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New Assignment of the Signals in ^{23}Na DOR NMR to Sodium Sites in Dehydrated NaY Zeolite

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A new assignment of the signals in the ^{23}Na DOR NMR spectra to the different sodium sites in dehydrated NaY zeolite is presented. ^{23}Na DOR and MAS NMR measurements of dehydrated NaY, Ca^{2+} -exchanged NaY samples, and NaY samples in which $\text{Mo}(\text{CO})_6$ is adsorbed are used for this purpose. Four distinct signals in the ^{23}Na DOR NMR spectra of dehydrated NaY are found: the first signal with an isotropic chemical shift of -6 ppm and a quadrupolar coupling constant of 0.4 MHz is assigned to the Na^+ cations at site I. The second signal, with an isotropic chemical shift of -12 ppm and a quadrupolar coupling constant of 2.3 MHz, is assigned to the Na^+ cations at sites I'/II'. The third and the fourth signals, with isotropic chemical shifts of -4 and 5 ppm and quadrupolar coupling constants of 4.2 and 4.7 MHz, respectively, are assigned to the Na^+ cations at sites II and III.

Introduction

Zeolites and related molecular sieves are becoming more and more important for a great variety of applications, such as catalysts, adsorbents, and ion exchangers. Their well-defined pore system and high specific area, in combination with their ability to act as a solid acid, make them very useful for these applications. In this respect, zeolite Y is one of the more frequently used zeolites, especially as a catalyst.¹ In the as-synthesized form, sodium cations are present to compensate for the negative charge of the zeolite framework (NaY). A thorough knowledge of the locations of the Na^+ cations and the interactions between these cations and the zeolite lattice and/or the adsorbed reactants is a prerequisite for understanding the solid-state and catalytic properties of zeolites. This knowledge can also be very useful for the study of the incorporation of metal, metal oxide, or metal sulfide particles in the zeolite channels, for instance for the development of hydrocracking catalysts.²⁻⁴

Several techniques have been used to study the locations and the interactions of the Na^+ cations in the Y zeolite, such as XRD,⁵ ND,⁶ IR,^{7,8} and ^{23}Na NMR measurements.⁹⁻¹² However, NMR spectra of quadrupolar nuclei, like ^{23}Na , are limited in resolution, because of the second-order quadrupolar line broadening of the readily observable central $+1/2 \leftrightarrow -1/2$ transition in these spectra. The double-rotation NMR (DOR) technique¹³ is able to reduce this line broadening and thus gives a much better spectral resolution. The observed center of gravity of the MAS powder pattern, or the peak position in the DOR spectrum (δ_{obs}), is the sum of two isotropic shifts (in ppm):

$$\delta_{\text{obs}} = \delta_{\text{iso}}^{\text{CS}} + \delta_{\text{iso}}^{2\text{Q}} \quad (1)$$

where the first term is the isotropic chemical shift and the second term is the isotropic second-order quadrupolar shift. In contrast with the first term, the second term is field dependent and is given by eq 2:

$$\delta_{\text{iso}}^{2\text{Q}} = -\frac{3}{40} \left[\frac{I(I+1) - 3/4}{I^2(2I-1)^2} \right] \frac{C_Q^2}{\nu_L^2} \left[1 + \frac{\eta^2}{3} \right] (10^6) \quad (2)$$

where I is the nuclear spin, η is the asymmetry parameter which describes the deviation of the local electrical field gradient from cylindrical symmetry, C_Q is the quadrupolar coupling constant

Figure 1. Structure of NaY. Cation sites are given by roman numerals.

defined as the product of the electrical field gradient (eq) and the nuclear quadrupole moment (eQ) divided by h , and ν_L is the Larmor frequency of the nucleus at the magnetic field.

In dehydrated NaY five different cation sites are, in principle, available for occupation by sodium cations: site I is located in the hexagonal prisms, sites I' and II' are located in the sodalite cages, and sites II and III are located in the supercages. The structure of NaY with these five different sites is given in Figure 1. Therefore, five distinct ^{23}Na NMR signals could be distinguishable, when the exchange of Na^+ cations between sites is very slow.

Earlier work has been done to assign the signals in the ^{23}Na DOR NMR spectra of dehydrated NaY to the different sodium sites. Jelinek *et al.*^{14,15} measured the ^{23}Na DOR NMR spectrum of dehydrated NaY at 11.7 T. From the known anchoring reaction of the CO parts of $\text{W}(\text{CO})_6$ molecules to Na^+ cations in the supercages and the exchange of NaY with Ti^+ , they found three clearly distinct ^{23}Na DOR NMR signals with the following assignments (line positions at 11.7 T): the signal at -4 ppm originates from Na^+ cations in the α - or supercages at site II, and the signal at -40 ppm belongs to Na^+ cations in the β - or sodalite cages at site I'. However, it was noticed by the authors that their assignments cannot easily be reconciled with results from other measurements, in particular regarding the relative numbers of Na^+ ions at the various sites. Hunger *et al.*¹⁶ measured the ^{23}Na DOR NMR spectra of NaY at 7.0 and 9.4 T. It is important to note that they used solid NaCl as the

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reference, which gives a difference of approximately 7 ppm compared to our reference (saturated NaCl solution). Throughout this paper, only the recalculated line positions with respect to the NaCl solution will be given. From the positions of the signals at these two different field strengths and DOR at different speeds, they assigned the low-field signal at -6.4 ppm (9.4 T) or -7.6 ppm (7.0 T) without noticeable quadrupolar interactions to the sodium cations at site I. The Na^+ cations located at sites I' and II are in their view indistinguishable and yield a combined high-field quadrupolar pattern at -41.0 ppm (9.4 T) or -71.0 ppm (7.0 T) with a quadrupolar coupling constant of 4.2 MHz.

In the present paper, we propose on the basis of ^{23}Na DOR and MAS measurements of NaY a new assignment of the ^{23}Na DOR NMR signals to Na^+ sites in dehydrated NaY. Ca^{2+} -exchanged NaY samples and NaY samples in which $\text{Mo}(\text{CO})_6$ is adsorbed are used to sustain this new assignment. A preliminary account of our work has been published.¹⁷

Experimental Section

Sample Preparation. NaY zeolite was purchased from PQ (Batch CBV-100) and had the formula $\text{Na}_{54}(\text{AlO}_2)_{54}(\text{SiO}_2)_{138}$. Series of Ca^{2+} -exchanged NaY zeolites were prepared at room temperature, using aqueous solutions of CaCl_2 of appropriate concentrations. After the exchange, the samples were washed until Cl^- -free and dried in air at 383 K for 16 h. The composition of the samples was verified by atomic absorption spectroscopy. All samples were stored in a desiccator over a saturated CaCl_2 solution. Additionally, two samples were prepared by gas-phase adsorption of $\text{Mo}(\text{CO})_6$ in NaY and $\text{Ca}_{16}\text{Na}_{22}\text{Y}$. Prior to the adsorption, the zeolite was dried in a He flow at 673 K (heating rate 6 K/min, 2 h at 673 K). After being cooled to 333 K, the zeolites (sample size about 1 g) were saturated by flowing a $\text{Mo}(\text{CO})_6/\text{He}$ mixture through the zeolite. This procedure provided full saturation of the zeolites with $\text{Mo}(\text{CO})_6$, leading to a concentration of about 16 $\text{Mo}(\text{CO})_6$ molecules per unit cell. After saturation, these two samples were transferred into a recirculation-type glovebox (O_2 and H_2O content lower than 1 ppm). Prior to the NMR measurements all other samples were dried in a He flow, using the following temperature program: 6 K/min to 673 K, 2 h at 673 K. After cooling, the samples were transferred into the recirculation-type glovebox, in which the samples were filled into air-tight spinners.

FT-IR Measurements. The far-infrared spectra were recorded using a Bruker IFS 113v FT-IR spectrometer equipped with a heatable *in situ* cell connected to a vacuum system (pressure lower than 10^{-4} Pa). Spectra were measured at 300 K after evacuation of the samples for 1 h at 723 K. The far-infrared spectra were recorded using self-supporting samples (3–8 mg/cm²) in the *in situ* cell equipped with silicon windows. Typically, 5000 scans were recorded at a resolution of 2 cm⁻¹, using standard far-infrared DTGS detectors, a Globar light source, and germanium-coated KBr or Mylar beamsplitters.

NMR Measurements. All ^{23}Na NMR measurements (DOR and MAS) were carried out on a Bruker MSL 400 NMR spectrometer at 105.8 MHz. The spinning speed of the inner DOR rotor was approximately 5 kHz and for the outer rotor 850 Hz, unless indicated otherwise. For acquisition, single-pulse excitation was used with a pulse length of 5 μs , corresponding to a flip angle of approximately 70°. For the different samples the influence of this relatively large pulse angle on intensity ratios between the different signals was checked. No differences in intensity ratios and/or relative phases between pulse lengths of 1 and 5 μs were found. The repetition delay was 1 s. Synchronized pulsing suppressed the odd-numbered DOR sidebands.¹⁸

The ^{23}Na MAS NMR measurements were recorded using a 4-mm double-bearing MAS probehead. Single-pulse excitation was used with a pulse length of 0.6 μs , corresponding to a flip angle of approximately 20°. The repetition delay was 1 s. The spinning rate was 10 kHz.

Figure 2. ^{23}Na DOR NMR spectra of dehydrated NaY (9.4 T) for DOR speeds of respectively 700, 850, and 1000 Hz. The signals are indicated by arrows. For the fourth signal at -46 ppm, see explanation in the text.

For all NMR measurements, typically 1000 FID's were accumulated in 1 K data points. After application of a 100-Hz Lorentzian line broadening, the 1 K data points were zero-filled to 8 K prior to Fourier transformation. All spectra were referred to a saturated NaCl solution, used as an external standard. The ^{23}Na DOR and MAS simulations were performed using the program QNMR.¹⁹

Results and Discussion

NaY. The ^{23}Na DOR NMR spectrum of dehydrated NaY at 9.4 T (850 Hz) is given in Figure 2. This spectrum is almost identical to the spectrum measured by Hunger *et al.*¹⁶ at 9.4 T. It contains signals (center bands) and side bands, which appear on either side of the center bands at distances of twice the rotation speed of the outer rotor. In order to distinguish between the ^{23}Na signals and the spinning side bands in the DOR spectra, DOR was performed at different speeds of the outer rotor. Figure 2 also gives the ^{23}Na DOR NMR spectra of dehydrated NaY for outer rotor speeds of 700 and 1000 Hz. From these spectra it is clear that there are at least three signals (indicated by arrows): one signal at -6 ppm, a second signal at -43 ppm, and a third signal at -24 ppm. The latter feature seems to change slightly on changing the outer rotor speed. Therefore, this band stems from a combination of a signal and a side band.

After the distances between the center bands and the spinning side bands in the ^{23}Na DOR NMR spectra of dehydrated NaY have been measured, it is clear that these distances are not exactly constant (i.e. twice the outer rotor speed). The same irregularities are seen in the 9.4-T ^{23}Na DOR NMR spectra of Hunger *et al.*¹⁶ This means that the ^{23}Na DOR NMR spectrum of dehydrated NaY cannot be simulated with only two center bands as suggested by Hunger *et al.*: one signal without side bands and one signal causing all the side bands. The varying distance between the side bands can only be explained if an extra, fourth signal (see above) is positioned at the low-frequency side of the peak at -43 ppm. The position of this extra signal is at approximately -46 ppm at 9.4 T.

Figure 3. Individual lines/patterns (traces 1–4), simulated (trace 5) and experimental (trace 6) ^{23}Na DOR NMR spectra of dehydrated NaY at 9.4 T: Trace 1, site I'/II'; trace 2, site II; trace 3, site III; trace 4, site I. The signals are indicated by arrows.

Figure 4. Individual lines/patterns (traces 1–4), simulated (trace 5) and experimental (trace 6) ^{23}Na MAS NMR spectra of dehydrated NaY at 9.4 T: Trace 1, site I'/II'; trace 2, site II; trace 3, site III; trace 4, site I.

A careful comparison of the spectra obtained at different DOR speeds shows that no speed-invariant, fifth signal can be obtained from our spectra. It is of course possible that one of the four postulated signals is, in fact, a combination of two signals that should then have almost identical isotropic shifts and quadrupolar coupling constants.

Using these four signals at respectively -6 , -24 , -43 , and -46 ppm allowed the ^{23}Na DOR NMR spectrum of dehydrated NaY at 9.4 T to be simulated using QNMR. Figure 3 gives the experimental and the simulated spectra, together with the individual traces. From this figure it can be seen that the resemblance between the experimental spectrum (trace 6) and final simulation (trace 5) is generally satisfactory. There are only some minor deviations toward the more negative frequency side. In order to verify the correctness of the parameters, the ^{23}Na MAS spectrum of dehydrated NaY at 9.4 T was also simulated using the same parameters as in the DOR simulation. The experimental spectrum and the simulated spectrum, together with the individual traces, are shown in Figure 4. Again, the similarity between the experimental and simulated spectra is good. Using the parameters determined by Hunger *et al.*¹⁶ gave also a good simulated ^{23}Na MAS spectrum, but a simulation of the DOR spectrum, based on their parameters, does not agree with the experimental DOR spectrum. In Table 1 the isotropic

TABLE 1: Parameters Used for the Simulation of the NMR Spectra of Dehydrated NaY (See Figures 3 and 4)

site	δ_{iso} (ppm, ± 1) ^a	P_Q (MHz, ± 0.1) ^b	relative area (%, ± 3)	Na/UC ^c
I	-6	0.4	15	8.1
I'/II'	-12	2.3	16	8.6
II	-4	4.2	53	28.7
III	5	4.7	16	8.6

^a δ_{iso} = isotropic chemical shift. ^b $P_Q = C_Q(1 + \eta^2/3)^{1/2}$. ^c Number of Na^+ cations per unit cell, calculated from the relative areas given in this table.

chemical shifts, the P_Q values (see eq 6), the relative areas, and the number of Na^+ cations per unit cell, calculated from these relative areas, of the four different signals used in the DOR and MAS simulations of the spectra of dehydrated NaY are given. In this table the P_Q values for the different sites and not the separate C_Q and η values are given. The reason is that the η values are difficult to obtain from the MAS simulations due to the broad, featureless MAS patterns.

Additionally, an assignment of the four signals to the five different Na^+ sites, based on symmetry and population arguments, is given in Table 1. Site I is octahedrally coordinated to six framework oxygens^{20,21} and is therefore expected to have a small quadrupolar interaction (and consequently almost no side bands): the signal at -6 ppm is therefore ascribed to Na^+ cations at site I. The Na^+ cations at the sites I'/II' and II are all coordinated to three oxygens,²² but due to the different site locations (sodalite and supercage, respectively), there will be some differences in symmetry and electric field gradients between these sites. Site III is probably the most asymmetric site and will thus have the largest quadrupolar interaction. Site II will have the highest Na^+ population as compared to sites I'/II' and III.⁵ From the information given above, a preliminary assignment of the remaining three signals to the different sites can be made. The signal at -46 ppm (highest quadrupolar interaction) is due to Na^+ at site III. The signal at -43 ppm (with the highest intensity) is assigned to the Na^+ cations at site II. The remaining signal at -24 ppm is ascribed to the Na^+ cations at sites I' and II', which are probably not much different from a symmetry point of view. The correctness of this assignment will be substantiated further on in this paper, where Ca^{2+} -exchanged samples and samples containing adsorbed $\text{Mo}(\text{CO})_6$ are discussed.

From XRD measurements,⁵ it is known that about 12–15% of the Na^+ cations in dehydrated NaY occupy site I, 21–26% are located at sites I'/II' in the sodalite cages, and 49–54% are located in the supercages at site II with the remainder being either in the supercages at site III or unlocated. Comparison of the relative areas of the four different ^{23}Na NMR signals in dehydrated NaY (Table 1) shows that our site populations determined by ^{23}Na NMR (DOR and MAS) are in reasonably good agreement with the site populations determined by XRD (assuming that all the "remaining Na^+ cations" are located at site III). It should be stressed at this point that about 29 sodium cations per unit cell are located at site II. The accuracy of our quantitative results is about 10%. This makes it improbable that large populations of Na^+ are present at site II'. A separate ^{23}Na DOR NMR signal for Na^+ cations at site II', if present, is therefore probably very small and can easily be hidden underneath one of the four main signals (see before). However, quantitative aspects concerning the site populations in dehydrated NaY zeolite in general remain very difficult, because the distribution of the sodium cations over the different sites is strongly dependent on the synthesis and the drying procedure of the NaY zeolite.^{5,10}

With the quadrupolar parameters given in Table 1, it is possible to calculate the DOR positions of the four signals at different field strengths. Substitution of the relevant parameters for ^{23}Na in eqs 1 and 2 (Introduction) results, for field strengths of

TABLE 2: Positions of the Four Signals in ^{23}Na DOR NMR Spectra of Dehydrated NaY at Three Different Field Strengths, Calculated Using Formulas 1 and 2 Given in the Introduction

site	δ_{obs} (7.0 T) ^a (ppm, ± 1)	δ_{obs} (9.4 T) ^b (ppm, ± 1)	δ_{obs} (11.7 T) ^c (ppm, ± 1)
I	-6	-6	-6
I'/II'	-33	-24	-20
II	-74	-43	-29
III	-83	-45	-27

^a Field strength used by Hunger *et al.*¹⁶ ^b Our measurements and those of Hunger *et al.*¹⁶ ^c Field strength used by Jelinek *et al.*^{14,15}

Figure 5. Simulated ^{23}Na DOR NMR spectrum of dehydrated NaY at 7.0 T.

respectively 7.0, 9.4, and 11.7 T, in the following formulas:

$$\delta_{\text{obs}}(7.0 \text{ T}) = \delta_{\text{iso}}^{\text{CS}} - 3.971P_Q^2 \quad (3)$$

$$\delta_{\text{obs}}(9.4 \text{ T}) = \delta_{\text{iso}}^{\text{CS}} - 2.233P_Q^2 \quad (4)$$

$$\delta_{\text{obs}}(11.7 \text{ T}) = \delta_{\text{iso}}^{\text{CS}} - 1.429P_Q^2 \quad (5)$$

where

$$P_Q = C_Q \left[1 + \frac{\eta^2}{3} \right]^{1/2} \quad (6)$$

In these formulas, the shift values are all in units of ppm, while the P_Q values are given in MHz. The DOR positions of the four sodium signals at these three different field strengths were calculated with these formulas and are presented in Table 2. The data in this table can be used to compare our measurements (9.4 T) with those of Hunger *et al.*¹⁶ (7.0 and 9.4 T) and Jelinek *et al.*^{14,15} (11.7 T).

Hunger *et al.*¹⁶ found, in addition to a line at -6.4 ppm (9.4 T), in agreement with our results, a high-field quadrupolar pattern at -71.0 ppm (7.0 T) or -41.0 ppm (9.4 T). From our data in Table 2, it follows that what they are describing as one quadrupolar pattern is in fact a combination of two closely spaced signals. The signal at -33 ppm (7.0 T) is present but difficult to see, because it is very close to the large Na^+ signal of the hexagonal prisms. Figure 5 depicts the simulated ^{23}Na DOR NMR spectrum of dehydrated NaY at 7.0 T using the data of Table 1. This spectrum is in reasonable agreement with the spectrum measured by Hunger *et al.*¹⁶

Jelinek *et al.*^{14,15} found, in addition to a signal at -4 ppm, signals at -30 and -42 ppm (11.7 T). Judging from Table 2, there should be a signal at approximately -19 ppm. This can hardly be seen because the resolution of their spectra at 11.7 T is not sufficient. From a more close inspection of the 11.7 T spectra, it can be concluded that all side bands are present (i.e. the measurements were not rotor-synchronized). The experimental part of Jelinek's paper does not specify whether synchronized pulsing was used. According to our calculations, the third and fourth signals are almost at the same position at approximately -28 ppm. This is in agreement with their ^{23}Na DOR NMR spectra. However, according to our simulation data, their band at -42 ppm is not a signal but must be a spinning side band. This is in principle possible because the distance between

Figure 6. ^{23}Na DOR NMR spectra of a series of Ca^{2+} -exchanged NaY zeolites. **Figure 7.** Far-IR spectrum of dehydrated NaY at 300 K.

the signal at -30 ppm and this side band is 12 ppm, which could very well correspond (at 11.7 T) to approximately twice the outer rotor speed (1600 Hz). The precise DOR speed at which the NaY spectra were recorded, however, was not mentioned; only a range of 600–800 Hz was specified.

To sustain the assignments of the four different signals to the Na^+ sites in dehydrated NaY, Ca^{2+} -exchanged NaY samples and NaY samples in which $\text{Mo}(\text{CO})_6$ is adsorbed were used.

Ca^{2+} Exchanged Samples. Figure 6 shows the ^{23}Na DOR NMR spectra of a series of Ca^{2+} -exchanged NaY zeolites. From this figure the effect of an increasing degree of ion exchange with Ca^{2+} is seen as a decrease in intensity of the signal at -3 ppm. It is well-known that at low degrees of exchange Ca^{2+} preferably substitutes the Na^+ in the hexagonal prisms.^{23,24} The signal at -3 ppm (corresponding to -6 ppm in dehydrated NaY) is therefore assigned to the Na^+ cations in the hexagonal prisms. Besides shifts in signal positions, the intensities of the side bands of the other center bands become stronger compared to the ^{23}Na DOR NMR spectrum of NaY. Probably, Ca^{2+} changes the electric field gradients surrounding the different Na^+ cation sites. In the ^{23}Na DOR NMR spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ there is still some signal intensity left at -3 ppm (Figure 6).

To verify whether in this case a new signal is positioned under the signal of Na^+ in the hexagonal prisms (at -3 ppm) or whether it should rather be explained by residual Na^+ cations at site I, far-infrared measurements were performed. Figure 7 shows the far-IR spectrum of dehydrated NaY. The assignments of the far-IR signals to the Na^+ sites, as reported in the literature,^{8,25} are indicated in Figure 7. The far-IR spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ is shown in Figure 8. The assignments, according to the same literature, are again indicated in the figure. It is clear that in $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ there is still some Na^+ left in the hexagonal prisms

Figure 8. Far-IR spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ at 300 K.TABLE 3: Parameters Used for the Simulation of the DOR Spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ (See Figure 9)

site	δ_{iso} (ppm, ± 1) ^a	P_Q (MHz, ± 0.1) ^b	relative area (%, ± 3)	Na/UC ^c
I	-2	0.4	6	1.0
I'/II'	-4	2.3	4	0.6
II	-3	4.6	57	9.1
III	3	5.0	33	5.3

^a δ_{iso} = isotropic chemical shift. ^b $P_Q = C_Q(1 + \eta^2/3)^{1/2}$. ^c Number of Na^+ cations per unit cell, calculated from the relative areas given in this table.

Figure 9. Individual lines/patterns (traces 1-4), simulated (trace 5) and experimental (trace 6) ^{23}Na DOR NMR spectra of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ at 9.4 T: Trace 1, site I'/II'; trace 2, site II; trace 3, site III; trace 4, site I. The signals are indicated by arrows.

(peak at 158 cm^{-1}), which was not to be expected *a priori* at this exchange level.

Assuming that Ca^{2+} changes the electric field gradients and that there is still some Na^+ left in the hexagonal prisms, the ^{23}Na DOR NMR spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ at 9.4 T was simulated with the parameters given in Table 3 using QNMR. For this simulation, again four signals were needed. From these data it can be seen that the Ca^{2+} exchange has an influence on the isotropic chemical shift of the Na^+ cations at sites I and I'/II'. For the Na^+ cations at sites II and III, the isotropic chemical shifts remain almost the same, but the P_Q values become larger than in NaY. This is caused by the increasing electric field gradients for the Na^+ cations at these sites, induced by local changes in the framework geometry.²⁵ Figure 9 shows the simulated ^{23}Na DOR spectrum of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$ (with individual traces) together with the experimental spectrum.

In the case of $\text{Ca}_{19}\text{Na}_{16}\text{Y}$, one would expect that almost all the residual Na^+ cations are located in the supercages at site II and III.²³ From the relative areas of the four different ^{23}Na NMR

Figure 10. ^{23}Na DOR NMR spectra of $\text{Mo}(\text{CO})_6/\text{NaY}$ (9.4 T) for DOR speeds of respectively 700, 850, and 1000 Hz. The signals are indicated by arrows. For the third signal at -27 ppm, see explanation in the text.

signals (Table 3), it is obvious that 90% of all residual Na^+ cations are present in the supercages. The Na^+ populations at site I and sites I'/II' are greatly reduced as compared to the case for dehydrated NaY. This is in agreement with the fact that Ca^{2+} preferably substitutes the sodium cations at site I and, at higher degrees of ion exchange, also the sodium cations at site I'/II'.^{23,24}

The effect of small bivalent ions changing the electric field gradients was already noticed by Hunger *et al.*¹⁶ for the analogous exchange with Ba^{2+} . They simulated the ^{23}Na MAS spectrum of a Ba^{2+} -exchanged NaY sample with a higher quadrupolar coupling constant for the high-field pattern than for the ^{23}Na MAS spectrum of dehydrated NaY. However, the degree of exchange of Na^+ for Ba^{2+} was 83% ($\text{Ba}_{22}\text{Na}_9\text{Y}$). In this case, it is obvious that the Ba^{2+} replaces not only the sodium cations in the hexagonal prisms but also exchanges the sodium cations in the sodalite cages to a large extent (only 9 Na^+ cations per unit cell are left!). Therefore, their ^{23}Na MAS spectrum of $\text{Ba}_{22}\text{Na}_9\text{Y}$ is probably almost exclusively due to the Na^+ cations in the supercages. Only the parameters of the Na^+ cations at sites II and III (our simulation; see Table 1) are needed to simulate the ^{23}Na MAS spectrum of $\text{Ba}_{22}\text{Na}_9\text{Y}$ as measured by Hunger *et al.*¹⁶

Samples Prepared by Gas-Phase Adsorption of $\text{Mo}(\text{CO})_6$

Figure 10 shows the ^{23}Na DOR NMR spectra of NaY in which $\text{Mo}(\text{CO})_6$ is adsorbed ($\text{Mo}(\text{CO})_6/\text{NaY}$) for outer rotor speeds of 700, 850, and 1000 Hz. From this figure it can be seen at first sight that there are two signals (indicated by arrows): one signal at -2 ppm and a second signal at -24 ppm. The side band on the right of the latter signal does not appear at twice the outer rotor speed from the center band. Therefore, the same reasoning as in dehydrated NaY can be used, *i.e.* a third signal must be present at the low-frequency side of the peak at -24 ppm. The position of this signal is approximately -27 ppm at 9.4 T. The large $\text{Mo}(\text{CO})_6$ molecules can only enter the 13-Å supercages of the NaY zeolite. From IR measurements,^{26,27} it is known that the oxygen ends of the CO ligand interact with the supercage Na^+ cations (sites II and III). This interaction renders a more symmetrical environment of these Na^+ cations, and therefore a lower P_Q value can be expected.

With this taken into account and from the DOR simulation of dehydrated NaY as a starting point, the ^{23}Na DOR NMR spectrum of $\text{Mo}(\text{CO})_6/\text{NaY}$ was simulated using QNMR. Figure

Figure 11. Individual lines/patterns (traces 1–3), simulated (trace 4) and experimental (trace 5) ^{23}Na DOR NMR spectra of $\text{Mo}(\text{CO})_6/\text{NaY}$ at 9.4 T: Trace 1, site I'/II'; trace 2, site II/III; trace 3, site I. The signals are indicated by arrows.

Figure 12. Simulated (bottom) and experimental (top) ^{23}Na MAS NMR spectrum of $\text{Mo}(\text{CO})_6/\text{NaY}$ at 9.4 T.

TABLE 4: Parameters Used for the Simulation of the NMR Spectra of NaY in Which $\text{Mo}(\text{CO})_6$ Is Adsorbed (See Figures 11 and 12)

site	δ_{iso} (ppm, ± 1) ^a	P_Q (MHz, ± 0.1) ^b	relative area (%, ± 3)	Na/UC ^c
I	-2	0.4	19	10.3
I'/II'	-10	2.3	29	15.7
II/III	-9	2.8	52	28.1

^a δ_{iso} = isotropic chemical shift. ^b $P_Q = C_Q(1 + \eta^2/3)^{1/2}$. ^c Number of Na^+ cations per unit cell, calculated from the relative areas given in this table.

11 depicts the experimental spectrum and the simulated ^{23}Na DOR NMR spectra, together with the individual traces. The experimental ^{23}Na MAS spectrum together with the simulated spectrum are given in Figure 12.

In Table 4, the isotropic chemical shifts, the P_Q values, the relative areas, and the number of Na^+ cations per unit cell, calculated from these relative areas, of the three signals used in the DOR and MAS simulations of $\text{Mo}(\text{CO})_6/\text{NaY}$ are given. Comparing these data with the simulation data of dehydrated NaY allows the following to be seen: the signal at -2 ppm in $\text{Mo}(\text{CO})_6/\text{NaY}$, which was earlier assigned to the Na^+ cations in the hexagonal prisms (site I), is shifted slightly compared to the original signal in dehydrated NaY. Probably, the Na^+ cations at site I are only slightly influenced by the adsorption of $\text{Mo}(\text{CO})_6$ in the supercages. A similar effect is also seen for the signal at -24 ppm in dehydrated NaY, which shifts to about -22 ppm in $\text{Mo}(\text{CO})_6/\text{NaY}$. No change of the P_Q value for this signal was observed, so it is now definitely assigned to the sodium cations in the sodalite cages at site I'/II'. The third signal at -27

Figure 13. ^{23}Na DOR NMR spectra of $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ (9.4 T) for DOR speeds of respectively 700, 850, and 1000 Hz. The signals are indicated by arrows. For the second signal at -27 ppm, see explanation in the text.

ppm has a P_Q value of 2.8 MHz as compared to P_Q values of 4.2 and 4.7 MHz for the two separate signals in dehydrated NaY (positioned at respectively -43 and -46 ppm). Due to the interactions with $\text{Mo}(\text{CO})_6$, the Na^+ cations at the distinct sites II and III in NaY will become indistinguishable (at 9.4 T) and the P_Q values will diminish (more symmetric surrounding upon $\text{Mo}(\text{CO})_6$ adsorption). This signal at -27 ppm is assigned to the Na^+ cations in the supercages interacting with the $\text{Mo}(\text{CO})_6$. The signals at -43 and -46 ppm in NaY are therefore assigned to Na^+ cations in the supercages at sites II and III. The signal at -43 ppm stems from Na^+ cations at site II, because this site has a higher Na^+ population compared to site III.⁵ It should be remarked at this point that our ^{23}Na DOR NMR spectra of $\text{Mo}(\text{CO})_6/\text{NaY}$ are not in agreement with the assignments presented by Hunger *et al.*¹⁶ In the latter case, the ^{23}Na DOR NMR signal due to the Na^+ cations in the sodalite cages (not interacting with $\text{Mo}(\text{CO})_6$) should have remained near -44 ppm after adsorption of $\text{Mo}(\text{CO})_6$.

A similar situation would have arisen after postulation of a fifth signal near that of site I' (see before). In order to have any noticeable effect at the low-frequency side of the ^{23}Na DOR NMR spectrum of dehydrated NaY, the sodium cations at site II' would have to possess a quadrupolar coupling constant of at least 4.5–5 MHz. We consider a difference between the quadrupolar interactions at sites I' and II' (about 2.3 and 4.7 ± 0.2 MHz, respectively) as unrealistically large. Apart from that, after adsorption of $\text{Mo}(\text{CO})_6$, the spinning side bands of such a signal should have remained visible.

To support the final assignments following from the $\text{Mo}(\text{CO})_6/\text{NaY}$ sample, a $\text{Ca}_{16}\text{Na}_{22}\text{Y}$ sample in which $\text{Mo}(\text{CO})_6$ is adsorbed ($\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$) was prepared. Figure 13 shows the ^{23}Na DOR NMR spectra of $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ for outer rotor speeds of 700, 850, and 1000 Hz. It can be seen that there is at least one center band (indicated by arrow) positioned at -24 ppm. A second signal, required to explain the distance of the side band on the right, is positioned at -27 ppm (analogous to $\text{Mo}(\text{CO})_6$ in NaY). The signal at -2 ppm has disappeared, due to the substitution of the Na^+ cations in the hexagonal prisms by the Ca^{2+} cations²³ (see paragraph on Ca^{2+} exchange).

With the knowledge that $\text{Mo}(\text{CO})_6$ can only interact with the sodium cations in the supercages and that most of the residual Na^+ cations after exchange with Ca^{2+} are located in the supercages, the simulation of $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ was per-

Figure 14. Simulated (bottom) and experimental (top) ^{23}Na DOR NMR spectrum of $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ at 9.4 T. The signals are indicated by arrows.

TABLE 5: Parameters Used for the Simulation of the NMR Spectra of $\text{Ca}_{16}\text{Na}_{22}\text{Y}$ in Which $\text{Mo}(\text{CO})_6$ Is Adsorbed (See Figure 14)

site	δ_{iso} (ppm, ± 1) ^a	P_Q (MHz, ± 0.1) ^b	relative area (%, ± 3)	Na/UC ^c
I	-2	0.4	2	0.4
I'/II'	-13	2.3	40	8.8
II/III	-10	2.8	58	12.8

^a δ_{iso} = isotropic chemical shift. ^b $P_Q = C_Q(1 + \eta^2/3)^{1/2}$. ^c Number of Na^+ cations per unit cell, calculated from the relative areas given in this table.

formed with QNMR. From the quadrupolar parameters used for the $\text{Mo}(\text{CO})_6/\text{NaY}$, the spectrum was simulated and is given in Figure 14 together with the experimental spectrum.

Table 5 summarizes the isotropic chemical shifts, the P_Q values, the relative areas, and the number of Na^+ cations per unit cell, calculated from these relative areas, of the signals used in the DOR simulation. From this table it is obvious that, as is to be expected, almost all quadrupolar parameters are the same as those for $\text{Mo}(\text{CO})_6/\text{NaY}$. So, although in CaNaY samples Ca^{2+} can change the electric field gradients around the Na^+ cations at sites II and III in the supercages, these differences disappear upon $\text{Mo}(\text{CO})_6$ adsorption.

Quantitative aspects regarding the samples in which $\text{Mo}(\text{CO})_6$ is adsorbed are difficult (Tables 4 and 5). Upon adsorption of $\text{Mo}(\text{CO})_6$, there seems to take place a redistribution of the Na^+ cations: the populations of site I ($\text{Mo}(\text{CO})_6/\text{NaY}$, Table 4) and especially of sites I'/II' in $\text{Mo}(\text{CO})_6/\text{NaY}$ and $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ (see Tables 4 and 5) are larger than in dehydrated NaY (Table 1) and $\text{Ca}_{16}\text{Na}_{22}\text{Y}$, respectively (Table 3). In the case of $\text{Mo}(\text{CO})_6/\text{Ca}_{16}\text{Na}_{22}\text{Y}$ (Table 5) the population of the Na^+ cations at site I decreases, in agreement with the Ca^{2+} exchange (see paragraph on Ca^{2+} exchange). However, it is difficult to sustain the quantitative aspects because population data for these samples in which $\text{Mo}(\text{CO})_6$ is adsorbed (e.g. from XRD) are not available.

Conclusions

We have shown by careful analysis of the ^{23}Na DOR and MAS NMR spectra (the former at different speeds of the outer rotor) that four different Na^+ sites can be distinguished in dehydrated NaY zeolite. With our values for the parameters δ_{iso} and P_Q , we are able to simulate not only the ^{23}Na DOR NMR spectra of NaY at 9.4 T, but also those at 7.0 T (Hunger *et al.*¹⁶). The same is true for the ^{23}Na MAS NMR spectra at 7 T, published by Hunger *et al.*¹⁶ and at 11.7 T, published by Jelinek *et al.*^{14,15}

The ^{23}Na DOR and MAS NMR spectra of $\text{Ca}_{16}\text{Na}_{22}\text{Y}$ were analyzed by taking into account that not all I-sites are devoid of Na^+ cations (far-IR) and, consequently, that some residual NMR

signal remains at -3 ppm. The assembly of center and side bands in the ^{23}Na DOR spectra can again only be explained by invoking four different cation sites. The δ_{iso} and/or P_Q values of the Na^+ cations at the other sites (I'/II', II, III) were influenced by the increasing electric field gradient values induced by the Ca^{2+} ions and accompanying changes in the lattice structure.²⁵

Adsorption of $\text{Mo}(\text{CO})_6$ in either NaY or $\text{Ca}_{16}\text{Na}_{22}\text{Y}$ has the effects as already proposed by Jelinek *et al.*^{14,15} The arguments for postulating different ^{23}Na NMR signals for Na^+ ions in supercages and sodalite cages are further strengthened. Regarding the quantitative aspects of our study, the known distributions for some NaY samples (based on XRD measurements) are reasonably reproduced. Attention should, however, be paid to the proven, extreme sensitivity of the Na^+ distributions in NaY toward the details of synthesis and subsequent treatments.^{5,10}

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