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EXPLORING CATION SITING IN ZEOLITES BY SOLID-STATE NMR OF QUADRUPOLAR NUCLEI

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ABSTRACT

Solid-state NMR spectroscopy of quadrupolar nuclei (e.g. ^{7}Li, ^{23}Na, ^{133}Cs, ^{139}La) offers considerable potential for determining the location and population of non-framework cation sites in zeolites. However, to obtain reliable results an array of sophisticated NMR techniques has to be applied, e.g. fast magic angle spinning (MAS), double oriented rotation (DOR), two-dimensional nutation, and experiments at different magnetic field strengths. In addition, computer simulation and decomposition of the spectra are prerequisites, and field gradient calculations are very helpful for spectra interpretation. Quantification of the spectra requires careful correction of the experimental line intensities for possible contributions from satellite transitions and/or spinning side bands. The methods for spectra registration and the strategy for line assignments and quantitative evaluation of the spectra are outlined and exemplified by ^{23}Na NMR studies of dehydrated NaY zeolites.

INTRODUCTION

The detection and quantification of charge-balancing cations at specific site locations in zeolites is of considerable interest for a deeper understanding of the chemical and physical properties of zeolites and related microporous materials. The development of reliable and possibly straightforward techniques for characterizing qualitatively and quantitatively cation siting in the zeolite cavities is, therefore, of great importance. So far, mainly X-ray and neutron diffraction but also other techniques such as infrared spectroscopy and NMR spectroscopy have been used for that purpose. Application of solid-state NMR spectroscopy is complicated by the fact that most of the relevant metal cations in zeolites represent quadrupolar nuclei, i.e. nuclei with a nuclear spin quantum number of $I > 1/2$. (e.g. ^{7}Li, ^{23}Na, ^{25}Mg, ^{39}K, ^{43}Ca, ^{87}Rb, ^{133}Cs, ^{135,137}Ba, ^{139}La). Owing to the interaction of the nuclear quadrupole moment of such nuclei with the electric field gradient (EFG) at the nuclear site ("quadrupole interaction"), complex and overlapping line shapes often appear in the NMR spectra which are notoriously difficult to analyse with respect to their intrinsic

NMR parameters, i.e. the *quadrupole coupling constant* (QCC), the *asymmetry parameter of the EFG* (η), the *isotropic chemical shift* (δ_{iso}), and *relative intensities* (I). On the other hand, important information about the local electronic structure and geometry of the cation site is provided by these parameters, and the site population can be characterized by the (corrected) line intensities. It will be shown in this contribution that the progress achieved recently in the experimental NMR techniques and in the interpretation and quantitative evaluation of NMR spectra of quadrupolar nuclei has now opened new routes for the application of solid-state NMR spectroscopy to detailed studies of cation siting in zeolites. In continuation and extension of our recent studies [1,2] state-of-the-art ^{23}Na NMR techniques including magic angle spinning (MAS) at five different magnetic fields up to the highest magnetic field strength presently available (17.6 T), double oriented rotation (DOR), at high spinning speeds, and two-dimensional nutation with MAS are applied to dehydrated zeolite NaY and the qualitative and quantitative interpretation of the spectra is discussed in some detail. Several other groups (see e.g. [3-10]) previously reported on ^{23}Na NMR of zeolites, but in the majority of cases, hydrated samples were studied in which a large portion of the Na^+ cations are not localized and show considerable mobility which partly averages the quadrupole interactions. The ^{23}Na MAS [4,8-10], DOR [8] and static 2D nutation [5] NMR spectra of dehydrated NaY published so far show poor resolution, and no detailed quantitative evaluation of the spectra has been performed.

EXPERIMENTAL SECTION

^{23}Na MAS, DOR and 2D nutation NMR spectra were measured at 79.4 and 105.8 MHz using Bruker MSL-300 and MSL-400 NMR spectrometers, respectively, equipped with Bruker standard MAS (double bearing, 4mm rotor diameter) and DOR probes. In addition, ^{23}Na MAS NMR spectra were recorded at 132.3, 158.7 and 198.4 MHz with the Bruker AMX-500, AMX-600 and AMX-750 spectrometers. Spinning speeds of 8 to 10 kHz and pulse widths corresponding flip angles below $\pi/8$ were applied to ensure optimum excitation of the central transition. DOR spectra were measured with spinning frequencies of about 4 to 6 kHz of the inner and between 0.85 and 1.3 kHz of the outer rotor. The odd-numbered spinning side bands were suppressed by rotor-synchronized pulse excitation [11]. ^{23}Na chemical shifts are referenced to solid NaCl. Spectra simulations were performed with the WINFIT program of the Bruker WINNMR software package for PC's or the program POWDER of the ASPECT 3000 software. The zeolite samples studied were commercial

products or prepared by standard synthesis and cation exchange procedures and subsequently dehydrated at 673 K in a vacuum line. To avoid rehydration, the dehydrated samples were transferred into the NMR sample containers in a glove box under dry nitrogen gas.

RESULTS AND DISCUSSION

NMR powder spectra of quadrupolar nuclei with half-integer spin quantum numbers (e.g. ^{23}Na with I = 3/2) are subject to line broadening mainly due to second order quadrupolar interactions which decrease with increasing strength of the external magnetic field B_o. As an example, Figure 1 shows the ^{23}Na MAS NMR spectra of dehydrated zeolite NaY measured at five dfferent B_o fields between 7.0 T and 17.6 T, corresponding ^{23}Na Larmor frequencies ν_L between 79.4 MHz and 198.4 MHz. Though the line narrowing effect with increasing field strength is clearly visible, complex spectral shapes are observed even at the highest B_o field strength of 17.6 T (ν_L = 198.4 MHz). To derive information on the distribution of the sodium cations in zeolites from that type of spectra, a general procedure for spectra analysis and structural interpretation of the NMR data has been established which includes (i) *separation of overlapping lines,* (ii) *determination of QCC, η, and δ_{iso} of the distinct lines,* (iii) *quantification of line intensities*, and (iv) *assignment of the lines to distinct cation sites.* The various techniques and methods applied for (i) - (iv) are outlined in the following and exemplified by ^{23}Na NMR studies of dehydrated zeolite NaY.

(i) Separation of overlapping lines

There are several techniques available for the separation of overlapping lines, the applicability of which depends on the type of the experimentally observed NMR spectrum. If the MAS NMR spectrum shows characteristic features (e.g. peaks or shoulders), *line decomposition by computer simulation* of the overlapping line shapes may be applied. Figure 2 demonstrates the simulation of the ^{23}Na MAS NMR spectra of dehydrated zeolite NaY measured at 105.8 MHz by two quadrupolar powder patterns (QP) and two Gaussian lines (GL). Similar simulations can be obtained for the spectra shown in Figure1 which were registered at the other Larmor frequencies. The spectra may also be fitted by a single QP and a single GL [1]. However, in this case, different values of δ_{iso} of the QP have to be assumed for the distinct spectra. Since δ_{iso}, i.e. the line position corrected for quadrupolar shift contributions, should be independent of the applied field strengths, this observation supports the conclusion that the spectra consist of more than one QP. It should be noted that this information could only be obtained from spectra measured at different field strengths.

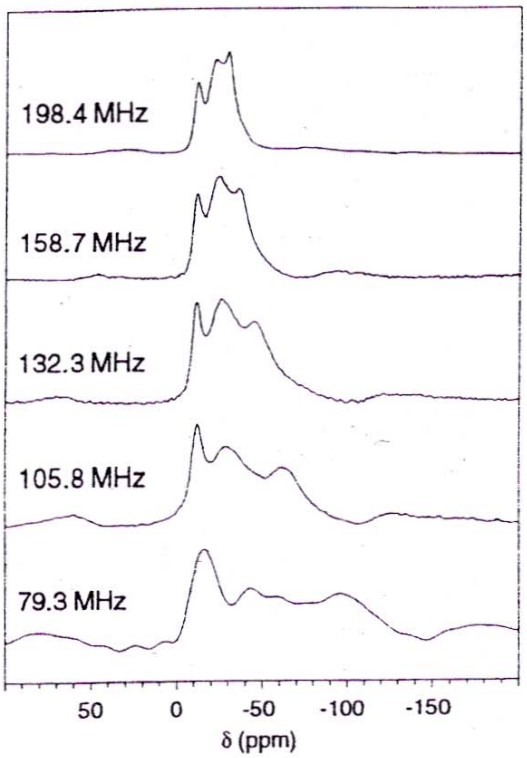


Fig.1. ^{23}Na MAS NMR spectra of dehydrated zeolite NaY at different Larmor frequencies ν_L

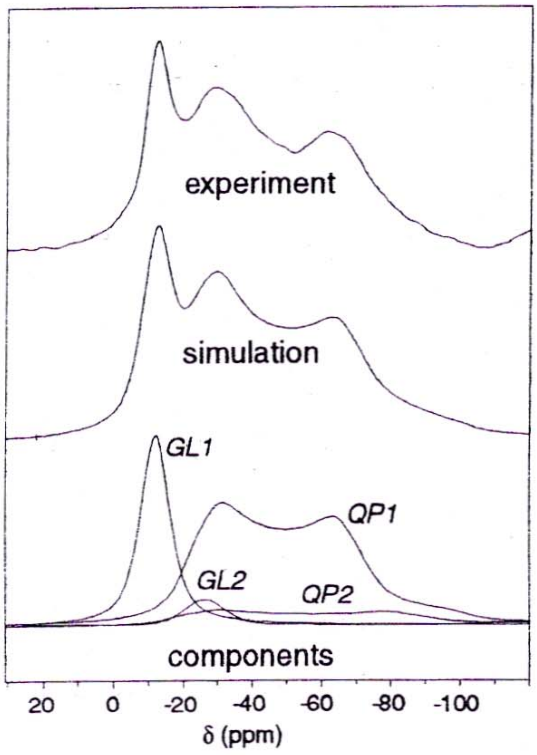


Fig.2. Experimental and simulated ^{23}Na MAS NMR spectra (105.8 MHz) of dehydrated zeolite NaY.

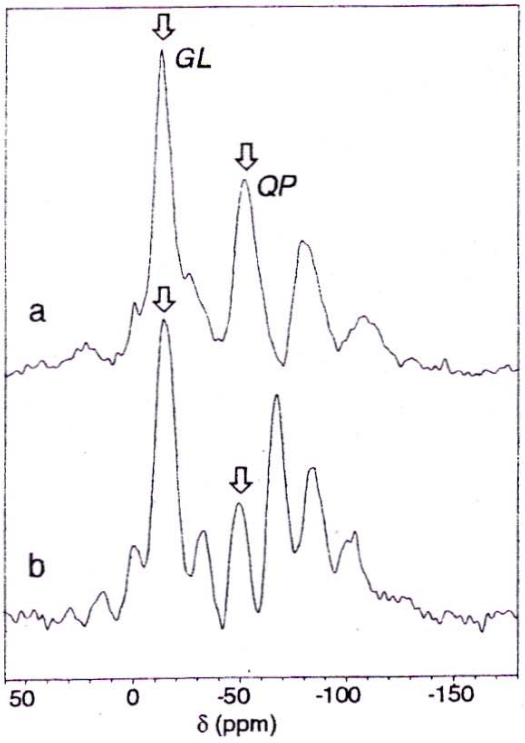


Fig.3. ^{23}Na DOR NMR spectra (105.8 MHz) of dehydrated zeolite NaY at different spinning rates of the outer rotor: a - 1300 Hz, b - 850 Hz

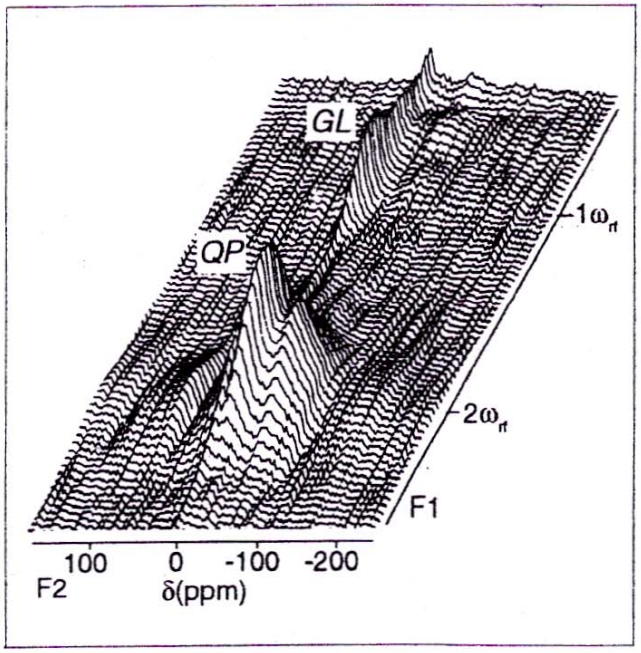


Fig.4. ^{23}Na two-dimensional nutation NMR spectrum (105.8 MHz, ν_{rf}=125 kHz) of dehydrated zeolite NaY

Effective narrowing of broad quadrupolar lines can be achieved by application of the *double oriented rotation technique (DOR)* as shown by the ^{23}Na DOR NMR spectra of dehydrated NaY zeolite in Figure 3. The broad QP pattern decomposes into a narrow central line (indicated by an arrow) and an array of spinning side bands well separated from the GL line. The central line can clearly be identified from DOR experiments with different spinning rates of the outer rotor (see Figure 3) [1]. However, the two distinct QP patterns observed in the simulated spectra cannot be resolved in the DOR spectrum.

Two-dimensional nutation NMR experiments allow the separation of overlapping lines characterized by distinctly different quadrupole interactions [1]. In these experiments the normal 1D spectrum is observed in the F2 dimension while its time dependence towards pulse length yields a clear resolution of lines subject to weak or strong quadrupole interactions in the second dimension F1. The application of this technique is exemplified in Figure 4 by the 2D nutation ^{23}Na MAS NMR spectrum (105.8 MHz) of dehydrated NaY zeolite. The GL line appears in the F1 dimension at $1\omega_{rf}$ and is clearly separated from the QP peak at $2\omega_{rf}$, but again no clear distinction can be made between QP1 and QP2.

(ii) Determination of QCC, η, and δ_{iso}

QCC, η, and δ_{iso} can, in principle, be obtained by direct calculation from the singularities of the quadrupolar pattern [12] or by computer simulation of the MAS line shapes. Table 1 collects the corresponding data of the four components derived from the simulation shown in Figure 2.

Table 1: ^{23}Na NMR data and site populations of dehydrated zeolite NaY

Line	δ_{iso} (ppm)	QCC (MHz)	η	I^{exp} (%)	I^{corr} (%)	Na^+/UC	Site
QP1	-12.0	4.0	0.2	62.0	65.4	35	SII
QP2	-3.5	4.8	0.2	9.9	28.7	15	SI'
GL1	-11.8	ca. 0.1	0	24.1	5.5	3	SI
GL2	-26.0	-	-	4.0	0.4	0.3	Na^+ hydr.

Difficulties may arise in the simulation and separation of heavily overlapping lines, and complementary information on QCC and δ_{iso} may be useful for the calculation of the line shapes. Good estimates of QCC and δ_{iso} are, for instance, available from the line shifts in the MAS and DOR NMR spectra measured at (at least two) different field strenghts [13]. If δ_1 and δ_2 are the line positions measured at the

Larmor frequencies ν_{L1} and ν_{L2} , then δ_{iso} and $QCC^* = QCC(1+\eta^2/3)^{1/2}$ can be calculated by equations (1) and (2) [1,14].

$$\delta_{iso} = \frac{\delta_1 \cdot K_2 - \delta_2 \cdot K_1}{K_2 - K_1} \qquad (1)$$

$$QCC^* = \sqrt{\frac{\delta_1 - \delta_2}{K_2 - K_1}} \qquad (2)$$

with $K_n = \frac{3 \cdot 10^6}{40\nu_{Ln}^2} \cdot \frac{[I(I+1) - 3/4]}{I^2(2I-1)^2}$, i.e $K_n = 25 \cdot 10^3/\nu_{Ln}^2$ for ^{23}Na with I = 3/2. Since $0 \leq \eta \leq 1$, QCC is close to QCC*, i.e. in the range of QCC* (for $\eta = 0$) and 0.866QCC* (for $\eta = 1$). Application of this method is particular useful for DOR spectra and for Gaussian lines of MAS spectra involved in weak quadrupole interactions. In fact, the size of QCC of the GL1 signal (Table 1) has been estimated that way.

Information on QCC can further be derived from the intensity distribution of the spinning side bands in the DOR spectra [15] and from 2D nutation experiments which separate lines with weak and strong quadrupole interactions (see e.g. Figure 4). In addition, QCC may be estimated from field gradient calculations using crystal structure data or sensible structure models of the sodium coordination in the zeolite [16] (see below).

(iii) Quantification of line intensities

The relative populations of the distinct cation sites in the zeolite cavities can be derived from the intensities of the corresponding lines in the ^{23}Na MAS NMR spectra. However, different to spin-1/2 nuclei such as ^1H, ^{13}C or ^{29}Si, the relative line intensities determined by integration from the MAS NMR spectra of quadrupolar nuclei are not a priori proportional to the relative populations of the distinct sites but must be corrected for possible contributions from satellite transitions and/or spinning side bands. In general, selective excitation of the central +1/2;-1/2 transition is observed for nuclei involved in strong quadrupole interactions (i.e. $QCC >> \nu_{rf}$, where $\nu_{rf} = \omega_{rf}/2\pi$ is the radio frequency field strength) while non-selective excitation of all transitions (i.e. central and satellite transitions) occurs for lines with vanishing QCC ($QCC << \nu_{rf}$.). For the ^{23}Na nucleus with I = 3/2 the central transition contains only 40% of the total intensity observed for non-selective excitation. Moreover, depending on the spinning speed ν_{rot}, the Larmor frequency ν_L and the size of QCC, a certain proportion of the intensity is distributed in spinning side bands which are difficult to integrate. A suitable method for intensity correction has been presented by Massiot et

al. [17]. This method permits the graphical determination of correction factors for the central and satellite transition intensities from QCC, η, ν_L and ν_{rot} for each line in the spectrum. The experimental (I^{exp}) and corrected intensities (I^{corr}) of the four components of the spectrum of Figure 2 are shown in Table 1 together with the number of Na^+ per unit cell (Na^+/UC) at the distinct sites calculated from I^{corr} and the total content of 53.3 Na^+ cations per unit cell. The dramatic changes of the relative intensities by the correction are obvious. It must, therefore, be emphasized that reliable information on the populations of sodium (and other quadrupolar nuclei involved in strong quadrupole interactions) cation sites in zeolites can only be obtained from carefully corrected line intensities.

(iv) Line assignment

The attribution of the NMR lines to distinct cation locations in the zeolite cavities may be derived from NMR studies of model zeolites with known cation site populations and from field gradient calculations of the specific cation sites. The line assignments of the ^{23}Na MAS NMR spectrum of dehydrated zeolite NaY given in Table 1 follow from the comparison of the number of Na^+ cations per unit cell (Na^+/UC) determined from the corrected line intensities with the population of the SI, SI' and SII cation sites obtained from X-ray diffraction [18]. The weak line GL2 originates from small portions of hydrated Na^+ cations as concluded from partially rehydrated NaY samples.The line assignments further agree with the changes in the line intensities of the ^{23}Na MAS NMR spectra of dehydrated zeolites NaHY, NaBaY and NaEMT expected due to the specific location of sodium cations in these samples [1]. The line attribution is also greatly supported by theoretical calculations of QCC of ^{23}Na in the specific site geometries (oxygen coordination) by means of a simple point charge model [16]. Using the crystal structure data of ref.18 and oxygen charges of -0.8 e, QCC of about 0, 3.8 and 4.8 MHz were calculated for sodium in SI, SII and SI' positions, respectively, in good agreement with the experimental results.

CONCLUSIONS

Solid state ^{23}Na NMR is a powerful method for the detailed investigation of the site distribution of sodium cations in zeolites. The MAS NMR spectra of dehydrated zeolite NaY consist of overlapping lines for the distinct sodium sites SI, SI' and SII, which can be separated by decomposition of the simulated line shapes in combination with DOR and 2D nutation NMR techniques and field gradient calculations. The site populations have been determined selectively from the line intensities after careful correction for contributions from satellite transitions and

spinning side bands, they agree well with the results of X-ray diffraction studies. ^{23}Na NMR has also been applied to characterize cation distributions and migrations upon de- and rehydration in various cation exchanged zeolites, e.g. NaHY, NaBaY [1], LaNaY [2, 19], and CsNaY [20], for the latter two materials in combination with ^{139}La and ^{133}Cs NMR studies, respectively. Further NMR work is in progress to study the redistribution of cations upon adsorption of organic guest molecules in zeolites.

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