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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 Mo(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. 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.

Several techniques have been used to study the locations and the interactions of the Na$^+$ cations in the Y zeolite, such as XRD, ND, IR, and $^{23}$Na NMR measurements. 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 $+1/2 ightarrow -1/2$ transition in these spectra. The double-rotation NMR (DOR) technique 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 ($\delta_{obs}$), is the sum of two isotropic shifts (in ppm):

$$\delta_{obs} = \delta_{iso}^{CS} + \delta_{iso}^{2Q}$$

(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:

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

(2)

where $I$ is the nuclear spin, $\eta$ is the asymmetry parameter which describes the deviation of the local electrical field gradient from cylindrical symmetry, $C_Q$ is the quadrupolar coupling constant defined as the product of the electrical field gradient (eq) and the nuclear quadrupole moment (eQ) divided by $h$, and $\nu_l$ 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. measured the $^{23}$Na DOR NMR spectrum of dehydrated NaY at 11.7 T. From the known anchoring reaction of the CO parts of W(CO)$_6$ molecules to Na$^+$ cations in the supercages and the exchange of Na$^+$ 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 $-44$ ppm originates from Na$^+$ cations in the hexagonal prisms at site I, the signal at $-29$ ppm stems from Na$^+$ cations in the I'/II' sites, and the signal at $-40$ ppm belongs to Na$^+$ cations in the $\beta$- or sodalite cages at site II'. 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. 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
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 23Na DOR and MAS measurements of NaY a new assignment of the 23Na DOR NMR signals to Na⁺ sites in dehydrated NaY. Ca²⁺-exchanged NaY samples and NaY samples in which Mo(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 Na₅₄(Al₂O₅)₁₅₄(SiO₂)₁₃₈. Series of Ca²⁺-exchanged NaY zeolites were prepared at room temperature, using aqueous solutions of CaCl₂ 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 CaCl₂ solution. Additionally, two samples were prepared by gas-phase adsorption of Mo(CO)₆ in NaY and Ca₁₄Na₂₂Y. Prior to the adsorption, the zeolite was dried in a He flow at 673 K (heating rate 5 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 Mo(CO)₆/He mixture through the zeolite. This procedure provided full saturation of the zeolites with Mo(CO)₆, leading to a concentration of about 16 Mo(CO)₆ molecules per unit cell. After saturation, these two samples were transferred into a recirculation-type glovebox (O₂ and H₂O 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 23Na 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 23Na 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.

Results and Discussion

NaY. The 23Na 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 23Na 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 23Na 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 23Na 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 23Na DOR NMR spectra of Hunger et al.¹⁶ This means that the 23Na 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.
only some minor deviations toward the more negative frequency side. In order to verify the correctness of the parameters, the experimental DOR spectrum of dehydrated NaY was simulated using the same parameters as in the DOR simulation. With the individual traces, are shown in Figure 3. From this figure it can be seen that the similarity between the experimental and simulated spectra is good. The correctness of this assignment will be substantiated further in this paper, where Ca²⁺-exchanged samples and samples containing adsorbed Mo(CO)₆ are discussed.

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. 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 Ca²⁺-exchanged samples and samples containing adsorbed Mo(CO)₆ are discussed.

From XRD measurements,2 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 Na²⁺ NMR signals in dehydrated NaY (Table 1) shows that our site populations determined by ²³Na 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 ²³Na 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 ²³Na in eqs 1 and 2 (Introduction) results, for field strengths of

| Table 1: Parameters Used for the Simulation of the NMR Spectra of Dehydrated NaY (See Figures 3 and 4) |
|---|---|---|---|
| site | \( \delta_{iso} \) (ppm, ±1)* | \( P_Q \) (MHz, ±0.1)* | relative area (%, ±3) | Na⁺/UC* |
| 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 |

* \( \delta_{iso} \) = isotropic chemical shift. * \( P_Q = C_Q(1 + \eta^2/3)^{1/2} \). * Number of Na⁺ cations per unit cell, calculated from the relative areas given in this table.
Third and fourth signals are almost at the same position at approximately -28 ppm. This is in agreement with their Z3Na band at DOR NMR spectra. However, according to our simulation data, synchronized pulsing was used. According to our calculations, the band. This is in principle possible because the distance between 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 23Na 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 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, Ca2+-exchanged NaY samples and NaY samples in which Mo(CO)6 is adsorbed were used.

Ca2+ Exchanged Samples. Figure 6 shows the 23Na DOR NMR spectra of a series of Ca2+-exchanged NaY zeolites. From this figure the effect of an increasing degree of ion exchange with Ca2+ as seen a decrease in intensity of the signal at -3 ppm. It is well-known that at low degrees of exchange Ca2+ 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 prism. Besides shifts in signal positions, the intensities of the side bands of the other center bands become stronger compared to the 23Na DOR NMR spectrum of NaY. This is shown in Figure 8. The assignments, according to the same literature, are again indicated in the figure. It is clear that in Ca19Na16Y there is still some Na+ left in the hexagonal prisms.
Na\(^{+}\) cations at sites I\(_1\) and I\(_1\)'I\(_1\)' for the almost the same, but the This is caused by the increasing electric field gradients for the residual Na\(^{+}\) cations are located in the supercages at site I\(_1\) and Na\(^{+}\) cations at these sites, induced by local changes in the framework geometry. Figure 9 shows the 23Na DOR NMR spectra of Ca\(_{19}\)Na\(_{16}\)Y (with individual traces) together with the 23Na DOR NMR spectra of Mo(CO)\(_6\)/NaY as measured by Hunger et al.\(^{16}\) 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 23Na MAS spectrum of a Ba\(^{2+}\)-exchanged NaY sample with a higher quadrupolar coupling constant for the high-field pattern than for the 23Na MAS spectrum of dehydrated NaY. However, the degree of exchange of Na\(^{+}\) for Ba\(^{2+}\) was 83\% (Ba\(_2\)Na\(_9\)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 23Na MAS spectrum of Ba\(_2\)Na\(_9\)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 23Na MAS spectrum of Ba\(_2\)Na\(_9\)Y as measured by Hunger et al.\(^{16}\)

Samples Prepared by Gas-Phase Adsorption of Mo(CO)\(_6\).

Figure 10 shows the 23Na DOR NMR spectra of NaY in which Mo(CO)\(_6\) is adsorbed (Mo(CO)\(_6\)/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 \(-27\) ppm, see explanation in the text.

Table 3: Parameters Used for the Simulation of the DOR Spectrum of Ca\(_{19}\)Na\(_{16}\)Y (See Figure 9)

<table>
<thead>
<tr>
<th>site</th>
<th>(\delta_{iso}) (ppm, (\pm 1))</th>
<th>(P_Q) (MHz, (\pm 0.1))</th>
<th>relative area (%, (\pm 3))</th>
<th>Na/UC</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(-2)</td>
<td>0.4</td>
<td>6</td>
<td>1.0</td>
</tr>
<tr>
<td>I'/'I'</td>
<td>(-2)</td>
<td>4.6</td>
<td>57</td>
<td>9.1</td>
</tr>
<tr>
<td>III</td>
<td>(-3)</td>
<td>5.0</td>
<td>6.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(a\) \(\delta_{iso}\) = isotropic chemical shift. \(b\) \(P_Q = C_0(1 + \eta^2/3)^{1/2}\). \(c\) Number of Na\(^{+}\) cations per unit cell, calculated from the relative areas given in this table.

(peak at 158 cm\(^{-1}\)), which was not to be expected \textit{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 23Na DOR NMR spectrum of Ca\(_{19}\)Na\(_{16}\)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'/'I'. 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.\(^{23}\) Figure 9 shows the simulated 23Na DOR spectrum of Ca\(_{19}\)Na\(_{16}\)Y (with individual traces) together with the experimental spectrum.

In the case of Ca\(_{19}\)Na\(_{16}\)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 23Na NMR 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'/'I' 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'/'I'.\(^{23,24}\)
ppm in Mo(CO)\textsubscript{6}/Na\textsubscript{Y}. No change of the Na\textsuperscript{+} cations per unit cell, calculated from these relative areas, of the three signals used in the DOR NMR spectra, together with the individual traces. The signals are given in Figure 12.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
site & \(\delta_{\text{iso}}\) (ppm, \(\pm 1\)) & \(P_Q\) (MHz, \(\pm 0.1\)) & relative area \((\% , \pm 3)\) & Na/UC\textsuperscript{c} \\
\hline
I & -2 & 0.4 & 19 & 10.3 \\
I'/II' & -10 & 2.3 & 29 & 15.7 \\
II/III & -9 & 2.8 & 52 & 28.1 \\
\hline
\end{tabular}
\caption{Parameters Used for the Simulation of the NMR Spectra of Na\textsubscript{Y} In Which Mo(CO)\textsubscript{6} Is Adsorbed (See Figures 11 and 12)}
\end{table}

* \(\delta_{\text{iso}}\) = isotropic chemical shift. \(\delta_{\text{iso}} = C_0(1 + \eta^2/3)^{1/2}\) \(\eta\) = Number of Na\textsuperscript{+} cations per unit cell, calculated from the relative areas given in this table.

Figure 11. Individual lines/patterns (traces 1–3), simulated (trace 4) and experimental (trace 5) \(^{23}\text{Na}\) DOR NMR spectra of Mo(CO)\textsubscript{6}/Na\textsubscript{Y} 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) \(^{23}\text{Na}\) MAS NMR spectrum of Mo(CO)\textsubscript{6}/Na\textsubscript{Y} at 9.4 T.

\begin{figure}
\centering
\includegraphics[width=\linewidth]{figure12}
\caption{Simulated (bottom) and experimental (top) \(^{23}\text{Na}\) MAS NMR spectrum of Mo(CO)\textsubscript{6}/Na\textsubscript{Y} at 9.4 T.}
\end{figure}


Figure 13. \(^{23}\text{Na}\) DOR NMR spectra of Mo(CO)\textsubscript{6}/Ca\textsubscript{16}Na\textsubscript{22}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.

\begin{figure}
\centering
\includegraphics[width=\linewidth]{figure13}
\caption{\(^{23}\text{Na}\) DOR NMR spectra of Mo(CO)\textsubscript{6}/Ca\textsubscript{16}Na\textsubscript{22}Y (9.4 T) for DOR speeds of respectively 700, 850, and 1000 Hz.}
\end{figure}

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 Na\textsubscript{Y} (positioned at respectively \(-43\) and \(-46\) ppm). Due to the interactions with Mo(CO)\textsubscript{6}, the Na\textsuperscript{+} cations at the distinct sites II and III in Na\textsubscript{Y} will become indistinguishable (at 9.4 T) and the \(P_Q\) values will diminish (more symmetric surrounding upon Mo(CO)\textsubscript{6} adsorption). This signal at \(-27\) ppm is assigned to the Na\textsuperscript{+} cations in the supercages interacting with the Mo(CO)\textsubscript{6}. The signals at \(-43\) and \(-46\) ppm in Na\textsubscript{Y} are therefore assigned to Na\textsuperscript{+} cations in the supercages at sites II and III. The signal at \(-43\) ppm stems from Na\textsuperscript{+} cations at site II, because this site has a higher Na\textsuperscript{+} population compared to site III.\textsuperscript{5} It should be remarked at this point that our \(^{23}\text{Na}\) DOR NMR spectra of Mo(CO)\textsubscript{6}/Na\textsubscript{Y} are not in agreement with the assignments presented by Hunger \textit{et al.}\textsuperscript{16} In the latter case, the \(^{23}\text{Na}\) DOR NMR signal due to the Na\textsuperscript{+} cations in the sodalite cages (not interacting with Mo(CO)\textsubscript{6}) should have remained near \(-44\) ppm after adsorption of Mo(CO)\textsubscript{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 \(^{23}\text{Na}\) DOR NMR spectrum of dehydrated Na\textsubscript{Y}, 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 Mo(CO)\textsubscript{6}, the spinning side bands of such a signal should have remained visible.

To support the final assignments following from the Mo(CO)\textsubscript{6}/Na\textsubscript{Y} sample, a Ca\textsubscript{16}Na\textsubscript{22}Y sample in which Mo(CO)\textsubscript{6} is adsorbed (Mo(CO)\textsubscript{6}/Ca\textsubscript{16}Na\textsubscript{22}Y) was prepared. Figure 13 shows the \(^{23}\text{Na}\) DOR NMR spectra of Mo(CO)\textsubscript{6}/Ca\textsubscript{16}Na\textsubscript{22}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 Mo(CO)\textsubscript{6}/Na\textsubscript{Y}). The signal at \(-27\) ppm has disappeared, due to the substitution of the Na\textsuperscript{+} cations in the hexagonal prisms by the Ca\textsuperscript{2+} cations\textsuperscript{23} (see paragraph on Ca\textsuperscript{2+} exchange).

With the knowledge that Mo(CO)\textsubscript{6} can only interact with the sodium cations in the supercages and that most of the residual Na\textsuperscript{+} cations after exchange with Ca\textsuperscript{2+} are located in the supercages, the simulation of Mo(CO)\textsubscript{6}/Ca\textsubscript{16}Na\textsubscript{22}Y was per-
Figure 14. Simulated (bottom) and experimental (top) $^{23}$Na DOR NMR spectrum of Mo(CO)$_6$/Ca$_{16}$Na$_{22}$Y at 9.4 T. The signals are indicated by arrows.

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

<table>
<thead>
<tr>
<th>site</th>
<th>$\delta_{23}$(ppm, $\pm$1)$^a$</th>
<th>$P_Q$ (MHz, $\pm$0.1)$^a$</th>
<th>relative area (% $\pm$3)</th>
<th>Na+/UC$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-2</td>
<td>0.4</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>I'</td>
<td>-13</td>
<td>2.3</td>
<td>40</td>
<td>8.8</td>
</tr>
<tr>
<td>II/III</td>
<td>-10</td>
<td>2.8</td>
<td>58</td>
<td>12.8</td>
</tr>
</tbody>
</table>

$^a$ $\delta_{23}$ = isotropic chemical shift. $^b$ $P_Q$ = $C_0(1 + \eta^2/3)^{1/2}$. $^c$ 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 Mo(CO)$_6$/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 Mo(CO)$_6$/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 Mo(CO)$_6$ adsorption.

Quantitative aspects regarding the samples in which Mo(CO)$_6$ is adsorbed are difficult (Tables 4 and 5). Upon adsorption of Mo(CO)$_6$, there seems to take place a redistribution of the Na$^+$ cations: the populations of site I (Mo(CO)$_6$/NaY, Table 4) and especially of sites I' and II in Mo(CO)$_6$/NaY and Mo(CO)$_6$/Ca$_{16}$Na$_{22}$Y (see Tables 4 and 5) are larger than in dehydrated NaY (Table 1) and Ca$_{16}$Na$_{22}$Y, respectively (Table 3). In the case of Mo(CO)$_6$/Ca$_{16}$Na$_{22}$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 Mo(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 $\delta_{23}$ 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.\textsuperscript{19}). The same is true for the $^{23}$Na MAS NMR spectra at 7 T, published by Hunger et al.,\textsuperscript{16} and at 11.7 T, published by Jelinek et al.\textsuperscript{14,15} The $^{23}$Na DOR and MAS NMR spectra of Ca$_{12}$Na$_4$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 NMR spectra can again only be explained by invoking four different cation sites. The $\delta_{23}$ 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.\textsuperscript{25} Adsorption of Mo(CO)$_6$ in either NaY or Ca$_{16}$Na$_{22}$Y has the effects as already proposed by Jelinek et al.\textsuperscript{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 reproducible. Attention should, however, be paid to the proven, extreme sensitivity of the Na$^+$ distributions in NaY toward the details of synthesis and subsequent treatments.\textsuperscript{29}

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References and Notes

(19) Program for simulation of solid-state NMR line shapes QNMR, developed and supplied by the Institute of Chemical Physics and Biophysics, Tallinn, Estonia.