Multiple-quantum magic-angle spinning and double-rotation NMR techniques were applied in the high field of 17.6 T to the study of oxygen-17-enriched zeolites A and LSX with the ratio Si/Al = 1. A monotonic correlation between the isotropic value of the chemical shift and the Si–O–Al bond angle \( \alpha \) (taken from X-ray data) could be found. Hydration of the zeolites causes a downfield \(^{17}\text{O} \) NMR chemical shift of about 8 ppm with respect to the dehydrated zeolites. Ion exchange of the hydrated zeolites generates stronger chemical shift effects. The increase of the basicity of the oxygen framework of the zeolite LSX is reflected by a downfield shift of approx. 10 ppm going from the lithium to the cesium form, and the substitution of sodium by thallium in the zeolite A causes a shift of 34 ppm for the O3 signal. \(^{17}\text{O} \) DOR NMR spectra are superior to \(^{17}\text{O} \) 3QMAS NMR spectra, featuring a resolution increase by a factor of 2 and are about equal with respect to the sensitivity. The residual linewidths of the signals in the \(^{17}\text{O} \) DOR and \(^{17}\text{O} \) 5QMAS NMR spectra can be explained by a distribution of the Si–O–Al angles in the zeolites. © 2001 Academic Press

Key Words: NMR; quadrupole nuclei; DOR; MAS; MQMAS; oxygen-17; zeolites.

INTRODUCTION

The abundance of elements in the Earth’s crust is about 50% oxygen, 28% silicon, and 8% aluminum, but solid-state NMR spectroscopy is mostly applied to the spin-1/2 nuclei \(^{1}\text{H}, \(^{13}\text{C}, \(^{31}\text{P}, \text{and} \(^{29}\text{Si}. \text{The demand for characterization of inorganic material and some recently developed experimental techniques have caused a growing interest in high-resolution solid-state NMR of quadrupole nuclei with half-integer spin, e.g., \(^{27}\text{Al} \text{and} \(^{17}\text{O}, \text{for which the electric quadrupole interaction strongly broadens the NMR signal in the powder spectra, cf.} [1]. \text{The} \(^{27}\text{Al} \text{NMR spectroscopy (nuclear spin} I = 5/2, \text{nuclear quadrupole moment} Q = 0.15 \times 10^{-28} \text{m}^2) \text{of inorganic materials is already well established. The} \(^{17}\text{O} \text{NMR (nuclear spin} I = 5/2, \text{nuclear quadrupole moment} Q = -0.026 \times 10^{-28} \text{m}^2) \text{is at the disadvantage of a smaller magnetic moment and the very low natural abundance of 0.037% or the high costs for the enrichment. Therefore, relatively few solid-state} \(^{17}\text{O} \text{NMR studies were published, since the first investigation on MnO}_2 \text{was performed by Jackson [2] in 1963. The fact that the nuclear quadrupole moment of} \(^{17}\text{O} \text{is much smaller}}

\[1\] \text{This paper is dedicated to Dr. Vladimir Bosáček on the occasion of his 70th birthday.}

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than that of the $^{27}$Al nuclei leads one to assume that the quadrupole broadening of the NMR signal is relatively small. However, the very anisotropic bonding of the oxygen atoms in many solids produces strong electric field gradients at the oxygen nuclei and quadrupole coupling constants $C_{qcc}$ of several megahertz. The mean values and the standard deviations for about 300 references to values of $C_{qcc}$ in inorganic materials [1] are $4.2\pm 1.5$ and $4.8\pm 3.5$ MHz for $^{17}$O and $^{27}$Al, respectively.

New NMR techniques, e.g., dynamic angle spinning (DAS) [3, 4], double rotation (DOR) [5], and multiple-quantum excitation in combination with fast spinning (MQMAS) [6], were recently developed for quadrupole nuclei with half-integer spins, and, in addition, the perturbing effect of the electric quadrupole interaction is reduced at the higher magnetic fields, which are now available. Numerous $^{17}$O NMR investigations applying these techniques were performed, in order to correlate the obtained NMR parameters of resolved oxygen signals with structure data obtained by diffraction methods: Grandinetti et al. [7] investigated the SiO$_2$ polymorph coesite, Mueller et al. [8] measured the $^{17}$O signals of diopside, forsterite, clinoenstatite, wollastonite, and larnite by DAS NMR, and Bull et al. [9, 10] investigated the silicon-rich zeolites Si–Y and ferrierite by $^{17}$O DOR NMR. We investigated several hydrated zeolites by $^{17}$O 3Q MAS and DOR NMR and demonstrated the reasonably good resolution in the field of 17.6 T, whereas we obtained insufficient resolution in the lower field of 11.7 T [11, 12]. Pingel et al. [12] proposed a correlation between Si–O–Al angles and the $^{17}$O chemical shift, whereas Bull et al. [9, 10] claimed that no simple correlation appears to exist between the zeolite bond angles and the $^{17}$O NMR parameters.

A relation between the isotropic value of the chemical shift of the $^{29}$Si NMR and the mean value (average above four values) of $^{29}$Si–O–Si or $^{29}$Si–O–Al angles $\alpha$ was established by Ramdas and Klinowski [13], see also Refs. [14, 15]. Radeglia and Engelhardt [16] gave an equation in the form

$$\delta(\text{Si}) = -223.9 \cos \alpha / (\cos \alpha - 1) - 7.2 + 5m = -223.9\bar{\rho} - 7.2 + 5m, \quad (1)$$

where the parameter $m$ corresponds to the coordination number of silicon atoms to aluminum atoms, commonly described by Q4($m$Al), $\alpha$ is the $^{29}$Si–O–T angle. The quotient $\cos \alpha / (\cos \alpha - 1) = \rho$ denotes the $s$-character of the oxygen hybrid orbitals and is given as the mean value of the four bonds. $^{17}$O DAS NMR studies of the SiO$_2$ polymorph coesite by Grandinetti et al. [7] yielded the correlations

$$\eta = 1 + \cos \alpha \quad (2)$$

and

$$C_{qcc} = C_{qcc}(180^\circ)2\rho \quad (3)$$

for the asymmetry parameter $\eta$ and the quadrupole coupling constant $C_{qcc}$, respectively. Some functions $\eta(\alpha)$, which are less simple than Eq. (2), are discussed by Sternberg [17]. The question of whether a correlation between T–O–T angles and $^{17}$O NMR parameters does [7, 12] or does not exist [9, 10] is one issue of the present paper.
Another topic is, how the isotropic value of the $^{17}$O NMR chemical shift can monitor molecule-framework interactions and basic properties of the zeolite framework. From the viewpoint of the methodology, the residual linewidth of MQMAS and DOR spectra is an important subject of interest. It is well known that multiple-quantum and double-rotation techniques are complementary tools for getting highly resolved $^{17}$O NMR spectra of solids, cf. [12], but it is not clear yet why the DOR technique (compared to 3QMAS or 5QMAS) yields a better resolution of the signals. Sources of line broadening and their different manifestations in DOR and MQMAS NMR will be discussed.

**MATERIALS AND METHODS**

Zeolites LSX were donated by Wilhelm Schwieger or by the Tricat Zeolites GmbH. Na,K–LSX denotes the zeolites Na$_{0.1}$K$_{0.3}$–LSX. The samples were dehydrated in a nitrogen stream for more than 12 h at 220°C and then treated at this temperature with H$_2$O (22–43% $^{17}$O enriched) for 3 h. After the enrichment procedure, some samples were dehydrated again at 400°C under vacuum, cooled and sealed, or loaded after activation with formic acid (40 HCOOH molecules per unit cell) and sealed.

$^{17}$O 3Q MAS experiments and $^{17}$O DOR experiments were performed in the external magnetic field of 17.6 T (Bruker DMX 750 with narrow-bore magnet) at 101.7 MHz. Additional DOR experiments were done in the field of 11.7 T (Bruker MSL 500 with a wide-bore magnet). Probes constructed at the Institute of Chemical Physics in Tallin and Bruker MAS probes were used for the DOR and MQ MAS experiments, respectively. Multiple-quantum experiments were performed by means of two adjusted strong pulses (or second pulse as FAM2 [18]) and an additional weak z-filter pulse [19]. The $^{17}$O NMR scales are referenced to H$_2^{17}$O. A total ring down delay of 7 μs after the z-filter pulse was used. The repetition time was in the range from 200 ms to 10 s corresponding to the measured longitudinal relaxation times $T_1$, which vary from 100 to 500 ms for the various zeolite samples under study. The dehydrated zeolites were loaded with 10 kPa gaseous oxygen, in order to shorten the value of $T_1$. A 24-phase cycle was applied twice with an additional 30° phase shift in between, in order to acquire the real and imaginary parts for the second Fourier transform. The nonselective nutation frequency of 120 kHz was determined for a H$_2^{17}$O sample at the Larmor frequency of 101.7 MHz. For this rf power, the widths of the first and the second pulses in the 3QMAS (5QMAS) experiments were adjusted for maximum $^{17}$O 3Q MAS NMR signal to 3.5 (3.8) μs and 1.2 (2.0) μs, respectively. The selective $\pi/2$ pulse length of the z-filter was adjusted to 32 μs. The FAM2-pulse [20], which was used in few 3Q experiments, consists of a phase-alternating four-pulse sandwich with relative durations taken from Ref. [20] and an adjusted total duration of 1.2 μs, cf. Fig. 1. The time step $t_1$ in the multiple-quantum dimension was increased in steps of the reciprocal spinning frequency, in order to avoid spinning sidebands. The time domain consisted of 64 and 1024 steps in $t_1$ and $t_2$, respectively. As many as 480 scans were accumulated for each $t_1$ step. The programs XfShear [21] and WINFIT [22] were used for the shearing of the 2D spectra and the simulation of the anisotropic lineshape, respectively.
DOR experiments were performed typically in a synchronized manner \cite{23} with outer rotor speed at about 1400 Hz and inner rotor speed at 6000–6500 Hz.

RESULTS AND DISCUSSION

$^{17}$O 3QMAS and DOR NMR spectra of the hydrated zeolite Na,K–LSX (low silicate X type with 70% Na and 30% K) are shown in Figs. 2 and 3, respectively. Only three signals are resolved in the isotropic projection of the two-dimensional 3QMAS spectrum (Figs. 2 and 3), but four signals can be observed in the 5QMAS and DOR spectra (Fig. 3). X-ray data from Porcher et al. \cite{24} prove the existence of four different oxygen sites in the faujasite-type zeolite LSX. Therefore, the peak in the middle position of the 3QMAS spectrum is fitted by two signals, and four slices are used for the determination of the quadrupole parameter from the obtained spectra (Fig. 2). The deconvolutions of the spectra give intensities of 25%:21%:26%:28% and 24%:30%:25%:21% for MAS and DOR, respectively. These intensities do not differ significantly from the ratio 1:1:1:1, as expected from the faujasite structure for the oxygen sites 1, 2, 3, and 4. The intensities in a preliminary study of the zeolite Na–LSX \cite{12} deviated from this ratio by an enhanced intensity (34%) in one position, which was explained by a preferred enrichment of the oxygen atoms in O1 position. In this study, the zeolite Na,K–LSX, which is the originally synthesized form, shows the best agreement with the expected 1:1:1:1 ratio. Other cation-exchanged forms (Li, Na, K, Rb) of the LSX show $^{17}$O signals with slightly different intensities. A significant deviation can be observed for the zeolite Cs–LSX: The 3QMAS spectrum gives a signal intensity of only 7% for the O4 site, whereas the corresponding signal disappears in the DOR spectrum. The numbering of the four signals in Fig. 2 refers to the usual numbering of the four oxygen positions in the faujasite, cf. Ref. \cite{24}, e.g., oxygen site 1 denotes bridges between adjacent cubo-octahedra. The assignment is based on the assumption that the chemical shift...
decreases with increasing bond angle. This assumption will be discussed afterward in detail.

Figure 3 shows spectra obtained by MQMAS and DOR techniques in the field of 17.6 T. The DOR spectra monitor the superposition of the isotropic chemical shift and the isotropic second-order quadrupole shift, whereas the MQMAS spectra exhibit the isotropic chemical shift only. The spectral range of the MQMAS
spectra (104 ppm for $I = 5/2$ and 3Q and only 20.4 ppm for 5Q) is limited by the MAS spinning frequency of 15 kHz, cf. [25]. It can be concluded from Fig. 3 that the resolution of the 5Q spectra exceeds the resolution of the 3Q spectra, but the signal-to-noise ratio of the free induction decay of the 5Q experiment is lower by a factor of 10 (although a week-end-run was made for each 5QMAS NMR spectrum). The sensitivity of the 3Q experiment per scan exceeds the 5Q experiment by a factor of about 40 for an equal number of scans. The DOR spectra are superior in resolution compared to the 3QMAS spectra. The signal-to-noise ratio of the free induction decay (FID) of one DOR acquisition is about equal to that for the FID of one 3QMAS acquisition, since the relatively low filling factor of the DOR coil (compared to MQMAS) is compensated by the higher excitation efficiency of the single transition. Therefore, we used DOR in the external fields of 17.6 and 11.7 T for the
TABLE 1

Values of the Isotropic Chemical Shift $\delta$ of the $^{17}$O NMR, the Quadrupole Parameters $P_Q$ (Determined from the Comparison of the DOR Spectra at Approx. 68 and 102 MHz), the Asymmetry Parameters $\eta$ (Determined from the Fit of the Slices in the 3QMAS Spectra), the Si–O–Al Bond Angles $\alpha$ (Taken from the Literature), and the Values of the $s$-character of the Oxygen Hybrid Orbitals (Determined by $\rho = \cos \alpha / (\cos \alpha - 1)$)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Site</th>
<th>$\delta$/ ppm</th>
<th>$P_Q$/ MHz</th>
<th>$\eta$</th>
<th>$\alpha$/°</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na,K–LSX</td>
<td>O1</td>
<td>50.6</td>
<td>3.3</td>
<td>0.3</td>
<td>132.5</td>
<td>0.403</td>
</tr>
<tr>
<td>Na,K–LSX</td>
<td>O3</td>
<td>45.2</td>
<td>3.4</td>
<td>0.3</td>
<td>136.3</td>
<td>0.420</td>
</tr>
<tr>
<td>Na,K–LSX</td>
<td>O2</td>
<td>42.1</td>
<td>3.3</td>
<td>0.2</td>
<td>141.5</td>
<td>0.439</td>
</tr>
<tr>
<td>Na,K–LSX</td>
<td>O4</td>
<td>36.8</td>
<td>3.6</td>
<td>0.15</td>
<td>146.8</td>
<td>0.456</td>
</tr>
<tr>
<td>Tl–A</td>
<td>O1</td>
<td>60.7</td>
<td>3.3</td>
<td>0.15</td>
<td>148</td>
<td>0.459</td>
</tr>
<tr>
<td>Tl–A</td>
<td>O2</td>
<td>53.4</td>
<td>3.6</td>
<td>0.05</td>
<td>161</td>
<td>0.486</td>
</tr>
<tr>
<td>Tl–A</td>
<td>O3</td>
<td>75.5</td>
<td>3.2</td>
<td>0.2</td>
<td>144</td>
<td>0.447</td>
</tr>
<tr>
<td>Na–A</td>
<td>O1</td>
<td>40.9</td>
<td>3.4</td>
<td>0.15</td>
<td>145.6</td>
<td>0.452</td>
</tr>
<tr>
<td>Na–A</td>
<td>O2</td>
<td>31.7</td>
<td>3.6</td>
<td>0.05</td>
<td>159.5</td>
<td>0.484</td>
</tr>
<tr>
<td>Na–A</td>
<td>O3</td>
<td>42.4</td>
<td>3.4</td>
<td>0.2</td>
<td>144.3</td>
<td>0.448</td>
</tr>
<tr>
<td>Na,K–LSX</td>
<td>mean(O1,O2,O3,O4)</td>
<td>44.8</td>
<td>3.4</td>
<td>0.25</td>
<td>138.1</td>
<td>0.427</td>
</tr>
<tr>
<td>Tl–A</td>
<td>mean(O1,O2,O3)</td>
<td>67</td>
<td>3.3</td>
<td>0.15</td>
<td>148.6</td>
<td>0.460</td>
</tr>
<tr>
<td>Na–A</td>
<td>mean(O1,O2,O3)</td>
<td>39.9</td>
<td>3.5</td>
<td>0.15</td>
<td>147.7</td>
<td>0.458</td>
</tr>
<tr>
<td>Tl–A</td>
<td>mean(O1,O2)</td>
<td>57.4</td>
<td>3.4</td>
<td>0.1</td>
<td>153.8</td>
<td>0.473</td>
</tr>
<tr>
<td>Na–A</td>
<td>mean(O1,O2)</td>
<td>37</td>
<td>3.5</td>
<td>0.1</td>
<td>151.5</td>
<td>0.468</td>
</tr>
</tbody>
</table>

determination of the isotropic NMR parameter $\delta_{CSiso}$ and $P_Q = C_{qcc}(1 + \eta^2/3)^{1/2}$, whereas 3QMAS slices were used for the determination of the asymmetry parameter $\eta$ of the quadrupole interaction. The latter parameter could not be obtained from the DOR spectra, since the resolution of the spinning sidebands was not sufficient for a sideband analysis.

Table 1 shows $^{17}$O NMR parameters, Si–O–Al bond angles $\alpha$, and values for the $s$-character of the oxygen hybrid orbitals determined by the equation $\rho = \cos \alpha / (\cos \alpha - 1)$. The upper part of the table describes four oxygen sites in the zeolite Na,K–LSX and three oxygen sites in the zeolite Na–A. The data for the zeolite Na–A are slightly revised with respect to those in a previous paper [12], since new 3QMAS and DOR experiments were performed. Two averages are given at the bottom of the table. The crucial point of the upper six lines in Table 1 is that the assignment of the obtained values of the $^{17}$O NMR chemical shift to the oxygen site numbers and angles, which were taken from the literature, is problematic. Only the correspondence in seven lines in Table 1 seems to be free of doubts: Tl–A (O3), Na–A (O3), Na,K–LSX (mean O1, O2, O3, O4), Tl–A (mean O1, O2, O3), Na–A (mean O1, O2, O3), and Tl–A (mean O1, O2), and Na–A (mean O1, O2). The signal of the site O3 in the zeolites A has an about twofold intensity due to the twofold occupation of the site O3 with respect to O1 or O2. Also the last five lines, which give the averages of isotropic values of the chemical shift and averaged values for the bond angles or $s$-characters, are unproblematic.

Additional information on the assignment of $^{17}$O NMR signals to oxygen sites can be obtained from the asymmetry parameter $\eta$ of the electric field gradient tensor. Equation (2) describes the plausible facts that $\eta$ decreases from the value 1.
FIG. 4. Correlation between the isotropic chemical shift of the $^{17}$O DOR NMR and the $s$-character of the oxygen hybrid orbitals for the oxygen sites of the zeolites Na–A (circles) and Na,K–LSX (rectangles). The straight line represents the best linear fit.

to 0 for $\alpha$ going from 90° to 180°. The signals with the lowest values of $\eta$ should be assigned to the largest angles in this range. Unfortunately, the accuracy of the asymmetry parameter, which has been obtained from the fit of the slices in the 2D 3QMAS spectra, is not very high (±0.05), but the value $\eta = 0.05$ for the signals, which has been connected in Table 1 to site O2 of the hydrated zeolites Tl–A and Na–A, proves that the assignment of all three signals of the zeolite A is justified. The difference in the values of the asymmetry parameters of the four signals of the zeolite Na,K–LSX ($\eta = 0.3, 0.3, 0.2, 0.15$ for O1, O2, O3, O4, respectively) are less significant, but also in agreement with the assignment of the $^{17}$O NMR signals to the sites. Therefore, the rule that the chemical shift is decreasing with increasing bond angle seems to be valid also for the zeolite Na,K–LSX. Figure 4 plots the seven isotropic chemical shift values (calculated from the $^{17}$O DOR NMR spectra) of the zeolites Na–A and Na,K–LSX against the values of the $s$-character of the oxygen bonds in the various Si–O–Al sites. The solid line in Fig. 4 corresponds to the correlation

$$\delta(^{17}\text{O})/\text{ppm} = -214\rho + 136.$$  

The best fit for the correlation of chemical shift with bond angle gives $\delta/\text{ppm} = -0.65\alpha/° + 134$. This only slightly deviates from the relation $\delta/\text{ppm} = -0.71\alpha/° + 143.7$, which was obtained by previous 3QMAS experiments [12].

The corresponding correlation coefficients are 0.924 and 0.918, if the chemical shift is plotted against $\alpha$ or $\rho$, respectively. This result supports the existence of a
correlation between chemical shift and bond angle in the samples under study. In contrast, Grandinetti et al. [7] did not find a monotonic correlation between $^{17}$O NMR shift and bond angle for the SiO$_2$ polymorph coesite. A linear fit of the data [7] gives $\delta/\text{ppm} = -0.61\alpha/\degree + 139$ with a low correlation coefficient of 0.829. The slope of the linear fit is similar to the slope of the linear fit of our results, see above. This emphasizes the tendency that the chemical shift decreases with increasing bond angle, but it does not prove that a simple correlation exists in general. Also two facts of our own experimental findings, which will be discussed afterward, argue against a general correlation: The dehydration of the zeolite and adsorption of molecules other than water change the Si–O–Al angles and the values of the corresponding chemical shift. The obtained functions $\delta(\alpha)$ vary upon dehydration or adsorption of other molecules. In addition, the $^{17}$O chemical shift depends on the type of the zeolitic cation. For example, a downfield shift of 34.1 ppm can be observed for the O$_3$ signal in the $^{17}$O NMR spectrum going from the sodium to the thallium form of the zeolite A.

It is well known that the interaction of the framework with adsorbed molecules influences the structure of zeolites. For example, different X-ray patterns exist for the hydrated and the dehydrated faujasites and zeolites A, cf. [24, 26, 27], and the symmetry changes from monoclinic to orthorhombic in the zeolite ZSM-5 upon adsorption of organic molecules [28]. One effect is that the framework bond angles are changed by the adsorbed molecules. This goes obviously along with a change of the $^{17}$O NMR chemical shift. However, the $^{17}$O NMR shift upon dehydration (compared to the hydrated zeolites) cannot be explained by the changes of bond angles only. The fit for the chemical shift values obtained from the 3QMAS spectra of the dehydrated zeolites A and LSX in fused glass ampoules (upon Si–O–Al bond angles taken from X-ray data) gives $\delta/\text{ppm} = -0.65\alpha/\degree + 130$, whereas the function for the hydrated zeolites is $\delta/\text{ppm} = -0.65\alpha/\degree + 134$. This indicates a low-field shift of about 4 ppm due to the interaction of the water molecules with the framework oxygen atoms in addition to the shift that is caused by the change of the bond angles.

Figure 5 shows the spectra of the dehydrated zeolite Na,K–LSX, the zeolite after loading with 40 HCOOH molecules per unit cell, and the hydrated zeolite, which contains 60 water molecules per unit cell. The most significant differences in these $^{17}$O spectra and in corresponding spectra of the zeolite A [29] exist between the hydrated and dehydrated zeolites. The centers of gravity are 47.7 and 40.2 ppm in the spectra of the zeolite Na-LSX, see Fig. 5, and 40.6 and 32.1 ppm in the spectra of zeolite Na–A [29], for the hydrated and dehydrated samples, respectively. From X-ray data, cf. [26], it can be concluded that the Si–O–Al angles vary upon dehydration. The average bond angles increase upon dehydration only slightly by 2.5° and 0.5° for the LSX and A types, respectively. The downfield shift in the $^{17}$O spectra of zeolites upon hydration is mainly influenced by the interaction of the polar water molecules with the oxygen framework of the zeolite. The simple explanation is that water molecules attract charge from the electronic shell of the oxygen framework, which causes a paramagnetic $^{17}$O NMR shift. The relatively weaker interaction between the molecules of formic acid and the LSX framework causes a chemical shift (center of gravity) of 42.4 ppm, which is only 2.2 ppm downfield with respect to that of the dehydrated sample, cf. Fig. 5.
Figure 6 shows the mean values (center of gravity) of the isotropic $^{17}$O NMR chemical shift in the spectra of several cation-exchanged zeolites and the ionic radius of the cations taken from Ref. [30]. The downfield shift increases with increasing ionic radius, if zeolites of A and LSX type are considered separately. The cation exchange influences also the Si–O–Al angles in the zeolites. X-ray data for the zeolite Na–A [31] and Tl–A [32] give mean Si–O–Al angles of 148.4° and 149.2° for the hydrated sodium and thallium forms, respectively. $^{29}$Si MAS NMR spectra of zeolites A show changes of the signal position from $-89.7$ ppm (Na–A) to $-92.2$ ppm (Tl–A). The change of the chemical shift (2.5 ppm) is considerably higher than that calculated from the change of the mean bond angle (0.8°) by means of Eq. (1), which gives approx. 0.5 ppm. We could not find X-ray data in the literature, which give the bond angles in hydrated zeolites LSX, if the sodium ions are fully exchanged by cesium ions. The $^{29}$Si MAS NMR spectra show changes of the signal position from $-82.8$ ppm for Li–LSX, and $-84.6$ ppm for Na,K–LSX up to $-89.7$ ppm for Cs–LSX. The shift of about 7 ppm would give (by means of Eq. (1)) a change of about 9° in the mean bond angle. A value of 139.3° was determined by Olson [33] for the hydrated zeolite Na–X. However, the application of Eq. (1) to zeolites exchanged with larger cations seems to be questionable, and X-ray studies should be performed, in order to determine the bond angles for all cation forms of the zeolite LSX.

The large shift of the center of gravity going from the sodium to the thallium form of the zeolite A, see Fig. 6, in connection with the small variation of the mean Si–O–Al bond angle of only 0.8° proves that the $^{17}$O NMR chemical shift strongly depends on the radius of the cation. A nearly linear dependence was found for the five cations in the zeolite LSX. The tendency of increasing chemical shift with increasing cationic radius can be explained in the following way: A decreasing distance of the cation to the oxygen framework attracts an increasing charge from the electronic
shell of the oxygen framework, which causes a paramagnetic contribution to the $^{17}$O NMR shift. A base is an electron pair donor. The electron density of the oxygen framework is increasing with increasing cation radius. This leads to the increase of the basic properties of the zeolite.

The last aspect of this study concerns the resolution of the NMR spectra. It is well known that both distributions of the quadrupole parameter $P_Q$ and distributions of the isotropic value of the chemical shift $\delta_{CSiso}$ limit the resolution of the MQMAS or the DOR NMR spectra of quadrupole nuclei, whereas the resolution for spin-1/2 nuclei depends only on the latter effect. The $^{29}$Si MAS NMR spectra show a single signal at $-89.7$ or $-84.6$ ppm, which is $1.0$ and $0.7$ ppm broad (fwhm = full width at half-maximum), for the hydrated zeolites Na–A or Na,K–LSX, respectively. The broadening of the spectra can be explained by a distribution of the mean Si–O–Al bond angles, which is caused by nonregularly distributed cations, since the positions of some cations in the unit cell are ill defined. Some other effects (field inhomogeneity, incorrect adjustment of the magic angle, susceptibility broadening, mobility, short $T_1$ of heteronuclei) that could cause a line broadening were excluded. Assuming this to be the dominant effect, the width of the distribution of angles can be calculated from Eq. (1). We obtain $1.5^\circ$ and $0.9^\circ$ for the zeolites Na–A and Na,K–LSX, respectively (by using the mean angle of all sites, since the calculated value is slightly different for each site). These values characterize the fwhm for the distribution of the mean Si–O–Al angle, which is an average over four angles. Doubled values for the distribution widths of one Si–O–Al angle are expected, if the angles are independently distributed. Thus, the residual linewidths of the $^{29}$Si MAS NMR yield distribution widths (fwhm) of the (nonaveraged) Si–O–Al angles of $3.0^\circ$ and $1.8^\circ$ for the zeolites Na–A and Na,K–LSX, respectively.
This distribution of angles can be inserted into Eqs. (3) and (4). The latter gives a distribution of the $^{17}\text{O}$ chemical shift with an fwhm of 1.8 and 1.5 ppm, for the hydrated zeolites Na–A and Na,K–LSX, respectively. The angular-dependent distribution of the quadrupole coupling constant can be estimated by Eq. (3). For the sake of simplicity, we use mean quadrupole coupling constants of 3.4 and 3.2 MHz, and we use again the mean angle of 148.4° and 139.3° for the hydrated zeolites Na–A and Na,K–LSX, respectively. The values 0.06 and 0.05 MHz for the fwhm of the distributions of the quadrupole coupling constants are obtained for the hydrated zeolites Na–A and Na,K–LSX, respectively.

With the Larmor frequency $\nu_L$ and the quadrupole coupling parameter $P_Q = C_{qq}(1 + \eta^2/3)^{1/2}$ we have in the case of the nuclear spin $I = 5/2$ and multiple- or single-quantum transitions for MQ MAS or DOR, respectively, the following equations for the isotropic value of the total shift:

$$\delta_{\text{MQMAS iso}}/\text{ppm} = \delta_{\text{CS iso}}/\text{ppm} + \frac{3 \times 10^6}{850} \frac{P_Q^2}{\nu_L^2}$$

and

$$\delta_{\text{DOR iso}}/\text{ppm} = \delta_{\text{CS iso}}/\text{ppm} - \frac{3 \times 10^6}{500} \frac{P_Q^2}{\nu_L^2}.$$  (5)

The isotropic quadrupole shifts on the right-hand side of the equations, which are of opposite sign (factor $-10/17$) for the multiple-quantum transitions compared to that for the single-quantum transition, are distributed due to the distribution of the quadrupole coupling constants. Inserting the distributions, which were estimated above, we obtain quadrupole shifts in the order of magnitude of 0.1 ppm (exact 0.08 and 0.06 ppm in the case of 3QMAS or $-0.13$ and $-0.1$ ppm in the case of DOR for the hydrated zeolites Na–A and Na,K–LSX, respectively).

Thus, the influence of an angular distribution (Si–O–Al angle) on the isotropic quadrupole shift (about ±0.1 ppm) can be neglected in comparison to the influence on the isotropic chemical shift (about 2 ppm). Figure 3 demonstrates the different resolution in the $^{17}\text{O}$ spectra for 3QMAS, 5QMAS, and DOR techniques. The deconvolution gives linewidths of about 2 ppm for the single signals in the 5QMAS and DOR spectra as well. This value does not differ significantly from the values that were estimated for the $^{17}\text{O}$ NMR spectra by means of the $^{29}\text{Si}$ NMR spectra (1.8 and 1.5 ppm, for the hydrated zeolites Na–A and Na,K–LSX, respectively). The residual linewidths of the 5QMAS and DOR spectra can be explained by a distribution of the Si–O–Al angles, which is caused by a nonhomogeneous distribution of cations in the zeolite. This is a natural broadening independent from NMR techniques. Now the question arises as to why the residual linewidth of the 3QMAS NMR spectra is about twice as broad as that for 5QMAS and DOR NMR. The excitation procedure does not influence the residual linewidth of the 3QMAS spectra: Application of FAM2 gives the same resolution (and also the same intensity in opposite to that of the original work [18]). Also the lowering of the hf power by a factor of 2 does not influence the residual linewidth of the spectra. The improved resolution of 5Q compared to 3QMAS NMR was first reported by Sarv et al. [34]. Also Mildner et al. [35] claimed that the resolution of 3QMAS experiments is less than the resolution that was obtained by a 5QMAS technique similar to the RIACT
technique. Pike et al. [36] calculated the relative scaling factors and obtained a better resolution by the factor of 4.19 for 5Q than for 3Q MAS (spin = 5/2), but they could not find experimental evidence for this. Nonsecular dipolar coupling between \(^{17}\)O and \(^{27}\)Al nuclei can also influence the resolution of \(^{17}\)O NMR spectra in the lower field, cf. [37]. This can be neglected in this study, since the Larmor frequency of the aluminum nuclei is more than two orders of magnitude higher than the corresponding quadrupole coupling constant. Further work seems to be necessary in order to explain the resolution of 3Q MAS NMR lower than that of DOR NMR.

**CONCLUSIONS**

The tendency that the isotropic chemical shift of the \(^{17}\)O NMR decreases with increasing bond angle (or s-character of the oxygen hybrid orbital) was confirmed by this study. A quite linear correlation exists for the oxygen sites in the zeolites A and LSX, if the data are limited to the sodium form of the hydrated zeolites. A fit of seven signals of the hydrated sodium zeolites A and LSX gives the equation \(\delta/\text{ppm} = -214\rho + 136\) with a correlation coefficient of 0.92, if the chemical shift is plotted against the s-character of the oxygen hybrid orbital \(\rho = \cos \alpha / (\cos \alpha - 1)\).

The dehydration of the zeolites causes \(^{17}\)O NMR chemical shift changes by the superimposed effects of the well-known changes of the Si–O–Al bond angles and the effect of polarization of the framework by the adsorbed water molecules. The total effect is about 8 ppm, whereas the angular corrected effect amounts to about 4 ppm. The low-field shift due to the adsorption interaction is relatively small (approx. 2.2 ppm) for formic acid.

A downfield shift of approx. 10 ppm going from the lithium to the cesium form of the zeolite LSX and a shift of approx. 34 ppm for the O3 signal after the substitution of sodium by thallium cations in the zeolite A reflect the increase of the basicity of the oxygen framework of the zeolite by ion exchange with larger cations.

\(^{17}\)O DOR NMR spectra are superior to \(^{17}\)O 3QMAS NMR spectra with respect to the resolution by a factor of 2. The application of the FAM2 excitation [18] does not improve resolution or intensity in the \(^{17}\)O 3QMAS NMR spectra. The signal-to-noise ratio of DOR and 3QMAS NMR spectra is comparable, whereas that of 5Q MAS NMR spectra is lower by more than one order of magnitude, and the spectral window is lower by a factor of 5. This limits the application of the 5QMAS technique to the \(^{17}\)O NMR. The residual linewidths of the signals in the \(^{17}\)O DOR and \(^{17}\)O 5QMAS NMR are caused by a distribution of the Si–O–Al angles in the zeolites.

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REFERENCES