

## APPLICATION OF $^{23}\text{Na}$ NUTATION NMR TO CHARACTERIZE THE CATION EFFECT IN ION-EXCHANGED $\text{NaY}$ ZEOLITES\*

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The two-dimensional sodium-23 nutation NMR was used to monitor the behavior of sodium ions in the partially alkali, alkali-earth or rare-earth ion exchanged  $\text{NaY}$  zeolites. The sodium-23 nutation spectra of the hydrated and rehydrated Y zeolites consist of two peaks at 1 and  $2\omega_{\text{rf}}$  in  $F_1$  axis with chemical shift of 0–10 ppm. For the degree of IA, IIA or RE cation exchange  $<45\%$ , only one peak at  $1\omega_{\text{rf}}$  was found. For the degree of cation exchange  $>45\%$ , the second peak at  $2\omega_{\text{rf}}$  might be observed. The correlation between the relative intensities and lineshapes of two peaks and the nature and distribution of cations in the supercages and sodalite cages with degree of exchange and heating treatment was studied.

The structural feature of aluminosilicate zeolites has been extensively investigated by solid state NMR recently. These studies have been concentrated on aluminosilicate framework using  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR (refs<sup>1–4</sup>). However, only a few solid state NMR studies were found on monitoring the properties of the intraframework cations in zeolites<sup>5–7</sup>. The determination of the cation locations and effects usually involves X-ray or neutron diffraction<sup>8,9</sup> and far-infrared<sup>10</sup> methods. The correlation of the NMR spectrum of the cationic nucleus with its ion content is rather direct and it seems to be a favorable probe for the location and mobility of cations in zeolites. However, the nucleus under investigation has a spin quantum number  $I > 1/2$ , e.g.,  $^{23}\text{Na}$ ,  $^7\text{Li}$ ,  $^{133}\text{Cs}$  and  $^{139}\text{La}$ , the central transition ( $1/2, -1/2$ ) line is broadened by the quadrupolar interaction.

Identifying different environment around cations via chemical shift becomes very difficult even under high magnetic field. Two-dimensional nutation NMR has been shown as an efficient technique to separate the quadrupolar interaction and the chemical shift and to obtain the information on quadrupolar parameters of intraframework cations<sup>4,6,11,12</sup>. In a previous study<sup>12</sup>, we found that the distribution and the mobility of sodium ions in hydrated  $\text{La,Na-Y}$  zeolites as the function of heating treatment, water content and lanthanum content were clearly monitored by

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two-dimensional nutation <sup>23</sup>Na NMR. Here we report a 2D <sup>23</sup>Na NMR study of the effect of cation on a series of hydrated and rehydrated and partially IA-, IIA- and RE-exchanged Na-Y zeolite samples. The <sup>23</sup>Na NMR spectra were found to vary with the nature and content of cations on the Y zeolites before and after heat treatment. The cation distributions in supercages and small sodalite or double hexagonal prism cages dominate the 2D <sup>23</sup>Na NMR profile.

## EXPERIMENTAL

A binder-free Na-Y zeolite with Si/Al ratio of 2.29 (Strem Chemical Co.) was washed with 1M-NaCl solution and deionized water, then dried at room temperature. IA, IIA and RE, Na-Y were prepared by partially exchanging a portion of the thoroughly washed Na-Y zeolite with metal chloride solution. Elemental composition of the zeolite samples was determined by inductively-coupled-plasma atomic-emission spectroscopy (ICPAES) and the percentage of metal ion exchanged in the zeolite is used as the notation for the sample, e.g., a Li exchange level of 63% was indicated by 63Li,Na-Y. The 86La,Na-Y, 88Ca,Na-Y and 78Ba,Na-Y were prepared from 10 g of Na-Y by three 4-h exchanges with their respective chloride solution at 86°C. All other hydrated and partially exchanged samples were prepared from Na-Y by exchanging once or more with 0.1M chloride solution at room temperature. Rehydrated samples were prepared by 1) evacuating and heating the hydrated sample from room temperature to 150°C with a heating rate of 0.2°C/min and at 150°C for 4 h; 2) increasing temperature to 350°C with 0.2°C/min and at 350°C for approx. 30 h, the final equilibrium pressure was 10<sup>-2</sup> Pa; 3) cooling the sample under vacuum, then exposing it to water vapor and over saturated NH<sub>4</sub>Cl solution for one week at room temperature.

NMR measurements were carried out with static samples at 52.9 MHz on a Bruker MSL-200 spectrometer using a standard 7 mm double bearing CP-MAS probe. A duration of 0.5 s between scans was allowed for nuclear spin relaxation. Chemical shifts were calibrated against a saturated aqueous NaCl solution with high field shift as negative.  $T_1$  measurements were taken by inversion-recovery pulse sequence. The field strength of radio frequency at  $80 \pm 5$  kHz was employed on 2D nutation experiments. Typically, 64 rows of 1 K data were collected with the first row being zero and the increment of pulse sequence was 2  $\mu$ s. The free induction decays were doubly Fourier transformed in the magnitude mode. To enhance S/N ratio, the line broadening (LB) filter was used in  $F_2$  domain (about 100 ~ 400 Hz). Each 2D experiment took about 5 ~ 24 h. Data were plotted as white-wash stacked plots.

## RESULTS AND DISCUSSION

The two-dimensional nutation spectra of hydrated and rehydrated 60Ca,Na-Y are given in Fig. 1, of which the quadrupolar interaction and chemical shift are separated and displayed on  $F_1$  and  $F_2$  axes respectively. According to Veeman et al.<sup>13</sup> and Kentgens<sup>14</sup>, when the quadrupole interaction ( $\omega_q$ ) is small relative to the Zeeman interaction at r.f. field ( $\omega_{rf}$ ), the nutation frequency ( $F_1$ ) is equal to  $1\omega_{rf}$ ; when  $\omega_q \gg \omega_{rf}$ , the nutation line for Na will be found at  $2\omega_{rf}$ ; the intermediate case gives a complicated profile sprayed from  $1\omega_{rf}$  to  $2\omega_{rf}$ . Our previous study on La,Na-

-zeolite Y (ref.<sup>12</sup>) showed two Na species in Y zeolites, one with a narrow line at  $F_1 = 1\omega_{rf}$  and the other, a powder pattern with two broad peaks at  $F_1 = 1\omega_{rf}$  and  $2\omega_{rf}$  with the same linewidths. The single Na NMR line of rehydrated 60Ca, Na-Y shows that most of their sodium nuclei could be derived from one species with quadrupolar interaction  $\ll\omega_{rf}$  (80 kHz). The nutation spectrum of hydrated 60Ca,Na-Y has two peaks at  $F_1 = 1\omega_{rf}$  and  $2\omega_{rf}$  and their linewidths are different from each other (Table I), because of the quadrupolar interaction  $\ll\omega_{rf}$  and  $\leq\omega_{rf}$  of the two species. These two components can be distinguished by applying a  $\pi - t - \pi/2$  inversion-recovery sequence. Figure 2 shows that the relaxation processes consist of two components and the time constant of the broad component is shorter than that of the narrow component. The spin-relaxation time  $T_1$  of the narrow component of hydrated 60Ca,Na-Y is similar to that of the Na nuclei in rehydrated 60Ca,Na-Y (Fig. 2) and in Na-Y (Challoner et al.<sup>15</sup>). The 2D  $^{23}\text{Na}$  NMR lines of both components project themselves as a combined broad line in the  $F_2$ -axis. The chemical shifts of all ion exchanged Na-Y are similar to that of Na-Y. Therefore, the nutation frequency is more useful than chemical shift in discriminating different environment around Na cations in Y zeolites.

The  $F_1$  projections of  $^{23}\text{Na}$  nutation spectra of partially cation exchanged Na-Y as a function of their exchange levels and hydrated state are shown in Figs 3–6. Figures 3 and 4 show that the spectra of hydrated and rehydrated La,Na-Y and Ba,Na-Y are similar and are characterized by a narrow peak at  $1\omega_{rf}$  on nutation axis

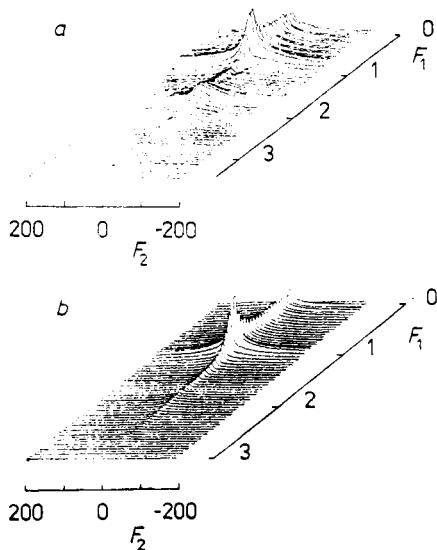


FIG. 1  
Sodium-23 nutation spectrum of hydrated (a) and rehydrated (b) 60Ca,Na-Y

for the cation exchange level up to 45%. For exchange level > 45%, two peaks at  $1\omega_{rf}$  and  $2\omega_{rf}$  are provided by hydrated samples, while the spectra of the rehydrated samples show only one line at  $1\omega_{rf}$ . For exchange level up to 70%, the Ca,Na-Y zeolites have similar spectra as La,Na-Y and Ba,Na-Y. As  $\text{Ca}^{2+}$  exchange level is greater than 70%, both the hydrated and rehydrated samples give two broad peaks at 1 and  $2\omega_{rf}$  with similar linewidths (Fig. 5). However, a slight variation on the spectra of IA,Na-Y was found after heat treatment (Fig. 6).

According to structural analysis<sup>16</sup>, the distribution of cations at the available sites provided by the zeolite framework is a function of the degree of hydration, the nature of the cations and the structure of framework. The framework of Y zeolites is constructed from sodalite cage units, truncated octahedrons with a diameter of 0.66 nm, which enclose large supercages with a diameter of 1.27 nm by double six tetrahedra ring (D6R, diameter 0.26 nm) connections; these supercages are interconnected to a three-dimensional network of cavities by opening twelve tetrahedra ring windows (0.72 nm in diameter). This anionic framework provides cationic sites in both supercages and small sodalite or D6R cages. All of the cationic sites

TABLE I

Variation of linewidths of the peaks in  $F_2$  axis at  $F_1 = 1\omega_{rf}$  and  $2\omega_{rf}$  for hydrated and rehydrated cation-exchanged Na-Y zeolites

Sample	Linewidth, $\text{Hz}^a$			
	hydrated at		rehydrated at	
	$2\omega_{rf}$	$1\omega_{rf}$	$2\omega_{rf}$	$1\omega_{rf}$
52Ce,Na-Y	4 120	1 360	—	730
86La,Na-Y	4 280	4 320	—	720
60Ba,Na-Y	3 690	860	—	720
68Ba,Na-Y	4 960	4 820	—	720
78Ba,Na-Y	4 540	4 410	—	700
60Ca,Na-Y	4 080	2 380	—	800
65Ca,Na-Y	3 820	3 320	—	720
78Ca,Na-Y	3 850	3 830	4 020	4 080
88Ca,Na-Y	4 630	4 560	4 350	4 690
63Li,Na-Y	3 350	1 580	3 510	1 580
65K,Na-Y	3 120	730	—	680
80K,Na-Y	3 860	1 050	3 770	1 030
56Cs,Na-Y	3 850	1 250	—	1 320
66Cs,Na-Y	3 680	1 140	3 760	960

<sup>a</sup> The linewidth at half-height of the peak.

may not be accessible to all cations and the ion-exchange capacity of zeolites should vary with the incoming cation. Ion-exchange isotherms showed that the replacement of  $\text{Na}^+$  ions by  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Cs}^+$  is limited in large supercages and the ion exchange reaction terminates at an exchange level of 70% at 25°C (refs<sup>17,18</sup>). Therefore, the temperature of exchange was raised to 86°C to obtain 88Ca,Na-Y, 80Ba,Na-Y and 86La,Na-Y. The replacement of  $\text{Na}^+$  ions in small cages depends on the size of incoming cation, hydration energies and the framework interactions of cations. During heating and dehydration, the cations (with ionic diameter <0.26 nm) can strip off their hydration shell and occupy the sites in small sodalite or D6R cavities. The strong interaction between divalent or trivalent cations and framework can keep some of the divalent cations and most of the trivalent cations in the small cages after rehydration<sup>19,20</sup>. Therefore, the distribution of the remaining  $\text{Na}^+$  ions among the supercages and small cavities in partially exchanged Na-Y zeolites should vary with the heat treatment and with the nature and content of incoming cations.

For exchange level <45%, only one line is shown at  $F_1 = 1\omega_{rf}$ ; this indicates that the replacement of mobile  $\text{Na}^+$  ions in supercages by incoming cations does not effect the mobility of remaining Na nuclei in Y zeolites. When the exchange level increased to 45–70%, replacements of  $\text{Na}^+$  ions may occur at SII sites in supercages<sup>21</sup>, the divalent or trivalent ions at SII can then block the movement of remaining  $\text{Na}^+$  ions and induce two  $\text{Na}^+$  species of different symmetry environment. After heat treatment, most of the  $\text{La}^{3+}$ ,  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  ions tend to stay in small sodalite or D6R cavities while the  $\text{Na}^+$  ions prefer to be located in the supercages.

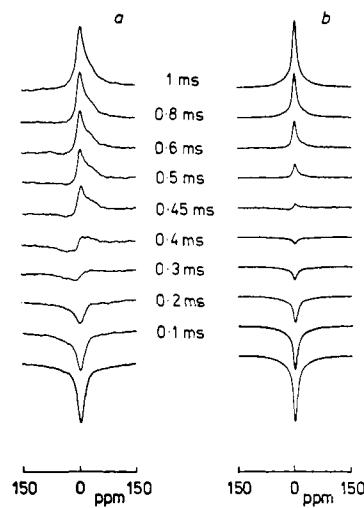


FIG. 2

Application of the inversion-recovery sequence to hydrated (a) and rehydrated (b) 60Ca,Na-Y. The lowest curves correspond to 1  $\mu\text{s}$

This results in the Na nuclei at high symmetry environment which, in turn, gives one narrow nutation line at  $F_1 = 1\omega_{rf}$  on rehydrated Ca,Na-Y (with exchange level <70%), Ba,Na-Y and La,Na-Y samples. Although the heat of hydration and

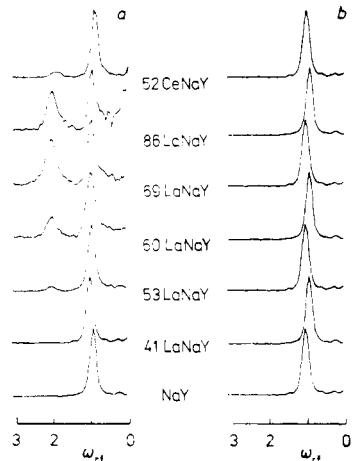


FIG. 3

$F_1$  projection of the  $^{23}\text{Na}$  2D nutation NMR spectra of hydrated (a) and rehydrated (b) RE,Na-Y

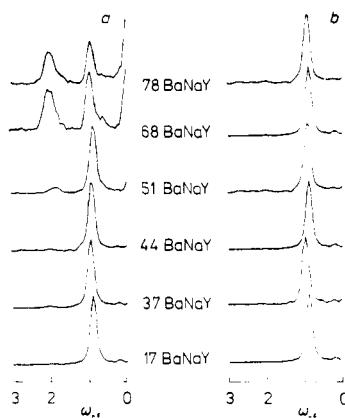


FIG. 4

$F_1$  projection of the  $^{23}\text{Na}$  2D nutation NMR spectra of hydrated (a) and rehydrated (b) Ba,Na-Y

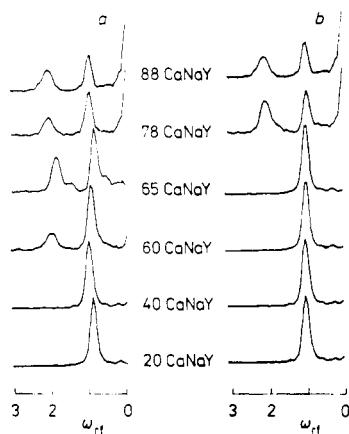


FIG. 5

$F_1$  projection of the  $^{23}\text{Na}$  2D nutation NMR spectra of hydrated (a) and rehydrated (b) Ca,Na-Y

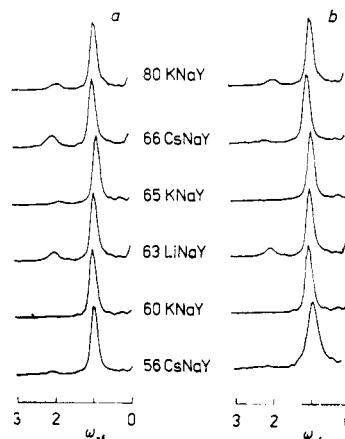


FIG. 6

$F_1$  projection of the  $^{23}\text{Na}$  2D nutation NMR spectra of hydrated (a) and rehydrated (b) IA,Na-Y

the energy of interaction between cations and framework follow the order of:  $\text{La}^{3+} > \text{Ca}^{2+} > \text{Ba}^{2+}$ , the small size of the  $\text{Ca}^{2+}$  ion (diameter 0.20 nm) relative to both the six tetrahedral ring and the diameters of  $\text{Ba}^{2+}$  (0.27 nm) and  $\text{La}^{3+}$  (0.23 nm) makes the behavior of  $\text{Na}^+$  ions in  $\text{Ca},\text{Na}-\text{Y}$  different from those in  $\text{Ba},\text{Na}-\text{Y}$  and  $\text{La},\text{Na}-\text{Y}$  with exchange level  $> 70\%$ . The Na spectra of  $\text{Ca},\text{Na}-\text{Y}$  (exchange level  $> 70\%$ ) indicate that the remaining  $\text{Na}^+$  ions may be located at low symmetry sites and the  $\text{Ca}^{2+}$  ions can stay in supercages after heat treatment.

The interaction between the monovalent cation and tetrahedral aluminosilicate framework or water molecules is much smaller than that for divalent or trivalent cations. The migration of monovalent cations, except for  $\text{Cs}^+$  ions (of radius  $> 0.26$  nm), from supercages to small cavities is possible at room temperature and is not irreversible by heat treatment. As expected, the influence of alkali cations on the mobility of  $\text{Na}^+$  nuclei in Y zeolites is quite small, similar spectra can thus be found for hydrated and rehydrated states. The relative high intensity on  $F_1 = 1\omega_{\text{rf}}$  peak demonstrates that most of  $\text{Na}^+$  nuclei in  $\text{IA},\text{Na}-\text{Y}$  belong to high symmetry species.

The distributions of  $\text{Na}^+$  ions in partially exchanged Na-Y zeolites were monitored by 2D  $^{23}\text{Na}$  NMR, of which, the profile depends on the location of the exchangeable cations and the occupancy of the different sites before and after heat treatment.

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