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Multinuclear Solid-State NMR Study of Dehydration of Na–Y Type Zeolites

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High-resolution solid-state NMR spectra of ^{23}Na, ^{27}Al, and ^{29}Si nuclei were measured for dehydrated Na–Y type zeolites as well as undehydrated and rehydrated samples using magic angle sample spinning technique. ^{1}H NMR spectra, X-ray diffraction patterns, and thermal properties were measured as well. ^{23}Na NMR results indicate that there are three types of Na sites with different symmetries in the faujasite framework; two types with high and slightly low symmetries are detected by NMR, while the third cannot because of its very low symmetry. Na ions in high-symmetry sites are moved into slightly-low and very-low-symmetry sites by the dehydration. On the other hand, the Na ions in the amorphous region are located in low and very-low-symmetry sites. ^{27}Al and ^{29}Si NMR lines are broadened by the dehydration, due to the distortion of AlO_4 tetrahedra and the interaction with ^{27}Al nuclei, respectively. The ^{29}Si spin-lattice relaxation time becomes longer by the dehydration, which indicates that water molecules play some role in the relaxation.

Zeolites are crystalline aluminosilicates with many pores inside it. SiO_4 and AlO_4 tetrahedra are connected by sharing their oxygen atoms, and positive ions and water are located in the cage constructed by the SiO_4 and AlO_4 tetrahedra. The structures and properties of zeolites are largely influenced by the water molecules.

High-resolution solid-state NMR has been extensively used to study the structure of zeolites in recent years.[1] ^{29}Si NMR can distinguish Si atoms in zeolites according as the number of Al atoms coordinating to the Si atoms through oxygen atoms.[2] ^{27}Al NMR can resolve four-coordinated and six-coordinated Al,[3] i.e., lattice and extra-lattice Al. A number of NMR spectra have been measured for various zeolites so far, and comparisons have been made between them. But even if the network structures are the same, it is possible that the spectra are different depending on the hydration state. Actually, spectral changes caused by thermal treatment have been reported for the ^{29}Si spectra of ZSM-5[4] and the ^{27}Al spectra of ZSM-5 and H–Y zeolites[5,6] No extensive studies, however, have been published up to now.

In the present work, ^{23}Na, ^{27}Al, and ^{29}Si NMR spectra have been measured for dehydrated Na–Y zeolites as well as undehydrated and rehydrated samples, using magic-angle sample-spinning (MAS) technique,[7]) to study the effect of the hydration state on the NMR spectra. ^{1}H NMR spectra, X-ray diffraction pattern, and thermal properties were measured as well. Changes of the microscopic structure shown by the NMR results are discussed in relation to the hydration state. Since the NMR spectra have been measured for several nuclei in the same samples, the relations between the spectra of different nuclei are also discussed.

Experimental

Materials. Na–Y zeolite, coded JRC-Z-Y4.8, was supplied by Sansho-Shokubai-Iinkai, Catalysis Society of Japan. Dehydration was carried out in air at elevated temperatures. Dehydrated samples are called DE400, DE600, and DE800, which were dehydrated at 400 °C for 4 h, at 600 °C for 5 h, and at 800 °C for 5 h, respectively. Rehydration was performed by contacting the dehydrated samples with an excess of liquid water at room temperature for 2.5 d, after which the sample was dried at 70 °C for 1 d. Rehydrated samples are called RExxx, whose xxx denotes the dehydration temperature.

Measurements. High-resolution solid-state NMR spectra were measured by a JEOL FX-200 pulsed spectrometer equipped with an accessary for MAS. The resonance frequencies were 52.80, 52.00, and 39.60 MHz for ^{23}Na, ^{27}Al, and ^{29}Si nuclei, respectively. An ordinary one-pulse cycle was used under a MAS condition with a spinning speed of about 3.5 kHz. ^{1}H NMR spectra were also measured by a Bruker CXP-100 pulsed spectrometer, operating at a resonance frequency of 90.03 MHz and using the ordinary one-pulse cycle. Shift values are referred to NaCl aqueous solution for the ^{23}Na spectra (The shift of solid NaCl was 6.7 ppm with respect to this standard.), to $AlCl_3$ aqueous solution for the ^{27}Al spectra, and to tetramethylsilane for the ^{29}Si and ^{1}H spectra. All the measurements were carried out at room temperature.

Powder X-ray diffraction patterns were measured by a Rigaku Geiger-flex diffractometer, and thermal analysis was performed by a Rigaku Thermoflex.

Results

^{23}Na NMR. Figure 1 shows ^{23}Na MAS NMR spectra of undehydrated and dehydrated samples. Since the maximum intensity of the central line ($m=1/2\rightarrow-1/2$) of half-integer spins is obtained at a flip angle of $\pi/(2I+1)$(I :spin number),[8] the flip angle of the excitation pulse was set at $\pi/4$ for ^{23}Na spin ($I=3/2$). The undehydrated sample has a symmetric peak at -12 ppm with a 1.2-kHz width. On the other hand, DE400 and DE600 have asymmetric line shapes, whose tops are located at the same position as the undehydrated sample. DE800 shows a markedly different line shape centered at -28 ppm with a

2.8-kHz width. The spectral intensities per unit sample weight are 20% for DE400 and DE600 and 40% for DE800 with respect to the undehydrated sample.

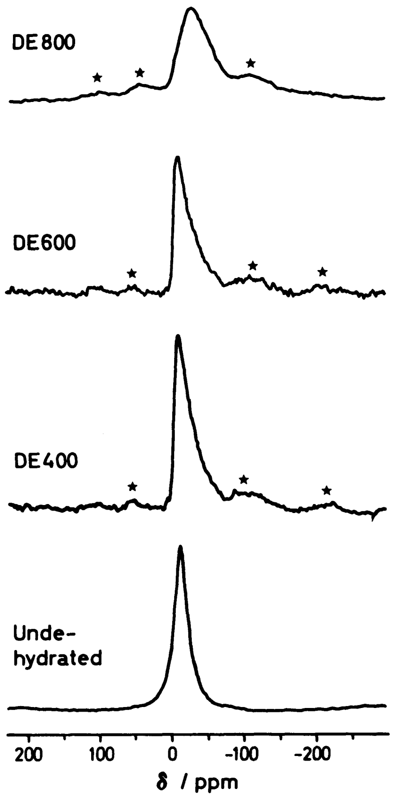

Fig. 1. ^{23}Na MAS NMR spectra of undehydrated and dehydrated Na–Y zeolites. The flip angle of the excitation pulse was $\pi/4$ and the recycle time was 1 s. The intensity is not normalized, and the mark ★ denotes spinning sideband.

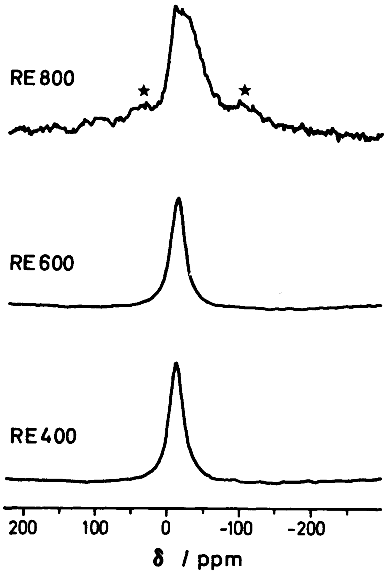

Fig. 2. ^{23}Na MAS NMR spectra of rehydrated Na–Y zeolites under the same measuring conditions as in Fig. 1.

Figure 2 shows the spectra of rehydrated samples. The spectra of RE400 and RE600 agree with that of the undehydrated sample, while the spectrum of RE800 is a superposition of the spectra of DE800 and the undehydrated sample.

Table 1. Summary of ^{23}Na and ^{27}Al MAS NMR

Sample	^{23}Na NMR$^{a)}$		^{27}Al NMR$^{b)}$	
	Peak	FWHM$^{c)}$	Peak	FWHM$^{c)}$
	ppm	kHz	ppm	kHz
Undehydrated	−12	1.2	53	1.0
DE400	−10	1.4	45	2.6
DE600	−11	1.4	42	2.7
DE800	−28	2.8	45	2.1
RE400	−13	1.2	51	1.3
RE600	−15	1.2	51	1.3
RE800	−11, −21	2.7	47	2.1

a) Resonance frequency of 52.80 MHz. b) Resonance frequency of 52.00 MHz. c) Full width at half-maximum.

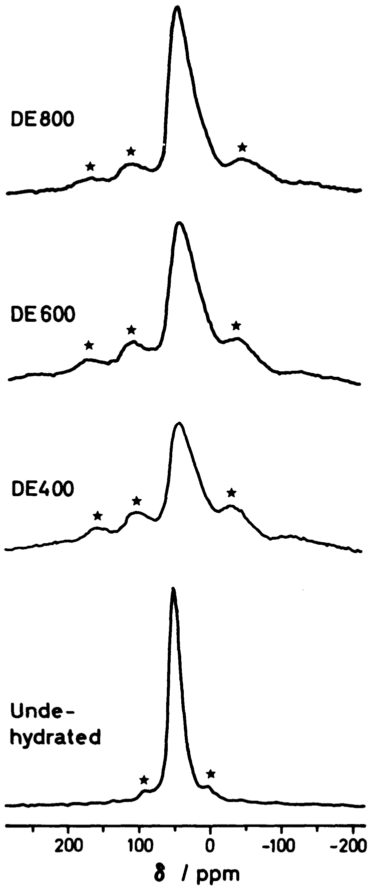

Fig. 3. ^{27}Al MAS NMR spectra of undehydrated and dehydrated Na–Y zeolites with the flip angle of $\pi/6$ and the recycle time of 1 s. The intensity is not normalized, and the mark ★ denotes spinning sideband.

The results are summarized in Table 1.

^{27}Al NMR. Figure 3 shows ^{27}Al MAS NMR spectra of the undehydrated and dehydrated samples. The undehydrated sample has a peak at 53 ppm with a 1.0-kHz width. DE400, DE600, and DE800 have a peak at about 45 ppm with a width of about 2.6 kHz, and their total intensities per unit sample weight decrease to the extent of 80—90% of that of the undehydrated sample. For the rehydrated samples, RE400 and RE600 have spectra similar to the undehydrated sample, while RE800 shows a spectrum similar to DE800. The results are usmmarized in Table 1.

^{29}Si NMR. Figure 4 shows ^{29}Si MAS NMR spectra of the undehydrated and dehydrated samples. The undehydrated sample has four peaks at −88.7, −93.7, −99.3, and −105.1 ppm, which are attributed to Si(3Al), Si(2Al), Si(1Al), and Si(OAl), respectively, in which Si(nAl) denotes the Si atom coordinated by n aluminum atoms and (4-n) silicon atoms through oxygen atoms. Assuming that Loewenstein's rule[9] is valid, the [Si]/[Al] ratio of the faujasite framework is estimated to be 2.75 using the equation in Ref. 10. The T_1 value is 6.3±0.7 s for all the four peaks. DE400 has four peaks also, but their widths are wider than those in the undehydrated sample, resulting in lower resolution. The two peaks assigned to Si(3Al) and Si(2Al) are shifted in the higher-field direction by about 1.5 ppm compared to those of the undehydrated sample, while other two peaks are not shifted. DE600 has the same line shape as DE400, and the line shape is independent of the recycle time, which indicates that the four peaks have the same T_1 value. The T_1 value is 13±3 s, longer than that of the undehydrated sample. DE800 has a negligible fine structure, and the total linewidth is broader than that of DE600.

Figure 5 shows the spectra of the rehydrated samples. RE400 and RE600 have the same spectra as the undehydrated sample. On the other hand, RE800 has a little fine structure, and the whole line shape is similar to the sum of the spectra of DE600 and DE800.

^{1}H NMR. ^{1}H results are summarized in Table 2. The undehydrated sample contains a large amount of water, whose proton shows a peak at 5.0 ppm with a 0.22-kHz width. The ^{1}H nuclei are in a motionally-narrowed state. On the other hand, the DE samples

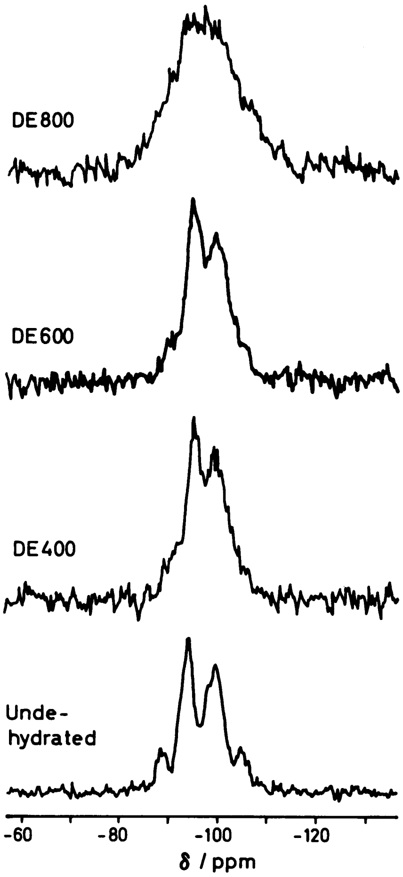

Fig. 4. ^{29}Si MAS NMR spectra of undehydrated and dehydrated Na–Y zeolites with the flip angle of about $\pi/2$ and the recycle time of 10 s. The intensity is not normalized.

Table 2. ^{1}H NMR Results

Sample	Peak / ppm	FWHM / kHz	C_H[a)]
Undehydrated	5.0	0.22	100
DE400	12	2.50	3.2
DE600	8.6	0.92	1.9
DE800	4.2	0.34	2.8

a) Relative hydrogen content with respect to the unit cell of the framework.

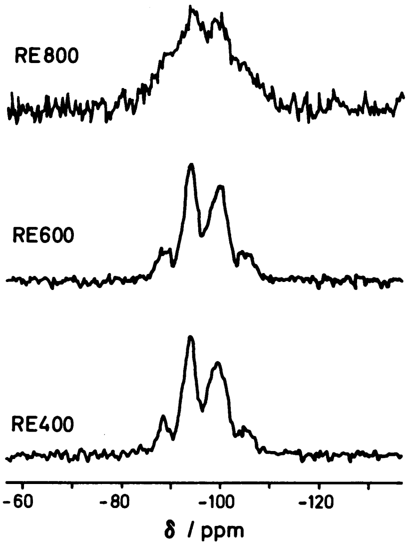

Fig. 5. ^{29}Si MAS NMR spectra of rehydrated Na–Y zeolites under the same measuring conditions as in Fig. 4.

lose most of their water. Though DE800 has a higher hydrogen content than DE600, it is probably caused by the absorption of water from atmospheric moisture after the dehydration process. The motionally-narrowed line which (0.34 kHz) of DE800 supports that the hydrogen is present in the form of mobile H_2O.

X-Ray Diffraction. The undehydrated sample shows a typical pattern of faujasite framework. Some peaks of the faujasite framework split into doublet in the pattern of DE400, indicating the lowering of the crystal symmetry. On the other hand, DE600 has the same pattern as the undehydrated sample, recovering the crystal symmetry. DE800 has a broad peak in addition to the pattern of the faujasite framework, which demonstrates that the framework structure is partially decomposed.

Thermal Analysis. Most of water molecules were desorbed in the temperature range between 35 and 350 °C, whose weight is 24.4% of the undehydrated sample. Weight decreased gradually up to 900° C, and finally 25.1% of the weight was lost.

Discussion

The DE samples lose most of their water, as demonstrated by ^{1}H NMR. X-Ray diffraction results indicate that DE400 and DE600 retain their network structure, while DE800 is a mixture of the faujasite network and an amorphous silica-alumina. Rehydration can reproduce the undehydrated state from DE400 and DE600, while it cannot from DE800, which is clearly demonstrated by ^{23}Na, ^{27}Al, and ^{29}Si NMR results.

^{23}Na NMR. Since ^{23}Na spin has quadrupole moment, the linewidth of the central line is broadened mainly by second-order quadrupole interaction,[11,12] reflecting coordination symmetry of the Na ion. The spectrum of the undehydrated sample shows a sharp line at −12 ppm without any spinning sidebands, which indicates that the Na ions are located in high-symmetry sites, coordinated by water molecules. On the other hand, the spectra of DE400 and DE600 have asymmetric line shapes and are accompanied by many spinning sidebands, suggesting that the Na ions are located in slightly-low-symmetry sites. The Na ions lose water molecules coordinating to themselves by the dehydration, as shown by the ^{1}H NMR results, and they approach to the framework atoms. Thus the coordination symmetry of the Na ions becomes slightly lower. The spectrum of DE800 shows a broad line centered at −28 ppm with many spinning sidebands, demonstrating that the Na ions are located in low-symmetry sites. It must be noted that a small shoulder is observed at about −10 ppm in the spectra of DE800, which can be ascribed to the Na ions in the faujasite framework left undecomposed.

By the rehydration, the Na ions in DE400 and DE600 recover their site symmetry, coordinated by water molecules. On the other hand, the spectrum of RE800 is composed of two lines centered at about −10 and −30 ppm. A part of Na ions in DE800 recover their symmetry, which are considered to be located not in the amorphous region but in the faujasite framework.

Consequently, three kinds of Na ions are observed with different site-symmetries. The difference in the signal position is originated from second-order quadrupole shift[12] and/or chemical shift.

The total signal intensities are largely reduced by the dehydration. Though the quadrupole interaction reduces the signal intensity,[13] the observed large reduction indicates the presence of undetectable nuclei, which are considered to be located at sites with very low symmetry. A simplified calculation suggests that 85 at% of Na ions are not observed in DE400 and DE600, while 70 at% in DE800.

A simple model is presented which can express the correlation between the Na sites and the NMR spectra. In the faujasite framework there are three kinds of occupied sites with different symmetries. The Na ions in the first site are coordinated by water molecules and have high symmetry, producing the narrow NMR line at −12 ppm without sidebands. The second site has slightly low symmetry, giving the asymmetric line at −10 ppm with many spinning sidebands, and the third site has very low symmetry, giving no detectable line. Only the first site is occupied in the hydrated state, while Na ions are distributed over the second and third sites in the dehydrated state. On the other hand, the amorphous region has low-symmetry sites and the third sites. The Na ions in this region cannot be hydrated to form symmetrical Na–H_2O clusters, probably because the ions are trapped on sites having an insufficient space for the cluster.

^{27}Al NMR. ^{27}Al spectra have only one peak which can be attributed to four-coordinated Al. DE400 and DE600 have larger linewidths than the undehydrated sample, which is considered to be broadened by second-order quadrupole effect. The AlO_4 tetrahedra is considered to be distorted by the approach of Na ions on dehydration. The approach of Na ions to the AlO_4 tetrahedra also gives rise to the lowering of Na site symmetry, as described above.

The broadening of the ^{27}Al resonance line on dehydration has been reported for H-ZSM-5 and H-Y, but in the case of Na-ZSM-5 the broadening is so large that the resonance line disappears.[5,6] On the contrary, a signal can be observed in the present case of Na-Y, but the intensity corresponding to 30—40 at% of Al atoms decreases. The decrease is partly explained by the increase in quadrupole interaction which reduces the intensity of the central line. Thus the value of 30—40 at% is only the upper limit of the undetected Al atoms.

Rehydration can reproduce the ^{27}Al spectrum, since Na ions are removed from the neighborhood of the AlO_4 tetrahedra by coordination of water molecules. On the other hand, the spectrum of DE800 does not change by the rehydration, although DE800 indicates the same line shape and intensity as DE400 and DE600. The symmetry of the AlO_4 tetrahedra in DE800 is lowered by the decomposition of the network, not only by the neighboring Na ions.

^{29}Si NMR. The width of each Si(nAl) line is broadened by the dehydration, which is caused by dipolar interaction with ^{27}Al perturbed by its quadrupole interaction and/or chemical shift dispersion. Line broadening of a $I=1/2$ spin bonded to a $I\geqq 1$ spin has been reported for ^{13}C spectra of α-carbon atoms in amino acids.[14] The increase of electric field gradient on the Al nuclei makes the ^{29}Si resonance line broader in the present case. Chemical shift dispersion may be produced by lowering of the crystal symmetry. The results of X-ray diffraction and ^{29}Si NMR however indicate that the crystal symmetry does not influence the line width very much in this case, as explained below. Although DE400 has an X-ray diffraction pattern with lower crystal symmetry than the undehydrated sample and DE600, the ^{29}Si NMR spectra of DE400 and DE600 agree with each other. Furthermore, the ^{29}Si spectra of DE600 and the undehydrated sample are different in spite that they have the same X-ray diffraction pattern.

The peaks ascribed to Si(3Al) and Si(2Al) are shifted towards higher field by the dehydration. The shift is considered to be caused by the interaction with Al, since the shift is only observed for the Si atom coordinated by more than one Al atom.

In the case of ZSM-5 the ^{29}Si spectral structure is not directly correlated with the hydration state.[4] Heat treatment causes line narrowing instead of broadening, which is attributed to temoval of lattice defects such as Si–OH. This behavior is different from the present results of Na–Y. Since the Na–Y sample has a much higher Al content than ZSM-5, the ^{29}Si NMR spectrum of Na–Y is inevitably influenced by the Al nuclei.

By heating at 800 °C, the network structure is broken, and the amorphous part produces a broad ^{29}Si line without any fine structure. The structure cannot be reconstructed by the rehydration, so that the spectrum of the amorphous part does not change. Though RE800 shows a little fine structure, it is produced by a crystalline part left undecomposed.

The T_1 value of ^{29}Si nuclei is also changed by the dehydration, though the network structure retains. The mechanism of the ^{29}Si relaxation is not established now, but paramagnetic impurities have been reported to have some role in the relaxation.[15] From the present study, it can be concluded that water in the cage plays some role in the ^{29}Si relaxation. Water molecules are considered to be a transport medium of paramagnetic impurities.

In summary, ^{23}Na, ^{27}Al, and ^{29}Si MAS NMR spectra can reflect the hydration state of Y-type zeolites very well. Line shape, position, and width of the spectra and spin-lattice relaxation time are changed by dehydration and hydration treatments.

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