected after in-situ evacuation at 773 K followed by adsorption of pyridine at 373 K and evacuation at 573 K.

On the steamed USY (U823), relatively large amount of Lewis acid site compared to Brønsted acid site was observed. $\text{Na}_2\text{H}_2\text{–EDTA}$ treatment of the USY almost completely suppressed the Lewis acidity (2E-U823). Increasing the basicity of EDTA salt from 2E-U823 to 4E-U823 gradually increased the Lewis acidity. The acid and base treatments resulted in considerable amounts of both Brønsted and Lewis acid sites.

3.4. Ammonia TPD

The ammonia TPD spectrum of the evacuated NH_4Y , namely the in situ prepared HY, showed a large desorption peak at a low temperature 500 K (Fig. 9). The number of acid site was found to be ca. 4.6 mol kg^{-1} , almost the same as

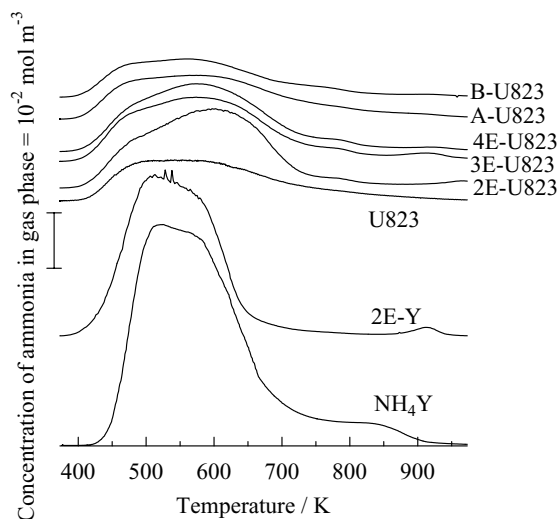


Fig. 9. Ammonia TPD spectra recorded after in-situ evacuation at 773 K followed by adsorption of ammonia and water vapor treatment at 373 K.

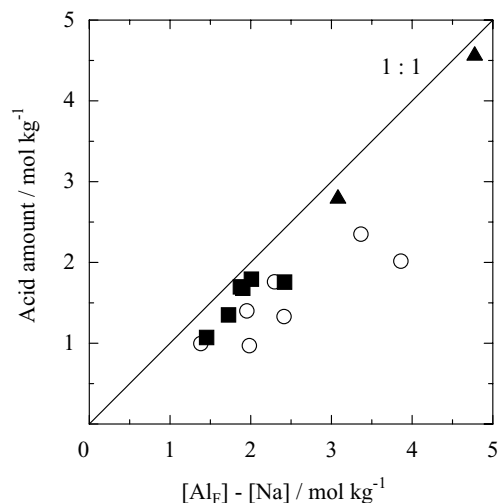


Fig. 10. Total acid amount as a function of $[Al_F]-[Na]$ on NH_4Y and 2E-Y (▲), USY steamed at various temperatures (○), and USY steamed at 823 K followed by treatments with various solutions (■).

$[Al_F]-[Na]$ (▲ in Fig. 10). The heat of ammonia adsorption was proved to be 111 kJ mol^{-1} according to the curve-fitting method [22]. The acid amount was decreased by the treatment with Na_2H_2-EDTA of NH_4Y down to 2.8 mol kg^{-1} , also similar to $[Al_F]-[Na]$ (2E-Y). The heat of ammonia adsorption was kept at 110 kJ mol^{-1} .

Steaming the NH_4Y made the TPD spectrum broad. The acid amount was significantly decreased. As shown in Fig. 10 (○), the acid amounts of the steamed USY samples were generally lower than $[Al_F]-[Na]$. The desorption of ammonia continued up to ca. 950 K pointing out the formation of strong acid site. The adsorption heat could not be determined by the curve-fitting method [22] because of the broad peak shape.

The treatment with EDTA salts enhanced the acid amount of U823. The peak maximum of 2E-U823 was observed at ca. 600 K, and the peak shape was relatively sharp. Increasing the basicity of EDTA salt from 2E-U823 to 4E-U823, the peak maximum slightly shifted lower. The simple base treatment (B-U823) shifted the peak maximum furthermore. The acid treatment (A-U823) resulted in a similar peak shape to that of U823. The acid amount of the USY steamed at 823 K followed by the treatments with various reagents approximately agreed to the $[Al_F]-[Na]$ content (■ in Fig. 10).

A similar TPD spectrum of the Na_2H_2-EDTA -treated USY has been reported by Rhodes et al. [37], but they did not analyze the acid strength. Here we analyze these spectra furthermore. In order to study the acid strength distribution, we assumed that the desorption peak of the modified U823 consisted of three fragments h_2-h_4 with ca. 126, 180 and 230 kJ mol^{-1} , respectively, and deconvoluted by means of the curve-fitting method [22] as shown in Fig. 11. Every sample had a peak shoulder at ca. 450 K, and this shoulder could not be fitted with the simulated curve, suggesting that the assumption of the curve-fitting method is not applicable

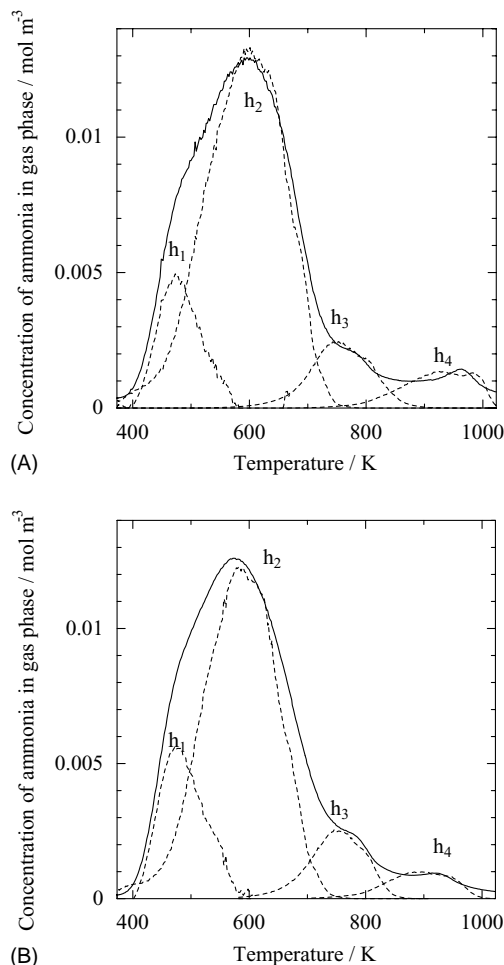


Fig. 11. Deconvolution of ammonia TPD spectra of 2E-U823 (A) and 4E-U823 (B).

to this shoulder. This method assumes that the desorption of ammonia is controlled by the equilibrium [21], but the diffusion of ammonia in micropore of zeolite may affect the apparent desorption rate at such a low temperature. Therefore, the difference (observed concentration of ammonia in gas phase) – (sum of the simulated fragments h_2-h_4) was assumed to be the fragment h_1 with the weakest acidity. The heat of ammonia adsorption of this type of acid is estimated to be ca. 110 kJ mol^{-1} , on the basis of the one-point analysis [21]. Because the acid strength was similar to that of the in situ prepared HY, the h_1 type acid site should be due to the framework aluminum.

The amounts of these fragments are summarized in Table 3. The Na_2H_2-EDTA -treated sample mainly possessed the h_2 type acid site. Enhancing the basicity of the EDTA salt from 2E-U823 to 4E-U823 decreased the h_2 type and increased the h_1 and h_3 types. The treatment with ammonia water (B-U823), namely the simple base treatment, significantly decreased the h_2 type. The acid treatment (A-U823) yielded also a relatively small fraction of the h_2 type.

Table 3

Acidic and catalytic properties of zeolite samples treated with various conditions

Sample	Acid amount (mol kg ⁻¹)					Conversion (%)		
	Total	<i>h</i> ₁	<i>h</i> ₂	<i>h</i> ₃	<i>h</i> ₄	Octane	2,2,4-Trimethylpentane	1,3,5-Triisopropylbenzene
NaY	0.08							
NH ₄ Y	4.56	4.01	0.32	0.18	0.05	0.0	11	37
2E-Y	2.89	2.59	0.00	0.20	0.10	0.5		
U573	2.02	^a	^a	^a	^a	11	56	
U673	2.35	^a	^a	^a	^a	23	69	
U823	1.40	^a	^a	^a	^a	28	64	24
U873	1.33	^a	^a	^a	^a	16	66	
U973	0.97	^a	^a	^a	^a	6.4	68	19
2E-U823	1.68–2.08	0.09–0.28	1.29–1.48	0.17–0.18	0.08–0.14	62–80	89	56
3E-U823	1.79	0.21	1.28	0.16	0.14	66		
4E-U823	1.70	0.30	1.15	0.17	0.08	58		
K4E-U823	1.76	0.42	0.97	0.29	0.08	51		
A-U823	1.35	0.21	0.82	0.22	0.10	44		
B-U823	1.07	0.15	0.64	0.23	0.05	35		
U (CCIC)	0.96	^a	^a	^a	^a	36	88	26

^a Could not be deconvoluted because of the broad peak shape.

3.5. Catalytic activity

The evacuated NH₄Y, namely the in situ prepared HY, showed almost no activity for the cracking of octane under the present conditions (Table 3). The 2E-Y sample, the NH₄Y treated with Na₂H₂–EDTA, also showed almost no activity. The activity for octane cracking was generated by steaming. Increasing the steaming temperature enhanced the activity, and the maximum activity was observed at 823 K. The higher temperature decreased the activity. The activity for cracking of 2,2,4-trimethylpentane was generally higher than that for octane (Table 3), because the reactivity of a branched alkane is substantially higher than a linear one. The activity for the branched alkane was also low on NH₄Y, and significantly enhanced by steaming.

The Na₂H₂–EDTA treatment of U823 greatly enhanced the activity for cracking of octane, as shown in Table 3 (2E-U823). In order to confirm the reproducibility, this catalyst was prepared three times by the same procedure from the NaY. The observed conversion was in the range from 63 to 80%, and the average value was 69%. The Na₃H–EDTA-treated U823 also showed a high activity (3E-U823). These activities were considerably higher than that on the commercially available sample [U (CCIC)]. Enhancing the basicity of EDTA salts from 3E-U823 to K4E-U823 decreased the activity. Both acid and base treatments (A-U823 and B-U823) also increased the activity of U823, but the increase was relatively small. The activity for cracking of 2,2,4-trimethylpentane was also enhanced by the Na₂H₂–EDTA treatment.

Here we have to note that the yielded high activity will be difficult to apply to the practical use. These experiments were carried out under the in situ conditions; the treated-USY sample containing Na was ion-exchanged, dried at 373 K, stored as NH₄ form and heated in helium in-situ at 773 K to remove ammonia just before the activity measurement.

After calcination of the 2E-U823 sample at 773 K in air followed by exposure to atmosphere for 2 days, the conversion was decreased to 39%, almost the same as that on the commercially available USY [U (CCIC)].

The activity for cracking of 1,3,5-triisopropylbenzene was high on the evacuated NH₄Y, and decreased by steaming. The Na₂H₂–EDTA treatment also significantly enhanced the activity for this reaction. The activity of 2E-U823 was higher than that of the commercially available USY [U (CCIC)].

4. Discussion

4.1. Acid site by framework Al

The evacuated NH₄Y, i.e. the in situ prepared HY zeolite, showed the amount of acid site close to the [Al_F]_{tot}–[Na] content, as shown in Fig. 10 (▲). The 1:1 stoichiometry has been obtained between the acid amount and [Al_F]_{tot}–[Na] on mordenite, ZSM-5 [22] and β [24] type zeolites when both aluminum and sodium contents were varied, and Y type when the sodium content was varied at a constant aluminum content [23]. In addition, this study clarified that the acid amount of 2E-Y, which was prepared by the simple dealumination of NH₄Y without formation of the extra-framework aluminum, also agreed with [Al_F]_{tot}–[Na]. In other words, the number of acid site is always in agreement with the 1:1 stoichiometry against the [Al_F]_{tot}–[Na] content.

The heat of ammonia adsorption of the in situ prepared HY, namely the evacuated NH₄Y, was ca. 110 kJ mol⁻¹ [23]. The acid strength of 2E-Y sample, which was prepared by the simple dealumination of NH₄Y without the formation of extra-framework aluminum, was almost the same as that of the parent NH₄Y. Therefore, we can conclude that the strength of Brønsted acid site generated by the isomorphous substitution of Al for Si in the FAU framework is

independent of the framework aluminum content at least in the experimental range of the aluminum content. This simple conclusion is commonly observed on other zeolite types [15].

The acidity due to the framework aluminum in FAU (ca. 110 kJ mol^{-1} of the ammonia adsorption heat) was weaker than those in MOR, MFI and *BEA (145, 135 and 125 kJ mol^{-1} , respectively [15,22,24]), and probably the weakest among aluminosilicates. No and quite low catalytic activity for the cracking of octane and 2,2,4-trimethylpentane, respectively, was observed on the in situ prepared HY and the $\text{Na}_2\text{H}_2\text{-EDTA}$ -treated NH_4Y (2E-Y). It is noteworthy that the present reaction temperature is low compared to the industrial process of alkane cracking, and therefore it is possible that the weak acid site due to the aluminum in FAU framework catalyzes the alkane cracking in the practical conditions.

The in-situ prepared HY however showed a high activity for the cracking of 1,3,5-triisopropylbenzene, probably because the dealkylation of aromatic hydrocarbon readily proceeded even on the weak Brønsted acid site, as widely believed [48].

4.2. Strong Brønsted acidity and high activity for alkane cracking generated by EDTA salt treatment

The ammonia TPD of the steamed USY in this study showed a relatively small but broad desorption spectrum which continued up to a quite high temperature, indicating the creation of strong acid sites by dealumination of Y zeolite, as known well [13]. However, the simple change in the framework aluminum content did not create the strong acid site, as observed for the 2E-Y sample. The enhancement of acid strength should therefore be related with the formation of extra-framework aluminum species by steaming.

From the broad peaks in the ^{27}Al NMR and IR of hydroxyl region, it is speculated that the extra-framework aluminum in the steamed USY contained various structures, i.e. $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})^{2+}$ cations bound to the ion-exchange site, small alumina particle interacting with the Brønsted acid site in micropore, small or large alumina particle on the external surface, those in amorphous silica–alumina complex and partly distorted framework aluminum. Because the ammonia TPD spectrum was very broad and both Lewis and Brønsted acids were observed in the IR of adsorbed pyridine, it is considered that various types of acid sites were generated by various extra-framework species. Generation of the activity for alkane cracking by steaming suggests that the active site should be hidden among these new acid sites.

The EDTA salt treatment simplified the acidic property of the USY. The IR of adsorbed pyridine demonstrates that most of acid sites on these samples were of a Brønsted type. The relatively sharp peak of TPD spectrum indicates the narrow distribution of acid strength. The deconvolution of the TPD spectrum shows that the acid sites of the $\text{Na}_2\text{H}_2\text{-EDTA}$ -treated USY zeolites are predominantly clas-

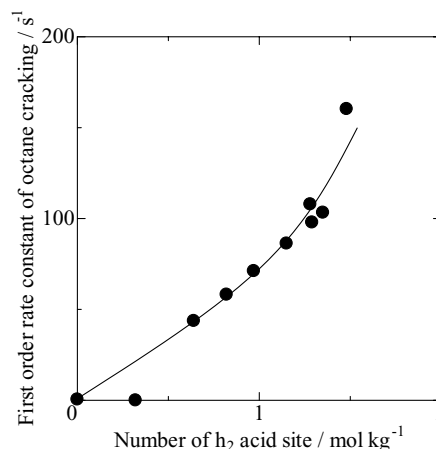


Fig. 12. Plots of catalytic activity for octane cracking against acid amount of h_2 on NH_4Y and 2E-Y (○), and USY steamed at 823 K followed by treatments with various solutions (●).

sified as one kind, h_2 type. The ammonia adsorption heat was $125\text{--}127 \text{ kJ mol}^{-1}$, which was obviously larger than that of the usual Y zeolite ($\Delta H^0 = 110 \text{ kJ mol}^{-1}$) [23], and close to those of zeolite β [24] and WO_3/ZrO_2 [49].

The activity for octane cracking was quite high on the $\text{Na}_2\text{H}_2\text{-EDTA}$ -treated USY, and decreased with an increase in the basicity of EDTA salt from $\text{Na}_2\text{H}_2\text{-EDTA}$ to $\text{K}_4\text{-EDTA}$ accompanied with a decrease in the amount of h_2 acid sites.

The reaction order of octane cracking depends on the experimental conditions and nature of catalyst, but here the first order kinetics is assumed. The first order rate constant is $-\{\ln(1-x)\}/t$, where x is the conversion, and t is the contact time estimated to be $1.00 \times 10^{-2} \text{ s}$. Fig. 12 shows a positive relationship between the number of h_2 acid sites and the catalytic activity for alkane cracking. The strong Brønsted acid site must have the high catalytic activity for the reaction of alkane. This type of acid site is not observed on the parent HY zeolite, and generated by steaming (USY). The following EDTA salt (especially $\text{Na}_2\text{H}_2\text{-EDTA}$) treatment increased this type of acid site. The high activity for the cracking of 1,3,5-triisopropylbenzene also supports the strong Brønsted acidity of the EDTA salt-treated USY.

The improvement of activity for catalytic cracking by the modification of Y zeolite has been explained as follows [7]:

- (1) Steaming the Y zeolite forms mesopores to enhance the diffusibility of reactant, but extra-framework alumina particles formed by the dealumination block a fraction of micropore.
- (2) The post treatment with acid or EDTA salt removes the aluminum particles to enhance the activity.

According to this explanation, the steaming must increase the mesoporosity but decrease the microporosity. The EDTA treatment must increase the microporosity. However, the mesoporosity was almost unchanged by the steaming as shown in Fig. 2, while the activity was generated,

and moreover, the microporosity was not improved by the EDTA treatment, while the activity was greatly enhanced. The present study points out the importance of the modification of acidic property. Kotrel et al. also emphasizes the importance of acidity to interpret the high activity of the modified Y zeolite [13].

4.3. Speculation on structure of strong Brønsted acid site on EDTA-treated USY

The interpretation of NMR of the USY treated with the EDTA salts is not easy. The ^{29}Si NMR shows that they have a considerable amount of the extra-framework aluminum. From the ^{27}Al NMR, if a broad baseline drift is ignored, it looks as if all the aluminum atoms are located in the framework position as tetra-coordinated atoms, because only Al_{IV} species at ca. 60 ppm were observed. In order to solve this problem, some explanations are possible. For example:

- (1) There are tetra-coordinated extra-framework aluminum species, like β zeolite [50] and Y zeolite modified by a different method [51].
- (2) There lies “NMR-invisible aluminum” at the extra-framework position.

The explanation (1) is hardly acceptable at least in this study, because the peak at ca. 60 ppm in the ^{27}Al NMR of the treated USY was quite sharp, suggesting that this peak did not consist of multiple fragments due to the framework and extra-framework species, and at almost the same position as that of the framework species in the parent NH_4Y . The peak at ca. 60 ppm was therefore attributed to the framework aluminum in this study. Therefore a considerable amount of the NMR-invisible aluminum species is supposed to be present on the USY treated with the EDTA salts. There possibly exists a quite broad peak of this species from 150 to -100 ppm in the spectra of these samples. Remy et al. quantitatively analyzed the ^{27}Al NMR of USY zeolite based on the assumption of six fragments including such a broad peak [52].

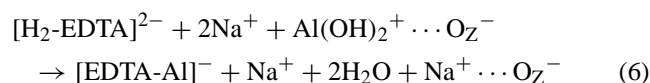
The Al species giving a very broad spectrum in the ^{27}Al NMR has been explained by the structural anisotropy [38,53]. In some cases, the spectrum of this species sensitively depends on the degree of hydration, showing a tendency to become sharp by the exposure to humid atmosphere. In this study, all the spectra were collected after exposure to the atmosphere containing ca. 80% of the relative humidity for more than 2 days. The broad peak shape even after the hydration indicates that the present NMR-invisible Al species was substantially anisotropic in the structure.

Enhancing the basicity of the EDTA salt decreased the total aluminum content, while the framework aluminum slightly increased. Therefore, the NMR-invisible species was decreased with enhanced basicity of the EDTA salt. The activity was also decreased by these treatments.

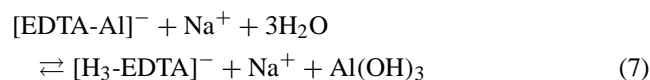
From these findings, we conclude that the NMR-invisible extra-framework aluminum species is increased by the $\text{Na}_2\text{H}_2\text{EDTA}$ treatment of the USY zeolite, and that this

species is the origin of the h_2 type acidity and therefore the activity for alkane cracking. It is speculated that the interaction between this species and the original Brønsted acid site is necessary to generate the h_2 acid site because of the following two reasons; the nature of this acid site was Brønsted type, while aluminum oxide alone usually generates Lewis acidity; the total acid amount agreed with the $[\text{Al}_\text{F}] - [\text{Na}]$, suggesting that the framework aluminum atom principally generated the acid site. The interaction between the framework Brønsted acid site and the NMR-invisible Al species should enhance the acid strength.

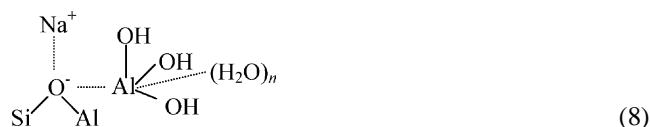
As described above, various extra-framework aluminum species are supposed to be present on the steamed USY zeolite. The EDTA salt is considered to dissolve a fraction of the extra-framework aluminum species into an anion at an elevated temperature in a basic medium based upon the chelating ability, for example as shown by Eq. (6).



where EDTA shows $(\text{O}_2\text{CCH}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CO}_2)_2$ and O_Z^- shows the ion exchange site of zeolite. The solubility of the formed salt $\text{Na}[\text{EDTA-Al}]$ is probably low, and therefore equilibrium (7) is supposed.

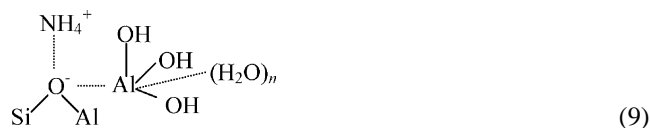


The formed aluminum hydroxide must precipitate soon, and probably, will be deposited on the zeolite. It is rational that the position where it deposits is close to the ion-exchange site because some electronic interactions can occur. However, the ion-exchange site itself should be blocked by sodium cation. Therefore the structure (8) is speculated.

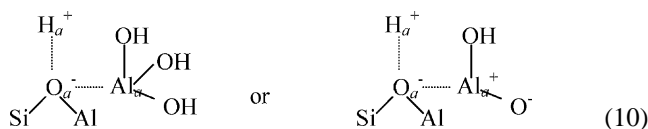


Probably, the oxygen anion in this species interacts with the Si or Al cation in the zeolite framework, and the hydrogen atom interacts with the oxygen anion, because a monomer of $\text{Al}(\text{OH})_3$ should be unstable. Moreover, water molecules may be adsorbed in humid atmosphere.

After the ion-exchange from Na^+ into NH_4^+ , the structure (9) is supposed. The difficulty in observation of this species by the ^{27}Al NMR should be due to the fact that this structure is strongly affected by the interactions with the surrounding cations and anions, resulting in the high structural anisotropy.



After the removal of NH_3 , the strength of formed Brønsted acid site [H_a in (10)] is considered to be enhanced by the interaction between O_a and Al_a . This could be the h_2 type acid site.



The enhancement of acid strength of framework aluminum site by the interaction with extra-framework aluminum has been proposed for various zeolites [54].

Remy et al. have shown the good correlation between the concentration of $\text{Al}(x)$ species, which showed a broad peak in the ^{27}Al NMR, and catalytic activity for the alkane cracking on some commercially available USY samples [52]. The present study agrees well with this experimental observation, because the NMR-invisible species exactly means the species with a quite broad NMR peak.

Thus it is considered that the high catalytic activity of the modified Y zeolite for the alkane cracking is due to the strong Brønsted acidity. The most important finding of this study is the clear relationship between the activity and number of a certain type of acid sites (Fig. 12). Because the structure of the strong acid site has not been clear, such an advanced technique as triple quantum NMR [35] is required for further investigation, but this study demonstrates that the quantitative analysis of acid sites can open a new insight.

5. Conclusion

The acidity of Y zeolite was weak, and therefore it was almost inactive for the cracking of octane at 573 K. Steaming of Y zeolite generated multiple types of extra-framework aluminum and both Brønsted and Lewis acid sites with a wide distribution of strength to create the cracking activity. The strong Brønsted acid sites were increased by the treatment with $\text{Na}_2\text{H}_2\text{EDTA}$, and the cracking activity was significantly enhanced. A good relationship was observed between the activity and the number of this type of acid sites, showing the origin of cracking activity of USY zeolite.

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