$^{17}$O multiple-quantum and $^1$H MAS NMR studies of zeolite ZSM-5

This Letter is dedicated to Dr. Dieter Fenzke on the occasion of his 60th birthday

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Abstract

Oxygen-17 multiple-quantum magic-angle spinning nuclear magnetic resonance studies were performed, for the first time, in the high field of 17.6 T. A good resolution between two oxygen signals due to SiOSi and SiOAl fragments could be obtained. From the residual linewidth of the SiOSi signal, it is concluded that a change of the bridging SiOSi angle by 13.4° gives rise to a quite large change in the isotropic chemical shift of less than 5.7 ppm. © 1998 Elsevier Science B.V.

1. Introduction

Oxygen isotope exchange is recognised as an useful modification of oxygen-containing materials for spectroscopic studies. Attractive attributes of the $^{17}$O NMR (spin $I = 5/2$) spectroscopy are the large chemical shift range and the additional information which can be obtained from the quadrupole parameters. The big drawback, the low $^{17}$O natural abundance of 0.037%, can be overcome either by the use of $^{17}$O-enriched components in the synthesis or by a post-synthesis isotope exchange. First $^{17}$O NMR studies of zeolites were performed by Timken et al. [1]. However, the resolution of signals in magic-angle spinning (MAS) spectra of $I > 1/2$ nuclei is limited by the quadrupole line broadening.

A recent suggestion to conquer the anisotropy of the quadrupole interaction in the solid-state NMR is the two-dimensional experiment of Frydman and Harwood [2] which makes use of multiple-quantum transitions in addition to the magic-angle spinning (MQ MAS NMR). Symmetric $p/2 \leftrightarrow -p/2$ coherences with the quantum level $pQ$ are selected, since the corresponding powder resonances devoid of first-order quadrupole effects. In the case of fast magic-angle spinning, the phase development $\varphi(t)$
of this multiple-quantum coherence can be written [3]:

\[ \frac{\varphi(t)}{2\pi t} = \Delta v p + \frac{\nu_0^2 (3 + \eta^2)}{90\nu_0}\left\{I(I+1) - \frac{3}{4}p^2\right\} \]

\[ \times p - \frac{\nu_0^2}{12960\nu_0}\left\{(18 + \eta^2)d_{20}^0 + \sqrt{360}\eta d_{20}^0 \cos 2\alpha + \sqrt{70}\eta^2 d_{40}^0 \cos 4\alpha\right\} \]

\[ \times \left\{36I(I+1) - 17p^2 - 10\right\}p. \quad (1) \]

\( \Delta v \) accounts for the offset and chemical shift effects as well. \( \nu_0 \) is the Larmor frequency and the nuclear spin value is \( I = 5/2 \) for \( ^{17}\text{O} \). \( \nu_0 = 3C_{\text{qcc}}/2I(I-1) \) and \( \eta \) denote the quadrupole frequency and asymmetry parameter, respectively, with \( C_{\text{qcc}} \) being the quadrupole coupling constant. Polar angles \( (\alpha, \beta) \) describe the spinner axis with respect to the quadrupole tensor. The elements \( d \) of the reduced Wigner matrices are related to \( \beta \).

It can be seen from Eq. (1) that by going from the multiple-quantum level \( pQ \) to the \(-1Q\) level of observation, the sign of the phase development of the second-order quadrupole interaction is averaged out, if the times \( t_1 \) and \( t_2 \) spent on the quantum levels \( pQ \) and \(-1Q\), respectively, fulfil the condition

\[ t_2 = p\frac{36I(I+1) - 17p^2 - 10}{36I(I+1) - 27t_1}. \quad (2) \]

This relation describes the appearance of the isotropic echo, and thus gives the slope of the anisotropic axis in the two-dimensional spectrum.

The selection of the triple-quantum coherences during \( t_1 \) gives the highest signal-to-noise ratio, since these transitions can be more effectively excited than the quintuple-quantum coherences. But the latter have the advantage of an enhanced line narrowing on samples with distributed surroundings [4]. A special pulse phase cycling has to be used, in order to follow the chosen pathways, [5,6] and the duration of the pulses must be tuned in order to increase the signal [7,8]. The insertion of a \( z\)-filter before observing the signal is useful, in order to obtain two fully symmetric pathways [9].

Wu et al. [10] and Dirken et al. [11] performed \( ^{17}\text{O} \) 3Q-MAS studies of hydroxyapatite and aluminosilicate glass, respectively. Two signals due to Si–O–Si and Si–O–Al fragments could be observed for the aluminosilicate glass and the NMR parameters [11] were similar to the values obtained for zeolites by Timken et al. [1]. Three resolved \( ^{17}\text{O} \) NMR signals for the well-known four distinct oxygen sites in the Si–O–Si fragments of siliceous faujasite have been observed by Bull et al. [12] by means of the double rotation technique, but the assignment was not possible. A minor problem of the previous \( ^{17}\text{O} \) NMR studies of zeolites has been that no information could be given about the degree of isotopic oxygen exchange in the zeolite.

The question arises, whether \( ^{17}\text{O} \) MQ-MAS is able to resolve the signal due to various distinct oxygen sites in Si–O–Si fragments in zeolites.

2. Experimental

Zeolite Na–ZSM-5 was treated with \( \text{H}_2\text{O} \) (24.7% \( ^{17}\text{O} \) enriched) at 450°C for one hour in a nitrogen steam. A portion of this sample was then ion exchanged with an aqueous solution of \( \text{NH}_4\text{NO}_3 \) (0.1 N) at room temperature [13]. The framework Si/Al ratio of 19 was determined by \( ^{29}\text{Si} \) MAS NMR. No extra-framework aluminium could be detected by \( ^{27}\text{Al} \) MAS NMR for the sodium and the ammonium forms of the zeolite as well. Samples for \( ^{1}\text{H} \) MAS NMR were prepared by heating 6 mm deep layers of zeolite \( \text{NH}_4\text{–ZSM-5} \) in glass tubes 3 mm outer diameter. The temperature was increased at a rate of 10 K h \(^{-1} \) under vacuum. Samples were maintained at 400°C at less than 10 \(^{-2} \) Pa for 24 h and then sealed off.

\( ^{1}\text{H} \) MAS NMR spectra of the zeolites \( \text{NH}_4\text{–ZSM-5} \) were measured on a Bruker MSL 500 spectrometer with a moderate MAS frequency for the glass am- pules of 8 kHz (in order to get a sufficient number of spinning sidebands) and with an echo 125 \( \mu \text{s} \) after the second pulse of the Hahn echo sequence.

In order to get optimum conditions for our \( ^{17}\text{O} \) 3Q-MAS experiment, we used a very high magnetic field of 17.6 T (Bruker DMX 750) at 101.7 MHz,
combined with a MAS frequency of 17.5 kHz and a high power transmitter/receiver system. Triple-quantum experiments were performed by means of two strong pulses and an additional weak z-filter pulse [9]. A total ring down delay of 7 μs after the z-filter pulse and a repetition time of 200 ms were used. A 24 phase cycle is 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 non-selective nutation frequency has been determined by a H$_2^{17}$O sample as 100 kHz. For this rf power, the widths of the first and second pulse were adjusted for maximum signal to 3.4 μs and 1.2 μs, respectively. The selective π/2 pulse length of the z-filter has been adjusted to 50 μs.

No spinning sidebands appear in the multiple-quantum dimension, because $t_1$ has been increased in steps of the reciprocal spinning frequency. The time domain consists of 64 and 1024 steps in $t_1$ and $t_2$, respectively. 480 scans were accumulated for each $t_1$ step. The programs XIShear and PULSAR have been used for the shearing of the 2D spectra and the simulation of the anisotropic lineshape, respectively [14]. The $^{17}$O NMR scales are referenced to H$_2^{17}$O [8].

3. Results and discussion

Fig. 1 shows the second and higher-order spinning sidebands of the $^1$H MAS spectra of dehydrated zeolites NH$_4$–ZSM-5. The upper spectrum shows the $^{17}$O-enriched sample and the spectrum at natural abundance of $^{17}$O is given below. The narrow and broad downfield peaks in each sideband correspond to two types of bridging hydroxyl groups [15]. Hunger obtained a second moment $M_{H-Al}^{2}$ = $3.7 \times 10^8$ s$^{-2}$ and a proton–aluminium pair distance of 0.25 nm for a similar zeolite [15]. The lineshape of the spinning sideband envelope is Gaussian, as for this H–Al interaction. Isotopic exchange creates $^{17}$OH groups with the internuclear distance of about 0.1 nm. The corresponding second moment can be calculated to $M_{^{17}O}^{2}$ = $2.4 \times 10^{10}$ s$^{-2}$. With a Gaussian like lineshape we can calculate the FWHM linewidth of the spinning sideband envelope from the second moment to be 58 kHz. This is in agreement with the finding that spinning sidebands can be observed up to the 7th order (±56 kHz) for the $^{17}$O enriched zeolite. From the intensity of the outer sidebands we can extrapolate intensities of the inner sidebands, which are due to the $^{17}$OH groups. The sum of all centre and sideband intensities due to $^{17}$OH interactions divided by the total intensity of the $^{17}$O enriched zeolite gives an amount of 13 ± 3% bridging $^{17}$OH groups with respect to the total number of bridging OH groups. This is only one half of the value that is expected for the equilibrium isotopic exchange with 24.7% $^{17}$O enriched water.

Fig. 2 shows the sheared 2D $^{17}$O 3Q-MAS spectrum of the zeolite Na–ZSM-5, whereas the projection on the isotropic axis is separately given in Fig. 3. Values of the isotropic chemical shift δ and quadrupole parameters C$_{qcc}$ and η have been obtained for both species, directly from the data processing of Fig. 2 [8]. These parameters were introduced into the simulation of the usual $^{17}$O MAS spectrum in order to obtain the relative concentrations (Fig. 4). In agreement with previous studies [1], both species can easily be assigned to SiOSi and SiOAl fragments with respectively: concentrations = 80 and 20%, δ = 40 and 30 ppm, C$_{qcc}$ = 5.3 and 3.5 MHz, η = 0.12 and 0.29.
The most important result of this study lies in the spectrum in Fig. 3. Fully resolved signals for the various bridging angles in the SiOSi or SiOAl fragments could not be obtained. The residual FWHM linewidth of the two lines amounts to $\delta_{1/2} = 5.7$ ppm. An X-ray structure determination of van Koningsveld [16] et al. has shown that 28 various SiOSi angles in the range of $142^\circ$–$167^\circ$ exist in the zeolite Na–ZSM-5. The mean value of these angles is $154.1^\circ$ and their standard deviation is $6.7^\circ$. Thus, 67% of the SiOSi bridges have angles in the region $154.1 \pm 6.7^\circ$. This range can be related to the value $\delta_{1/2}$ and the result of this comparison is that a change of the bridging SiOSi angle by $13.4^\circ$ gives rise to a change in the $^{17}$O isotropic chemical shift of less than 5.7 ppm. We must say ‘‘less’’, since other residual effects of line broadening cannot be excluded. This finding disagrees with the result of Bull and Cheetham [12], who claimed that in the zeolite SiI–Y the range of bridging oxygen angles $139^\circ$–$149^\circ$ corresponds to an $^{17}$O chemical shift variation of 10.6 ppm.

Relative actual concentrations for SiOsi and SiOAI fragments (Fig. 4: 80 and 20%) are different from their corresponding MQMAS intensities which are 75 and 25%, respectively (Figs. 2 and 3). Indeed, experimental intensities are influenced by the different efficiencies of the multiple-quantum manipulations for the two species which are submitted to different quadrupole interactions [7]. Nevertheless, this high amount of SiOAI fragments is surprising. For an equilibrium isotopic exchange an amount of 9.5% SiOAI fragments should be determined from the Si/Al ratio. The high relative intensity of the SiOAI signal could be explained by a favoured insertion of $^{17}$O into oxygen framework positions in the neighbourhood of aluminium.

Fig. 2. Sheared $^{17}$O 3Q-MAS spectrum of the $^{17}$O enriched hydrated zeolite Na–ZSM-5, together with its anisotropic MAS projection on the top.

Fig. 3. Isotropic projection of the $^{17}$O 3QMAS spectrum of the $^{17}$O enriched hydrated zeolite Na–ZSM-5.

Fig. 4. Lineshapes of the anisotropic spectra of the hydrated zeolite Na–ZSM-5. A: $^{17}$O MAS NMR spectrum, solid line for experimental spectrum and dotted line for simulated spectrum; B: Slice of the 2D spectrum at $\delta_{22} = 50$ ppm (Si–O–Si); C: Slice of the 2D spectrum at $\delta_{22} = 33$ ppm (Si–O–Al).
atoms. The formation of metastable peroxy states with three-valent atoms as the first step for labeling of zeolites has been proposed by Yang et al. [17]. But a complete explanation of the distribution of $^{17}$O in the zeolite framework is the subject of further studies.

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