Detection of active sites for paraffin cracking on USY zeolite by ^{27}Al MQMAS NMR operated at high magnetic field 16 T

Naonobu Katada [a,b,*], Shinichi Nakata [c], Sumio Kato [c],
Koji Kanehashi [d], Koji Saito [d], Miki Niwa [a]

[a] Department of Materials Science, Faculty of Engineering, Tottori University, 4-101 Koyama-cho Minami, Tottori 680-8552, Japan
[b] Conversion and Control by Advanced Chemistry, PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[c] Department of Materials Process Engineering and Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University, 1-1 Tegata Gakuen-machi, Akita 010-8502, Japan
[d] Advanced Technology Research Laboratory, Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan

Abstract

^{27}Al MAS (magic angle spinning) and 3Q (triple quantum) MAS NMR (nuclear magnetic resonance) at a very high magnetic field (16 T, 700 MHz for ^{1}H) enabled us to detect all the Al species on a series of modified Y zeolites. In a USY (ultra stable Y) zeolite after steaming, extra-framework Al species with various environments were detected, while only framework Al (IV) was observed in the parent NaY zeolite. 3QMAS NMR clearly identified the tetra-coordinated extra-framework Al with a large structural anisotropy (IV_b), in addition to the penta-(V) and hexa-coordinated (VI) species. Na_2H_2-EDTA (ethylenediaminetetraacetic acid) treatment of the USY was found to convert the V and VI species into the IV_b species. Increase in the Brønsted acid strength and the catalytic activity for octane cracking has been found on the Na_2H_2-EDTA-treated USY. Therefore, it is speculated that the IV_b species is the origin of enhanced Brønsted acidity (and thereby the high cracking activity) of the USY zeolite.
© 2005 Elsevier B.V. All rights reserved.

Keywords: EDTA-treated USY zeolite; ^{27}Al 3QMAS NMR; Extra-framework Al; Paraffin cracking; Brønsted acidity

1. Introduction

Ultra stable Y (USY) zeolite is utilized as a solid acid catalyst for paraffin (alkane) cracking in gasoline production, one of the largest industrial processes [1]. It is known that the acid site (H$^+$) of zeolite is generated by the isomorphous substitution Al^{3+} for Si^{4+} in the silicate framework. However, generation of the activity for the cracking on USY is difficult to explain. The cracking activity is generated during the stabilization process of parent Y zeolite (inactive for the cracking) into the USY by steaming [2], and enhanced by the following modification such as Na_2H_2-EDTA (ethylenediaminetetraacetic acid) treatment [3]. During these treatments, decrease in the framework Al (dealumination) [4], re-insertion of Al [5], structural change of Al species [6] and formation of mesopores [7] simultaneously occur. In order to find the most important factor, the analysis of microstructure and acidic property should be necessary. In addition, systematic study based on the samples with known structures is needed. However, these have not been achieved. The origin of cracking catalysis of USY zeolite has been unclear even now, and therefore the USY has been utilized for ca. 40 years.

We have analyzed the acidic properties of a series of modified Y zeolites by means of a developed method of ammonia temperature-programmed desorption (TPD). The Y zeolite had only weak acid sites [8]. After steaming, acid sites with various strengths and nature (Lewis and Brønsted) were observed on the USY. After the Na_2H_2-EDTA treatment, most acid sites were Brønsted type, and possessed a

* Corresponding author. Tel.: +81 857 31 5684; fax: +81 857 31 5684.
E-mail address: katada@chem.tottori-u.ac.jp (N. Katada).

high acid strength with a small distribution. The cracking activity showed a positive relationship against the number of strong acid sites on the USY zeolites modified with various reagents. Other properties could not explain the high activity on the Na_2H_2-EDTA-treated USY, whereas global characterization was carried out. The origin of cracking activity of USY should be the strength of Brønsted acid sites enhanced by some specific extra-framework Al species which were formed by steaming and increased by the Na_2H_2-EDTA treatment [6].

The structural character of the strong Brønsted acid site should be also clarified. However, ^{27}Al NMR (nuclear magnetic resonance), the most promising tool for the structural analysis, suffered from the presence of Al species invisible under ordinary NMR conditions such as 7–9 T of magnetic field (300–400 MHz frequency for ^{1}H) and 4 kHz of magic angle spinning (MAS) rate [9]. In our previous study, the amount of strong Brønsted acid sites was related with the invisible Al [6]. The positive relationship between the activity and amount of the Al species giving a very broad NMR signal has been pointed out by Remy et al. [10] On the other hand, Gola et al. have pointed out that the Na_2H_2-EDTA-treated USY was enriched with the invisible Al [11].

A very high magnetic field such as 16 T has become applicable to the NMR measurement. Coster and Fripiat [12], and Fyfe et al. [13] have applied it to some samples of the USY zeolite. In addition, a multiple quantum (MQ) method of NMR [14] becomes a promising tool for identification of the Al species in zeolite, and has already been applied to the USY zeolite [11]. Fyfe et al. applied the ^{27}Al 3Q (triple quantum) MAS NMR at 9–18.8 T to the USY zeolite and concluded that 14.4 to 18.8 T of the field strength was high enough for detection of all the Al species in the USY zeolite [13]. Aluminum species with various environments were found by this study, but the analysis has been carried out on only one sample of steamed USY, and the analyzed structure has not been related with the catalytic property. We here apply the NMR at 16.4 T (700 MHz for ^{1}H) with the 3Q technique to the USY and Na_2H_2-EDTA-treated USY zeolites, in order to show the structural change of the extra-framework Al species by the Na_2H_2-EDTA treatment, and to identify the active species for the catalytic cracking.

2. Experimental

2.1. Sample preparation

A sodium Y (NaY) zeolite with Si/Al_2 molar ratio 5.1 was kindly supplied by Catalysts and Chemicals Industries, Co. Ltd. It was ion-exchanged into NH_4Y [8], and steamed at 823 K for 1 h in a flow of water vapor and nitrogen (4:6 molar ratio) [6]. Thus obtained USY was stirred in an aqueous solution of Na_2H_2-EDTA (0.1 mol dm^{-3}) at 391 K for 24 h under refluxing, followed by filtration, ion-exchange with NH_4NO_3 solution and drying at 373 K as described previously [6].

The chemical composition was measured by a Shimadzu ICPS-5000 inductively coupled plasma emission spectrometer (ICP-ES) after dissolving the sample into hydrofluoric acid.

2.2. ^{27}Al NMR measurements and analysis

The NMR measurements were carried out after the exposure of samples to an atmosphere at 80% of the relative humidity for several days. ^{27}Al NMR experiments at 16 T were carried out at $\omega_0/2\pi = 182.4$ MHz with a JEOL ECA-700 spectrometer (16.4 T magnet). A 4 mm NB single-resonance JEOL MAS probe was used with sample spinning rate of $\omega_r/2\pi = 18$ kHz. The single pulse excitation sequence with radio frequency flip angle of about $18°$ was used in ^{27}Al MAS spectra in order to avoid the quadrupolar nutation effects.

For odd half-integer quadrupolar nuclei such as ^{27}Al, the frequency shifts due to the second-order quadrupolar interaction whereas multiple quantum transition ($-m \leftrightarrow +m$) is not affected by the first-order quadrupolar interaction. During the MQMAS experiment, multiple quantum coherence ($-m \leftrightarrow +m$) is excited and evolves for a period of t_1. It is then converted to single quantum coherence ($-1/2 \leftrightarrow +1/2$) and isotropic echoes are formed at t_2. Then, isotropic echoes are detected at the expected acquisition times.

$$t_2 = \left| \frac{C_4^I(m)}{C_4^I(1/2)} \right| t_1 \tag{1}$$

where $C_4^I(m)$ is fourth-rank coefficients that depend on the $-m \leftrightarrow +m$ transition and I spin number. For ^{27}Al nucleus ($I = 5/2$), $\left| C_4^I(m)/C_4^I(1/2) \right| = 19/12$ when 3Q excitation is applied.

In this study, the three-pulse sequence with z-filter which is selective to $\pi/2$ pulse at low rf-power was applied because of the symmetric coherence transfer yielding non-dispersion line shape [15]. Typical rf-field strength of $\omega_1/2\pi = 192$ kHz for both the multiple quantum excitation pulse and conversion pulse was employed while a weaker rf-field strength of $\omega_1/2\pi = 18$ kHz was used for z-filter selective pulse. Typical pulse durations are 2.5 μs (excitation), 0.9 μs (conversion) and 14 μs (z-filter). The hypercomplex sequence was used for collecting pure absorption mode line shapes [16]. Since skew 2D data were obtained in this MQMAS sequence, 2D spectra were paralleled to the F_2 dimension by the sharing transformation. For 3QMAS spectra in this report, scaling along the F_1 axis was done so that the slope of the chemical shift axis in 2D spectra equal 1. The ^{27}Al chemical shift was referenced to 1 mol dm^{-3} $AlCl_3$ aqueous solution at -0.1 ppm.

As a control, a spectrum was also collected at a low magnetic field (7 T, 300 MHz for ^{1}H) as described [6].

2.3. Other characterization

The crystal structure was analyzed using a Rigaku Miniflex plus X-ray diffractometer (XRD) with a Cu Kα X-ray

source. An ammonia TPD spectrum was collected using a BEL Japan TPD-AT-1 equipment after evacuation at 773 K followed by the adsorption of ammonia and the water vapor treatment at 373 K, as described previously [17]. An infrared (IR) spectrum was recorded 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 2.04×10^{-5} mol s^{-1} of helium flow, 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 first order reaction rate was assumed, and the first order rate constant $-\{\ln(1-x)\}/t$ was calculated from x (conversion) and t (contact time, 1.00×10^{-2} s).

3. Results

XRD showed that all the samples had the FAU structure. Table 1 shows a high micropore volume of the parent NaY, indicating the high crystallinity of this sample. The micropore volume was slightly decreased by steaming, and hardly changed by the following Na$_2$H$_2$-EDTA treatment. A small increase in the mesopore volume by steaming (0.007–0.012 cm^3 g^{-1}) was observed. A considerable increase in the mesopore volume (to 0.08 cm^3 g^{-1}) was observed after the Na$_2$H$_2$-EDTA treatment.

Table 1 also shows the change in framework aluminum content [Al$_F$]. On the parent NaY, most of the aluminum atoms were located in the framework, as shown by the similar [Al] and [Al$_F$] contents. The steaming at 823 K significantly decreased the framework aluminum content, resulting in only 2.0 mol kg^{-1} of the framework aluminum content in the USY. The Na$_2$H$_2$-EDTA treatment slightly decreased the framework aluminum [6]. Here, it should be noted that the agreement between the analyses of framework Al content
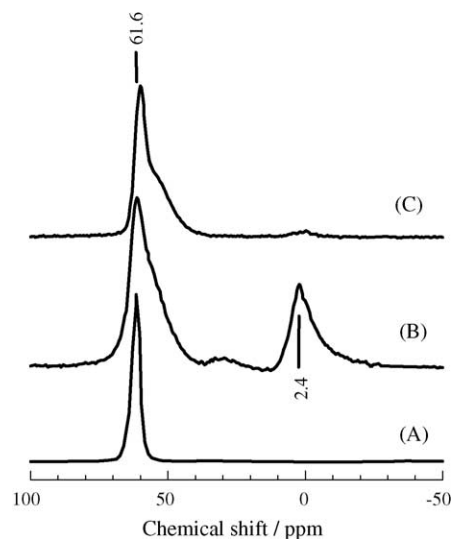

Fig. 1. ^{27}Al single pulse MAS NMR spectra at 16 T of NaY (A), USY (B) and Na$_2$H$_2$-EDTA-treated USY (C).

by the ^{29}Si NMR and XRD (unit cell dimension) on these samples has been confirmed [6].

Fig. 1 shows the single pulse NMR spectrum at 16 T. A narrow and symmetrical peak at 62 ppm on the parent NaY (A) indicates the presence of only one Al species, tetra-coordinated in the framework (termed IV species hereafter), as supported by only one peak in the ^{27}Al 3QMAS spectrum (Fig. 2, A). The USY (Fig. 1, B) had multiple species; hexa-coordinated species (VI) at 2 ppm, penta-coordinated species (V) at ca. 30 ppm, and tetra-coordinated species with large line broadening (IV$_b$) as a shoulder of the IV species. This observation is similar to those already reported based on the ^{27}Al NMR at the high magnetic field [12,13]. On the Na$_2$H$_2$-EDTA-treated USY (Fig. 1, C), the amounts of V and VI species were negligible, and most Al atoms formed the IV and IV$_b$ species; this is the most important finding in this study.

The 3QMAS NMR of USY and Na$_2$H$_2$-EDTA-treated USY (Fig. 2, B and C) clearly distinguished between the IV and IV$_b$ species. Table 2 shows the isotropic chemical shift

Table 1
Composition, peak intensities in ^{27}Al NMR, porosity, acidic property and cracking activity

Sample	Micropore volume[c] (cm^3 g^{-1})	Mesopore volume[c] (cm^3 g^{-1})	[Al][a] (mol kg^{-1})	[Al$_F$][b] (mol kg^{-1})	Relative peak intensity in ^{27}Al NMR at 16 T/%				Acid amount[d] (mol kg^{-1})	Averaged ammonia adsorption heat[d] (kJ mol^{-1})	Octane cracking rate constant[e] (s^{-1})
					IV	IV$_b$	V	VI			
NaY	0.396	0.007	5.2	4.9	100	0	0	0	4.56[f]	102[f]	0[f]
USY	0.352	0.012	5.5	2.0	33	35	4	29	1.40	112	33
Na$_2$H$_2$-EDTA-treated USY	0.358	0.080	5.0	2.2	40	56	0	4	1.68	120	102

[a] From ICP.

[b] From ^{29}Si NMR.

[c] From N$_2$ adsorption.

[d] From NH$_3$ TPD.

[e] By the pulse method at 573 K.

[f] Corresponding HY type zeolite.
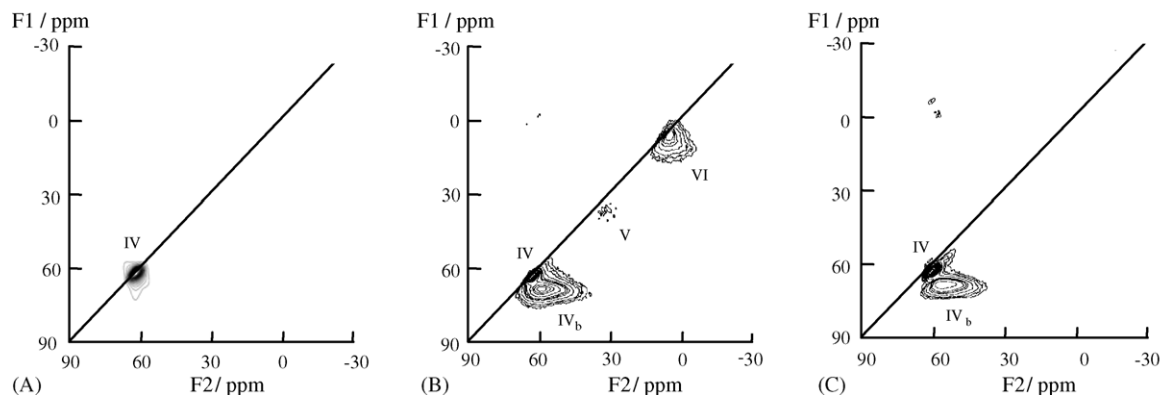
Fig. 2. ^{27}Al 3QMAS NMR spectra at 16 T of NaY (A), USY (B) and Na$_2$H$_2$-EDTA-treated USY (C).

($\Delta\delta$) and the quadrupolar coupling constant (C_Q) of each cross-section. On the USY and Na$_2$H$_2$-EDTA-treated USY, the IV$_b$ species had considerably a large C_Q (6.4 MHz) compared to the IV species (1.1 MHz), indicating lower structural symmetry of the IV$_b$ species.

The IV species was observed also in the conventional NMR spectra of all the samples at 7 T as shown in Fig. 3, while the VI species showed broad peaks, and the IV$_b$ and V species were quite unclear (practically invisible) on the USY (Fig. 3, B) and Na$_2$H$_2$-EDTA-treated USY (C) [6]. The advantage of the high magnetic field for detection of the Al species with high quadrupolar interaction is thus demonstrated.

The peak was deconvoluted into the fragments due to these species (Fig. 4), in order to discuss the change of contents of these species. Thus estimated peak intensities are summarized in Table 1. The intensities does not show the quantities of Al species directly, because the spectrum reflects only a fraction of quantum transitions. At least, the following qualitative changes were remarkable.

On the NaY, only the IV species was observed by the ^{27}Al NMR. By steaming, a considerable fraction of the framework (IV) species was converted into IV$_b$, V and VI species on the USY. The Na$_2$H$_2$-EDTA treatment diminished the V and VI species, while the IV$_b$ species increased.

Fig. 5 shows the ammonia TPD spectrum. As already reported, the HY zeolite prepared by conversion of NaY into NH$_4$Y through ion exchange followed by the in-situ evacuation showed a desorption peak at *ca.* 510 K (A). The number of acid sites was close to the number of aluminum atoms, and the heat of ammonia adsorption (an index of acid strength) was ca. 100 kJ mol^{-1} (Table 1). This type of acidity is attributed to the aluminum in the FAU framework [8]. The USY

showed a broad peak, indicating a wide distribution of acid strength (Fig. 5, B). The acid sites were decreased by steaming; the framework aluminum content was also decreased, but the acid amount was more significantly decreased (Table 1). The averaged adsorption heat was increased, showing the generation of strong acid sites. In the IR spectrum of adsorbed pyridine (Fig. 6, A and B) on these (HY and USY) zeolites, both pyridine molecules coordinated to Lewis acid sites (characteristic absorption, e.g., 1455 cm^{-1}) and pyridinium cations bonded to Brønsted acid sites (1545 cm^{-1}) were observed. It can be concluded that only weak acid sites were generated on the HY, and acid sites with various strengths and types (Lewis and Brønsted) were observed on the USY.

On the Na$_2$H$_2$-EDTA-treated USY, the adsorption heat was higher than on the HY and USY (Table 1). The peak of TPD was relatively narrow showing a narrow distribution of acid strength (Fig. 5, C). The nature of acid sites was mainly Brønsted type, as shown by the IR spectrum of pyridine (Fig. 6, C).

From these observations, it can be summarized that steaming (from HY into USY) diminished some of acid sites due to the framework aluminum, and increased the strength of some other acid sites; the Na$_2$H$_2$-EDTA treatment converted the acid sites into the strong Brønsted type.

Table 2
Isotropic chemical shift ($\Delta\delta$) and quadrupolar coupling constant (C_Q)

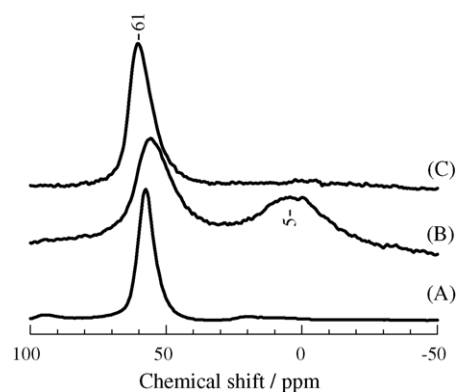|	NaY	USY				Na$_2$H$_2$-EDTA-treated USY	
	IV	IV	IV$_b$	V	VI	IV	IV$_b$
$\Delta\delta$ (ppm)	63.6	62.3	64.1	34.1	4.7	62.3	64.1
C_Q (MHz)	0.8	1.1	6.4	3.7	2.0	1.1	6.4

Fig. 3. ^{27}Al MAS NMR spectra at 7 T of NaY (A), USY (B) and Na$_2$H$_2$-EDTA-treated USY (C).

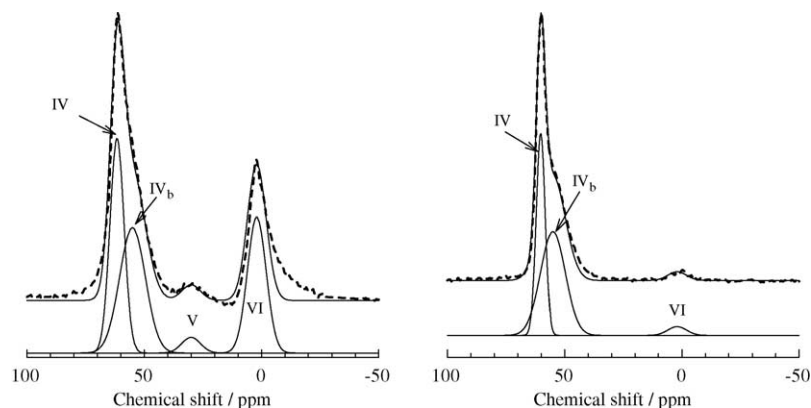Fig. 4. Deconvolution of single pulse spectra at 16 T of USY (left) and Na$_2$H$_2$-EDTA-treated USY (right). The experimental value is shown by a dotted line.
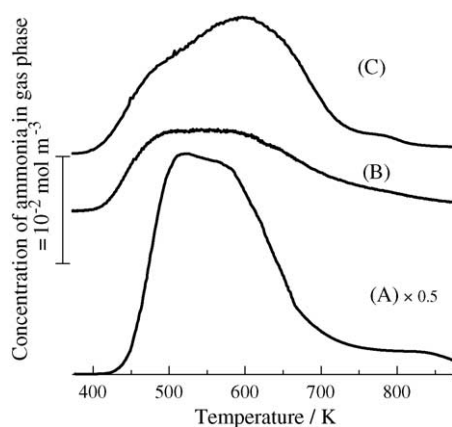

Fig. 5. Ammonia TPD spectra of HY in-situ-prepared from NH$_4$Y (A), USY (B) and Na$_2$H$_2$-EDTA-treated USY (C).

Table 1 also shows the catalytic activity. The activity for octane cracking at 573 K was negligible on the HY. The activity was generated by steaming (USY), and significantly enhanced by the Na$_2$H$_2$-EDTA treatment.
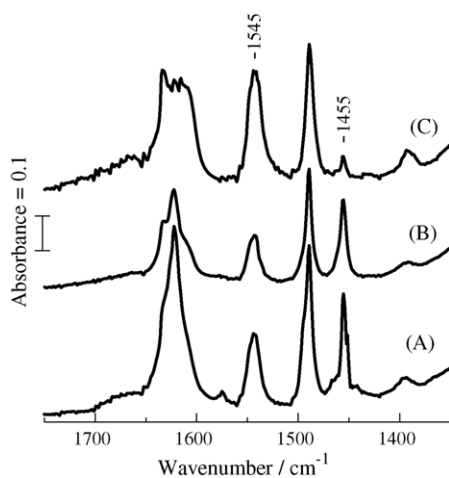

Fig. 6. IR spectra of pyridine adsorbed on HY in situ-prepared from NH$_4$Y (A), USY (B) and Na$_2$H$_2$-EDTA-treated USY (C).

4. Discussion

4.1. Proposal of a candidate species, IV$_b$, as the active site for catalytic cracking based on experimental findings

Formation of mesopores by steaming of Y zeolite has been proposed to enhance the activity for catalytic cracking of alkane [7]. However, because the active site is believed to be the acid site, we must take into account the change in acidic properties for the interpretation of catalytic activity for the alkane cracking. The increase in mesopore volume by steaming and the Na$_2$H$_2$-EDTA treatment could contribute to the enhancement of activity. However, it is difficult to explain the change in activity only from the porous structure. The HY showed no activity while it had mesopores. The increase in mesopore volume was small when the HY was converted into USY, while the activity was created. The analyses of microstructure of Al and acidic property provide a possible explanation as follows.
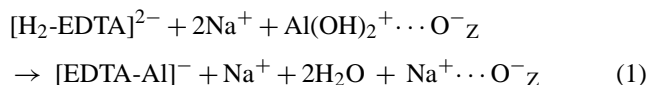
The cracking activity was not observed on the parent HY where most of the aluminum atoms were located in the framework. Steaming of Y zeolite created the activity, with the formation of strong acid sites. The activity was significantly increased by the Na$_2$H$_2$-EDTA treatment. After this treatment, most of the acid sites had a strong Brønsted nature. In addition, we have carried out the global characterization of a series of USY treated in various solutions (various EDTA salts, HNO$_3$, and NH$_3$). We found a clear relationship between the number of strong Brønsted acid sites and the activity for octane cracking at 573 K [6]. We thereby propose that the enhancement of catalytic activity is mainly due to the generation of strong Brønsted acidity.

Steaming converted a considerable fraction of the framework (IV) species into extra-framework (IV$_b$, V and VI) species. The Na$_2$H$_2$-EDTA treatment converted the V and VI species in the USY zeolite into the IV$_b$ species. From the viewpoint of microstructure, the Brønsted acidity and activity seem to increase with increasing IV$_b$ species. We here propose that the IV$_b$ species is the active site (more exactly, the species generating the activity) for the catalytic

cracking of alkane on the USY zeolite on the basis of these findings.

4.2. Schematic explanation for generation of strong acidity by Al IV$_b$ species

As described above, various extra-framework aluminum species are supposed to be present on the steamed USY zeolite. The EDTA salt is, based upon its chelating ability, considered to dissolve a fraction of the extra-framework aluminum species at an elevated temperature in a basic medium, for example as shown by Eq. (1).

$$[H_2\text{-EDTA}]^{2-} + 2Na^+ + Al(OH)_2^+ \cdots O^-_Z$$
$$\rightarrow [EDTA\text{-}Al]^- + Na^+ + 2H_2O + Na^+ \cdots O^-_Z \qquad (1)$$

where EDTA shows $(O_2CCH_2)_2N(CH_2)_2N(CH_2CO_2)_2$ and O^-_Z shows the ion exchange site of zeolite. The solubility of the formed salt $Na[EDTA\text{-}Al]$ is probably low, and therefore equilibrium (2) is supposed.

$$[EDTA\text{-}Al]^- + Na^+ + 3H_2O$$
$$\rightleftarrows [H_3\text{-EDTA}]^- + Na^+ + Al(OH)_3 \qquad (2)$$
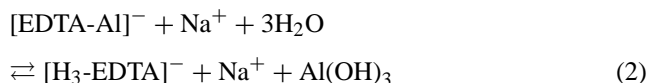
The formed aluminum hydroxide must precipitate soon, and will be probably deposited preferentially on the zeolite, because the zeolite has a large surface area and a strong electric field in the micropores. It is rational that the deposition occurs at the place close to the ion-exchange site, because some electronic interactions can occur. The ion-exchange site itself should be blocked by sodium cation in the Na_2H_2-EDTA solution. Therefore, the structure (3) is proposed.

$$\qquad (3)$$

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 $Al(OH)_3$ should be unstable.

After the ion-exchange of Na^+ for NH_4^+, the structure (4) is assumed. The Al_a in this drawing is presumed to be IV$_b$ species detected in the ^{27}Al NMR at the high magnetic field. The low structural symmetry of this species is consistent with this postulation, because it would strongly interact with the oxygen anion of the ion-exchange site of the left side in this drawing.

$$\qquad (4)$$

After the removal of NH_3, the strength of formed Brønsted acid site [H_a in (5)] is considered to be enhanced by the electron withdrawal from O_a by Al_a. The enhancement of acid

strength of framework aluminum site by the interaction with extra-framework aluminum has been proposed for various zeolites [18].

$$\qquad (5)$$

Finally we have to mention that the quantitative analysis has not been enough in this study. The activity showed a positive relationship with the peak intensity of IV$_b$ species as described above, but it was not a linear relationship. The following reasons can be adducted.

1) Here, first-order kinetics is assumed to analyze the reaction rate of octane cracking. However, the kinetics of alkane cracking is not simple. The reaction order is sensitive to the conditions.
2) As mentioned above, in addition to the effect of acidic property, the change in porosity can affect the apparent reaction rate.
3) As mentioned above, the peak intensity of single pulse spectrum of ^{27}Al NMR does not show the amount of species directly.

We are now studying the actual efficiency of these acid sites for the catalytic activity by means of a new method of ammonia TPD combined with IR; and it has suggested that a fraction of the Al species are not accessible by the reactants, probably because they are located in the small cavities of zeolite [19]. Therefore, the investigation should be continued, but the understanding of acid site in the modified USY zeolite is significantly advanced by using a new technique of ^{27}Al NMR at the high magnetic field. The ^{27}Al NMR at the high magnetic field revealed that the extra-framework Al species on the Na_2H_2-EDTA-treated USY zeolite were predominantly tetra-coordinated and anisotropic, and the possible role of this species in the catalytic cracking of paraffin is proposed.

5. Conclusions

1. ^{27}Al MAS NMR at 16 T enabled us to detect the tetra-coordinated Al species with a large structural anisotropy (IV$_b$) on the USY zeolite, while it was practically invisible at 7 T. The 3QMAS technique clearly identified this species.
2. On the NaY, only the framework Al (IV) was observed. By steaming, the IV$_b$, V (penta-coordinated) and VI (hexa-coordinated) species of extra-framework Al were formed on the USY. The Na_2H_2-EDTA treatment of the USY was found to convert the V and VI species into the IV$_b$ species.
3. The positive relationship between the peak intensity of IV$_b$ species and the catalytic activity suggests that the origin of enhanced Brønsted acidity (and thereby the high cracking activity) of the USY zeolite was the IV$_b$ species.

References

[1] C.V. McDaniel, P.J. Maher, US Patent, 3,292,192 (1966).

[2] L.A. Pine, P.J. Maher, W.A. Wachter, J. Catal. 85 (1984) 466.

[3] G.H. Kuehl, E.J. Edward, Eur. Patent 0142313-A1 (1984).

[4] J. Klinowski, J.M. Thomas, C.A. Fyfe, G.C. Gobbi, Nature 296 (1982) 533.

[5] D.-S. Liu, S.-L. Bao, Q.-H. Xu, Zeolites 18 (1997) 162.

[6] N. Katada, Y. Kageyama, K. Takahara, T. Kanai, H.A. Begum, M. Niwa, J. Mol. Catal., A: Chem. 211 (2004) 119.

[7] M. Kuehne, H.H. Kung, J.T. Miller, J. Catal. 171 (1997) 293.

[8] N. Katada, Y. Kageyama, M. Niwa, J. Phys. Chem., B 104 (2000) 7561.

[9] P.P. Man, J. Klinowski, J. Chem. Soc., Chem. Commun. (1988) 1291.

[10] M.J. Remy, D. Stanica, G. Poncelet, E.J.P. Feijen, P.J. Grobet, J.A. Martens, P.A. Jacobs, J. Phys. Chem. 100 (1996) 12440.

[11] A. Gola, B. Rebours, E. Milazzo, J. Lynch, E. Benazzi, S. Lacombe, L. Delevoye, C. Fernandez, Micro-. Mesopor. Mater. 40 (2000) 73.

[12] D. Coster, J.J. Fripiat, Chem. Mater. 5 (1993) 1204.

[13] C.A. Fyfe, J.L. Bretherton, L.Y. Lam, J. Am. Chem. Soc. 123 (2001) 5285.

[14] L. Frydman, J.S. Harwood, J. Am. Chem. Soc. 117 (1995) 5367.

[15] J.P. Amoureux, C. Fernandez, S.J. Steuenagel, Magn. Reson. A123 (1996) 116.

[16] D. Massiot, B. Touzo, D. Trumeau, J.P. Coutures, J. Virlet, P. Florian, P. Grandinetti, J. Solid State NMR 6 (1996) 73.

[17] M. Niwa, N. Katada, Catal. Surveys Jpn. 1 (1997) 215.

[18] A. Corma, Chem. Rev. 95 (1995) 559.

[19] K. Suzuki, N. Katada, M. Niwa, unpublished results.