Investigation of Sodium Cations in Dehydrated Zeolites LSX, X, and Y by ^{23}Na Off-Resonance RIACT Triple-Quantum and High-Speed MAS NMR Spectroscopy

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Abstract: We investigated by two-dimensional ^{23}Na ORIACT MQMAS NMR and one-dimensional ^{23}Na high-speed MAS NMR spectroscopy a homologous series of dehydrated zeolites with faujasite structure. The framework silicon to aluminum ratios varied between 1.06 and 2.60. In the case of zeolites Y ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 2.60$), we studied materials with sodium exchange degrees between 0 and 95%. The recently introduced ORIACT method (Caldarelli, S.; Ziarelli, F. *J. Am. Chem. Soc.* **2000**, *122*, 12015) significantly improved the resolution of the MQMAS spectra, in comparison with earlier studies. It was thus possible to extract meaningful quadrupole parameters by MQMAS NMR, which were used as a starting point for the simulation of 1D MAS NMR spectra to obtain more accurate values of the NMR parameters and site occupancy. We were able to show by this approach that in zeolite NaLSX the SI positions in the hexagonal prisms are occupied by sodium cations. For the homologous series of zeolites Y, it was found that sodium cations located at SII positions are the easiest to be substituted by ammonium ions through the exchange process.

Introduction

During the past decade, the development of new solid-state NMR techniques opened the way to a quantitative investigation of cations in dehydrated zeolites. Cations in zeolites such as lithium, sodium, potassium, or cesium ions act as adsorption sites for adsorbate molecules and reactants and influence the mean electronegativity of the zeolite framework. In addition, the shape selectivity of zeolites, i.e., the free diameters of their pores and cages, strongly depends on the distribution of cations in the zeolite lattice. The first NMR investigations of cations in hydrated zeolites were performed using magic angle spinning (MAS) with moderate rotation frequencies.[1−4] However, the analysis of dehydrated zeolites is a challenging NMR problem. High-speed MAS is necessary to ensure a quantitative result, but even this technique is inadequate in the presence of strong quadrupolar interactions and several overlapping signals, and it is often necessary to make use of more sophisticated methods. For example, double rotation (DOR),[5] two-dimensional nutation, and multiple-quantum MAS NMR spectroscopy[6] were all utilized for the study of zeolites.[7−15] Very recently, the issue of cation mobility within the cage has begun to receive some attention, as followed by high-temperature MAS NMR.[15−17]

In this paper we concentrate on the study of zeolites with a faujasite structure (FAU). Materials of this family are the most applied microporous adsorbents and catalysts for chemical processes. In sodium-exchanged zeolites X and Y, the cation may occupy one or more of the extra-framework positions shown in Figure 1, depending on the silicon-to-aluminum ratio in the framework and on the exchange degree. Sites I and I′ are located in the hexagonal prism and sodalite cage, respectively. Sites II and III are located in the supercage near six-member and four-member oxygen rings, respectively. Two different SIII positions occupied by sodium cations were observed in a dehydrated zeolite NaX ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 1.18$) by single-crystal X-ray diffraction.[18] The SIII′(1,2) positions are off-center in the four-

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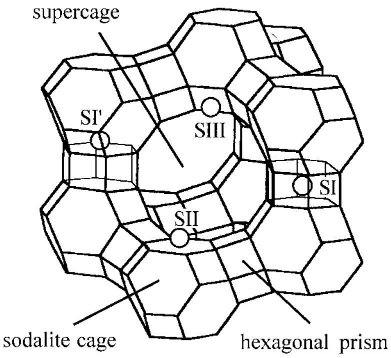

Figure 1. Structure of zeolites LSX, X, and Y. The extra-framework cation positions are SII and SIII in the supercage, SI′ in the sodalite cage, and SI in the hexagonal prism.

member rings and have one Na−O4 distance of 2.41 to 2.58 Å, one Na−O1 distance of 2.44 to 2.45 Å, and one Na−O1 distance of 3.39 to 3.61 Å. The SIII′(3) position is more symmetrical with two Na−O1 distances of 2.81 to 2.85 Å and one Na−O4 distance of 2.22 Å.

Previous investigations have shown that sodium cations located at different extra-framework positions in dehydrated zeolites NaX and NaY are characterized by strong quadrupolar interactions, corresponding to quadrupole coupling constants, $Q_{CC} = 3 \cdot e^2 \cdot q \cdot Q/h$, ranging between 1.0 and 6.0 MHz.[8,12,13] The parameter $e \cdot q = V_{zz}$ is the z-component of the electric field gradient at the site of the resonating nuclei and $e \cdot Q$ is the nuclear quadrupole moment. The ^{23}Na MAS NMR (central transition) signals of sodium cations in dehydrated zeolites X and Y are strongly broadened, due to second-order quadrupolar effects. Their resolution requires the application of modern methods of high-resolution solid-state NMR spectroscopy. For instance, the two-dimensional multiple-quantum MAS (MQMAS) technique has been applied to the study of sodium cations in dehydrated zeolites NaY, NaEMT, NaMOR, and NaZSM-5.[13,14] These investigations demonstrated the adeptness of this technique for the resolution of ^{23}Na NMR signals due to sodium cations with Q_{CC} values up to 3 MHz. The quadrupole coupling constant of sodium cations located at SI positions was found to be 1.2 MHz, which is much larger than the value obtained by MAS and DOR NMR spectroscopy.[8,12] Applying a standard two-pulse sequence,[19] Lim and Grey were able to obtain ^{23}Na MQMAS NMR spectra of dehydrated zeolites NaY and NaX showing broad signals in the range of sodium cations located at SII and SI′ positions, however, with poor signal-to-noise ratio and resolution.[15]

Many of the limitations of the MQMAS spectroscopy of zeolites arise from the coexistence of narrow and broad signals, associated with small and large EFG. Narrow signals tend to dominate the spectrum, because they are more easily detected and therefore tend to blank other contributions. This particular issue was tackled by a recently introduced technique, off-resonance RIACT triple-quantum MAS NMR. This is a modification of the RIACT method for converting multiple-quantum into one-quantum coherence by exploiting the periodic variation of the energy level system of half-integer quadrupolar nuclei under MAS.[20] This effect is based on the onset of an adiabatic level anti-crossing caused by the modulation of the quadrupolar frequency, ν_Q, due to the sample spinning in the presence of a radio frequency field ν_{RF}. Vega introduced the parameter $\alpha = \nu^2_{RF}/\nu_Q \cdot \nu_{ROT}$, where ν_{ROT} is the MAS rotation frequency, as a measure of the rate of change of the energy level, adiabaticity being achieved when $\alpha \gg 1$.[21] Later studies pointed out the complexity of a more detailed description of the level dynamics, in which the adiabatic condition is evaluated at each point in time, by $\alpha' \propto \nu^2_{RF}/|d\nu_Q/dt|$, where ν_Q is the actual, orientation-dependent quadrupolar frequency.[22−25] The value of α' in a polycrystalline sample has been shown to be very sensitive to an offset of the irradiating field. In particular, the coherence transfer is most effective when irradiating at the resonance for the MQ transition, which corresponds, for a spin $^3/_2$, to an offset equal and opposite in sign to the second-order quadrupolar shift.[25] By a proper choice of the irradiation offset, the ORIACT method achieves discrimination ("filtering out") of narrow signals with respect to broad ones because of their large difference in quadrupolar couplings, and therefore in the value of the associated second-order shift. The optimum offset condition for large couplings is performing poorly for the narrow ones (and vice versa), thus achieving an effective filtering of those latter components.[26] The ORIACT approach, similar to its parent technique, produces powder line shapes that differ from the MAS ones, as only a fraction of the crystallites contribute to the signal.[21] Most notably, some of the discontinuities observed in a MAS spectrum might not be present in the ORIACT one. In the case of the simple two-pulse method used here,[19] a further deviation from the textbook powder line shapes should be expected for sites with large couplings. In this case, such a simple pulse sequence may fail to excite the entire range of frequencies expected for a given site. As a consequence, the location of its actual center of gravity becomes uncertain, especially in the presence of an additional source of broadening due to structural disorder. A time-consuming exact simulation ("inversion") of the 2D spectra would be required to extract accurate NMR parameters.[27] Therefore, the MQMAS spectra were used in this work only to determine the number of species and to evaluate their quadrupolar coupling constant. This information provides a constraint on the maximum number of parameters and a good starting point for the simulation of the more accurate one-dimensional high-speed MAS spectra. The relative concept of "high-speed" means, in this contest, that rotation sidebands carry no appreciable intensity, and can be safely neglected in the simulations.

We applied the method outlined here to study sodium cations in zeolites with faujasite structure having framework n_{Si}/n_{Al} ratios between 1.06 and 2.60, and in zeolite NaY with up to 95% of the sodium exchanged for ammonium cations. The application of ORIACT allowed a resolution suitable for the large quadrupolar couplings in these sytems.

Experimental Part

Sample Preparation. Zeolites NaY and NaX with framework n_{Si}/n_{Al} ratios of 2.60 and 1.30, respectively, are commercial materials of Union Carbide Corp., Tarrytown, NY, USA. Zeolite NaLSX with the framework n_{Si}/n_{Al} ratio of 1.06 was synthesized as described elsewhere.[28] To ensure a sodium exchange degree of 100%, the parent zeolites NaLSX, NaX, and NaY were exchanged in a large surplus of

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a 0.1 M aqueous solution of $NaNO_3$ and, subsequently, washed in demineralized water. To prepare a homologous series of zeolites Y, the parent zeolite NaY was ion-exchanged several times in an 1 M aqueous solution of NH_4NO_3 leading to an exchange of 60% (NH_4Na/1), 75% (NH_4NaY/2) ,and 95% (NH_4NaY/3) of sodium cations by ammonium ions. All materials were characterized by X-ray diffraction and atomic emission spectroscopy with inductively coupled plasma (ICP-AES). ^{29}Si and ^{27}Al MAS NMR spectroscopy ensured that the ion exchange was not accompanied by a dealumination of the zeolite framework.

Prior to the NMR investigations, the powder materials were heated in a vacuum with a rate of 20 K/h up to the final temperature of 673 K. At this temperature, the samples were dehydrated for 12 h at a pressure below 10^{-2} Pa. In the case of zeolites NH_4NaY, this procedure led to the formation of HNa-form zeolites Y. Finally, the samples were filled into the MAS NMR rotors under dry nitrogen using a glovebox and tightly sealed with rotor caps.

NMR Measurements. The MQMAS NMR experiments were carried out on a Bruker DSX 400 spectrometer at a resonance frequency of 105.8 MHz. The sample spinning frequency of the 4 mm rotor was 10 kHz. All MQMAS NMR spectra were obtained with a two-pulse sequence: $P_1-t_1-P_2-$acquisition and the appropriate phase cycling.[26] The pulse durations P_1 and P_2 were set to 3−5 and 25 μs with power levels corresponding to $\nu_{RF} = 150$ and 75 kHz, respectively. The value of P_1 was optimized to maximize the relative contribution of broad signals; the value of P_2 is bound by the RIACT condition, equal to a quarter of the rotor period. A spectral width of 750 ppm, corresponding to an increment of 6.3 for t_1, was used for the MQ dimension, with a total of 32 increments and a TPPI acquisition scheme. The carrier frequency was chosen to be about 4 kHz off-resonance, a value suitable for large quadrupolar couplings. For each t_1 increment, a number of scans between 20 (typical) and 900 (for very low sodium contents) were used. The repetition time was set to 500 ms. The corresponding experimental time varied between 20 min and 8 h.

The high-speed MAS NMR experiments were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 105.8 MHz with a sample spinning rate of 22 kHz. To record the spectra, up to 10 000 free induction decays were accumulated with a repetition time of 500 ms. The spin system was excited with single $\pi/6$ pulses. All ^{23}Na NMR chemical shifts are referenced to a 1 M aqueous solution of NaCl.

Results and Discussion

^{23}Na ORIACT MQMAS Spectroscopy. The center of gravity of the peaks in the (not sheared) ^{23}Na ORIACT triple-quantum MAS NMR spectra shown in Figures 2 and 3 was located by visual evaluation. The values of the quadrupolar parameter $P_Q = Q_{CC}\cdot(1 + \eta^2/3)^{1/2}$, where η is the asymmetry parameter, and of the isotropic chemical shifts, δ_{iso}, were obtained using the formulas given in refs 13 and 29 (columns 3 and 4 of Table 1). The signals observed were assigned according to ref 12. The small differences in the chemical shift reported here with respect to ref 12 have to be ascribed to a different chemical shift reference (liquid and solid NaCl, respectively).

The low-field part of the spectrum of dehydrated zeolite NaLSX in Figure 2a consists of three strong signals due to sodium cations located at the SI, SIII′(3), and SIII′(1,2) positions. These signals are much better resolved than in the one-dimensional MAS NMR spectra published earlier.[12] The nonlinear intensities produced by the MQMAS experiment, even using the ORIACT filtering, tend to enhance signals from sites with weak quadrupolar interactions, such as the sodium cations located at SI position. This latter is thus well detectable, although the SI position is only weakly occupied. Conversely, lower relative intensity is observed for the broad SII and SI′ signals in the high-field range of the spectrum in Figure 2a. The quadrupolar parameters were estimated by evaluating the center of gravity of the MQMAS NMR signals (see Table 1), and they agree well with the values obtained in earlier studies.[12,15]

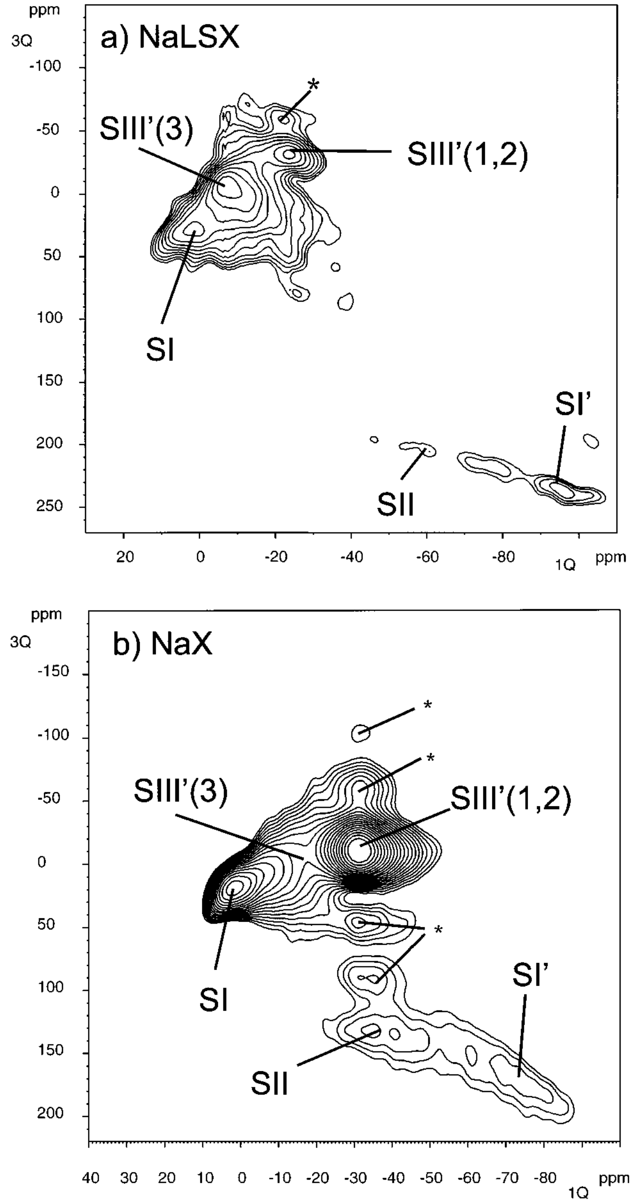

Figure 2. Two-dimensional (not sheared) ^{23}Na ORIACT triple-quantum MAS NMR spectra of dehydrated zeolites NaLSX (a) and NaX (b). Asterisks denote artifacts due to an incomplete decay of the signal in the MQ dimension.

The low-field range of the ^{23}Na ORIACT triple-quantum MAS NMR spectrum of zeolite NaX (Figure 2b), which has a significant lower aluminum and sodium content in comparison with zeolite NaLSX, consists only of two strong signals due sodium cations at SI and SIII′(1,2) positions. As shown in our earlier study,[12] the cation population of the SIII′(3) position is significantly lower in zeolite NaX than in zeolite NaLSX. The larger intensities of the SII and SI′ signals occurring in the high-field range of the spectrum of zeolite NaX are due to the lower quadrupolar interactions of these sodium cations in comparison with those in zeolite NaLSX (compare values in Table 1).

Figure 3 shows the ^{23}Na ORIACT triple-quantum MAS NMR spectra of the homologous series of zeolites Y with different sodium exchange degrees. The low-field range of the spectrum in Figure 2a is dominated by the signal of sodium cations located at SI positions. The SII and SI′ signals occurring in the high-

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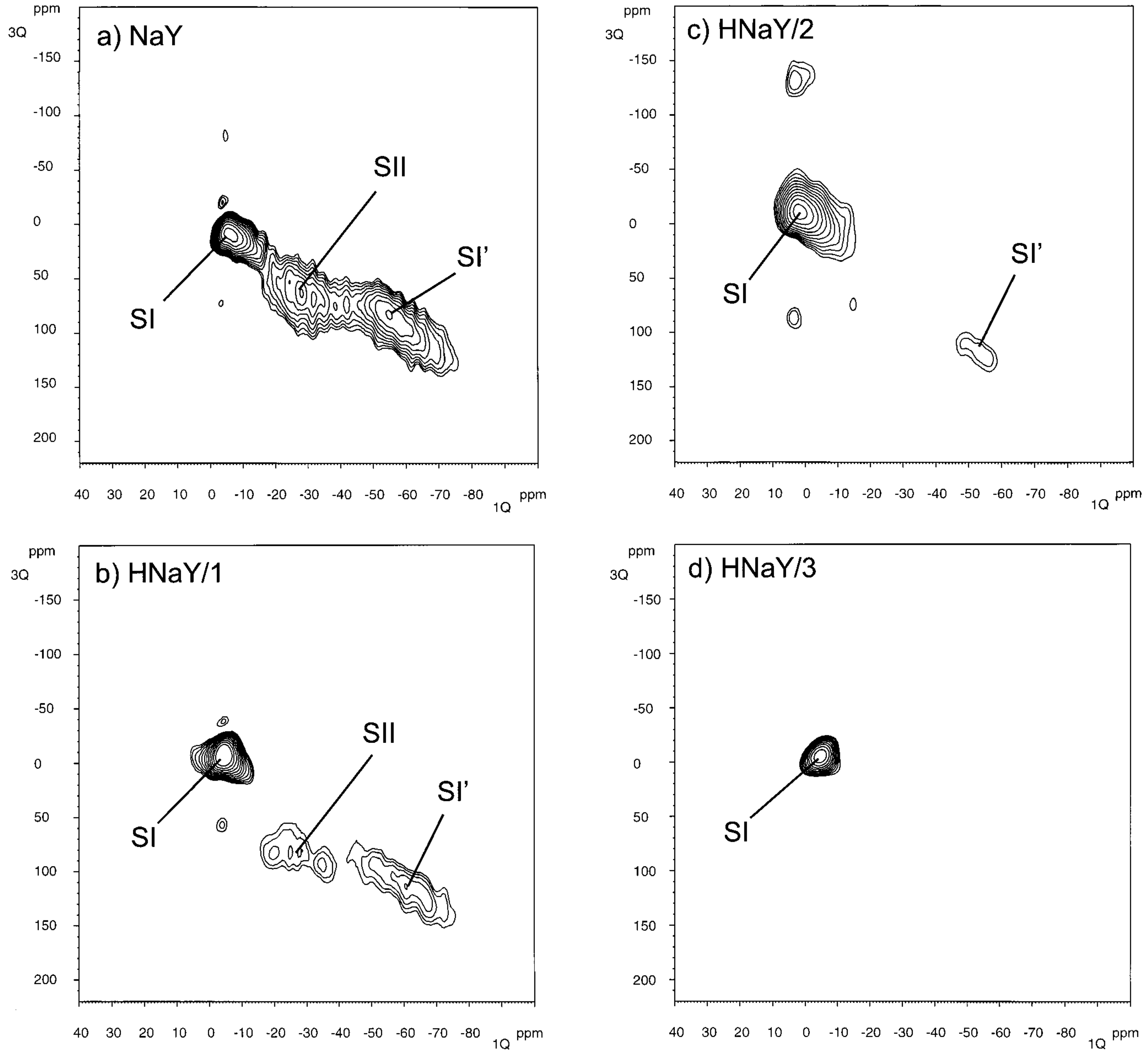

Figure 3. Two-dimensional (not sheared) ^{23}Na ORIACT triple-quantum MAS NMR spectra of dehydrated zeolites NaY (a) HNaY/1 (b), HNaY/2 (c), and HNaY/3 (d). Asterisks denote artifacts due to an incomplete decay of the signal in the MQ dimension.

field range are well-resolved and yield quadrupolar parameters in agreement with those obtained earlier.[12,15] The low sodium content of zeolites HNaY/1 and HNaY/2 leads to weak SII and SI′ signals (Figure 3b,c). The signal of sodium cations located at the SII positions decreases faster with increasing levels of substitution, which indicates a preferential depletion of sodium cations located in the supercages of the faujasite structure through the exchange process. Hence, the variation of the signal intensities in the ^{23}Na ORIACT triple-quantum MAS NMR spectra of the homologous series of zeolites Y gives qualitative information about the variation of the cation population. After an exchange of 95% of the sodium cations, the spectrum consists only of a single signal due to sodium cations at the SI position (Figure 3d).

The excellent quality of the ^{23}Na MQMAS NMR spectra in Figure 3 clearly shows the advantage of the ORIACT method for the study of sodium cations in dehydrated zeolites. However, the method has an upper limit in detectable P_Q, the quadrupolar parameter, due to a decreasing efficiency of the excitation/reconversion of MQ coherences. Other versions of the MQMAS experiment, introduced recently to cope with this problem, could be integrated with the ORIACT idea to try to compensate for this drawback.[30−32] ^{23}Na ORIACT triple-quantum MAS NMR spectroscopy has been demonstrated to be a powerful method to improve the resolution of different signals and to estimate quadrupolar parameters. In any case, ^{23}Na ORIACT triple-quantum MAS NMR spectroscopy of a homologous series of zeolites can provide a qualitative description of the variation of the site occupancy. For a quantitative evaluation of the cation population, we resorted to a simulation of one-dimensional ^{23}Na MAS NMR spectra.

^{23}Na High-Speed MAS Spectroscopy. The spinning rate of 22 kHz used here for the one-dimensional ^{23}Na MAS NMR spectra (Figures 4 and 5) assured that the sideband contribution

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Table 1. NMR Parameters of Sodium Cations in Dehydrated Zeolites LSX, X, and Y Derived by a Quantitative Evaluation of the ^{23}Na ORIACT Triple-Quantum and High-Speed MAS NMR Spectra Shown in Figures 2−5[a]

sample population	site	P_Q/MHz[b]	δ_{iso}/ppm[c]	Q_{CC}/MHz[d]	η[e]	δ_{iso}/ppm[f]	Na/u.c.[g]	Na/u.c.[h]
Na-LSX	SI	1.3	5	1.2	0.1	0	4	0−3
93.2 Na/u.c.	SI′	6.2	−10	5.9	0.1	−6	18	24−31
	SII	5.6	−1	5.1	0.2	−12	32	28−32
	SIII′(1,2)	1.8	−16	2.2	0.5	−13	26	15−24
	SIII′(3)	1.2	−5	2.0	0.8	−1	13	9−17
Na-X	SI	0.8	5	1.2	0.1	−1	4	0−2
83.5 Na/u.c.	SI′	5.6	−9	5.9	0.1	−10	16	21−30
	SII	4.5	−3	4.8	0.2	−16	32	29−32
	SIII′(1,2)	2.6	−17	2.6	0.5	−17	25	13−22
	SIII′(3)	1.7	−10	2.0	0.8	−11	6	10−12
Na-Y	SI	1.3	−1	1.2	0.1	−3	7	
53.3 Na/u.c.	SI′	4.3	−13	4.8	0.2	5	16	
	SII	3.3	−3	3.9	0.2	−7	30	
HNa-Y/1	SI	1.0	−2	1.2	0.1	−3	7	
21.3 Na/u.c.	SI′	4.5	−10	4.9	0.2	5	9	
	SII	3.4	1	3.8	0.2	−7	5	
HNa-Y/2	SI	1.1	−2	1.2	0.1	−3	7	
13.3 Na/u.c.	SI′	4.6	−9	4.9	0.3	5	6	
HNa-Y/3	SI	0.8	−4	1.2	0.1	−3	2.7	
2.7 Na/u.c.								

[a] The numbers of sodium cations given in the first column were determined by ICP-AES. [b] Parameter $P_Q = Q_{CC}(1 + \eta^2/3)^{1/2}$, obtained by ORIACT MQMAS NMR. [c] Isotropic chemical shift, δ_{iso}, obtained by ORIACT MQMAS NMR. [d] Quadrupole coupling constant $Q_{CC} = 3e^2{\cdot}q{\cdot}Q/h$, obtained by high-speed MAS NMR. The parameters $e{\cdot}q$ and $e{\cdot}Q$ are the z-component of the electric field gradient and the electric quadrupolar moment of the nuclei, respectively. [e] Asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$, obtained by high-speed MAS NMR. [f] Isotropic chemical shift, δ_{iso}, obtained by high-speed MAS NMR. [g] Number of sodium cations, obtained by a separation of the high-speed MAS NMR signals and the number of Na$^+$/u.c. determined by ICP-AES. This study. [h] Previously published results. For zeolite NaLSX see refs 12, 18, and 38. For zeolite NaX see refs 12, 15, 35, and 37.

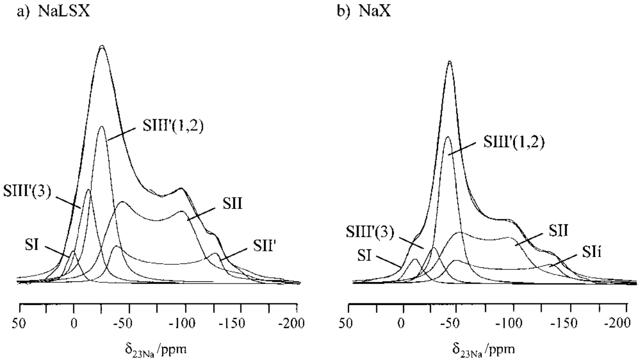

Figure 4. ^{23}Na high-speed MAS NMR spectra of dehydrated zeolites NaLSX (a) and NaX (b) recorded with a sample spinning frequency of 22 kHz and their simulations performed using the Bruker software WINFIT.

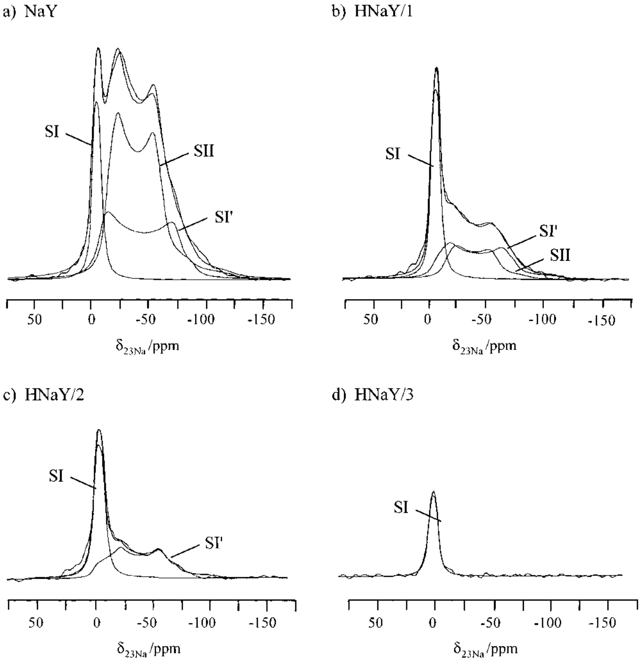

Figure 5. ^{23}Na high-speed MAS NMR spectra of dehydrated zeolites NaY (a), HNaY/1 (b), HNaY/2 (c), and HNaY/3 (d) recorded with a sample spinning frequency of 22 kHz and their simulations performed using the Bruker software WINFIT.

to the total signal is negligible, so that a correction of the relative intensities of the main signals is not necessary.[33] The quadrupolar parameters obtained by a simulation of the MAS spectra are given in columns 5 to 7 of Table 1. The number of sodium cations located at the different extra-framework cation positions given in the last column were calculated by the relative intensities of their ^{23}Na MAS NMR signals and the sodium concentrations obtained by ICP-AES for each zeolite (see column 1 of Table 1). The P_Q and Q_{CC} values determined by the two-dimensional MQMAS NMR and one-dimensional MAS NMR spectroscopy agree within an experimental error of up to ±10%, which is essentially due to the fact that the center of gravity in the MQMAS spectra is estimated visually. The main consequence of an error on P_Q and Q_{CC} would be to affect the calculated isotropic chemical shift value. This is one of the reasons for the differences between the chemical shifts calculated by MQMAS (Table 1 column 4) and the ones obtained by fitting the MAS spectra (Table 1 column 7). In the case of broad signals, an additional source of error may arise from a partial distortion of the line shape and from difficulties in locating the center of gravity accurately. All of these sources of error affect more strongly the broad signals, which explains why those are the ones which show the larger chemical shift deviations between MQMAS and MAS data. In any case, an experimental

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error on the quadrupolar parameters on the order of ±10% has no significant influence on the calculations of the cation populations given in Table 1.

A comparison of the cation populations obtained for zeolites NaLSX and NaX in the present work with those of former NMR studies (see refs 12 and 15) shows slight differences in the calculated populations of the SI and SIII positions. While in ref 12 no sodium cations were assumed to be located at SI positions in zeolite NaLSX, the strong SI peak in the MQMAS NMR spectrum in Figure 2a indicates the presence of these cations also in zeolite NaLSX. In contrast to ref 15, a higher sodium population at SIII′(1,2) positions was found in the present work which agrees well with the results of high-resolution X-ray diffraction analysis.[18] Comparing the cation populations in zeolites NaLSX and NaX, our results suggest that a lower framework aluminum content in zeolite NaX leads to a lower population of SIII′(3) positions in the supercages. The overall population of SI and SI′ sites is found to be lower than observed in previous studies.[12,18,36−38] Besides the differences in sample preparation (see ref 37 for a discussion of this subject), a possible explanation for this deviation could be the presence of a second type of site SI′, which so far has been observed only in a high-resolution structural study.[18] We were not able to resolve a signal from this site in the MQMAS spectra, and therefore it was not taken into account for the analysis of the MAS spectra, which may explain the lower number of Na cations assigned to the SI′ positions.

The homologous series of zeolites Y with different cation exchange degrees, which was studied in the present work for the first time by NMR spectroscopy, shows clearly a preferred substitution of sodium cations located at SII positions in the supercages by ammonium ions. While the parent zeolite NaY has 30 Na^+/u.c. at SII positions, the exchange of 60% (HNaY/1) and 75% (HNaY/2) of the sodium cations results in a decrease of the SII population to 5 and 0 Na^+/u.c., respectively. In the same zeolite samples, the population of the SI′ positions decreases only from 16 Na^+/u.c. for zeolite NaY to 9 and 6 Na^+/u.c. for zeolites HNaY/1 and HNaY/2, respectively. This finding agrees very well with the observation by ^1H MAS NMR of a preferential formation of acidic bridging OH in the supercages of zeolites Y for low exchange degree of sodium cations by ammonium ions.[35]

Conclusions

In this work, we explored, on one hand, the potentiality of a recently introduced NMR method, ORIACT,[26] for the study of sodium-containing zeolites. The technique has been applied to investigate for the first time a number of materials with faujasite structure.

The application of off-resonance RIACT for ^{23}Na triple-quantum MAS NMR to sodium cations in dehydrated zeolites LSX, X, and Y improves significantly the overall spectral quality, especially for signals of nuclei with large quadrupole coupling constants. Using this method, the signals of sodium cations located at SII and SI′ positions in dehydrated zeolites Y could be resolved in the MQMAS NMR spectra. In the case of a series of zeolites in which only the sodium population was varied, the intensities in the ^{23}Na ORIACT triple-quantum MAS NMR spectra reflect qualitatively the variation of the cation population. The information obtained by the two-dimensional ^{23}Na ORIACT triple-quantum MAS NMR spectra is an excellent starting point for a quantitative simulation of one-dimensional ^{23}Na MAS NMR spectra. In fact, they overcome the problems due to the low resolution of signals caused by nuclei with similar quadrupolar interactions and constraints of the number of maximum parameters to fit.

A number of facts could be deduced about the evolution of the relative population of the different sodium sites in those zeolites. In dehydrated zeolites Y, sodium cations located in supercages are preferentially replaced by ammonium ions upon exchange and dehydration, as shown by deconvolution of the ^{23}Na high-speed MAS NMR spectra of materials with different exchange degrees. This is in line with the preferential formation of acidic bridging OH groups in the supercages of zeolite Y at low cation exchange degrees. In the case of zeolites NaLSX and NaX our analysis unveils a strong occupancy of the SIII′-(1,2) position, which is off center of four-member oxygen rings in the supercages. In contrast to an earlier study of zeolite NaLSX, the SI position in the center of the hexagonal prisms appears to be occupied as well by sodium cations.

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