Low-temperature and echo $^1$H magic-angle spinning nuclear magnetic resonance studies of dealuminated and weakly rehydrated zeolites H-Y

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Abstract

Low-temperature $^1$H magic-angle spinning nuclear magnetic resonance (MAS NMR) and various rotor-synchronous spin echo $^1$H MAS NMR experiments have been applied to characterize partially dealuminated and weakly rehydrated zeolites H-Y. The signal caused by water adsorption on Lewis acid sites does not change at 160 K in comparison to room temperature. Spin echo $^1$H MAS NMR experiments with dipolar dephasing by means of high-power $^{27}$Al irradiation confirm that the water molecules must be close to aluminium sites. Two models of water adsorption on Lewis acid sites are discussed.

Keywords: Zeolites H-Y; Dealuminated zeolites H-Y; Rehydrated zeolites H-Y

1. Introduction

The $^1$H MAS NMR technique has proven to be an elegant and reliable method for the direct observation and characterization of bare hydroxyl groups in zeolites acting as Brønsted acid sites, i.e. proton donors, in catalytic reactions [1–3]. Additional information about the nature of these sites can be obtained from various NMR studies of other nuclei which may be constituents of the Si–OH–Al bridges, such as $^2$H, $^{27}$Al and $^{29}$Si [2,4,5]. The catalytic activity of zeolites can be strongly enhanced by partial dealumination of the zeolite framework. Part of the non-framework aluminium species are supposed to be acid sites of the Lewis type (electron pair acceptors). Their properties and interaction with Brønsted sites can be studied by NMR spectroscopy of the adsorption and reaction of probe molecules in the zeolites [1,6]. Partially dealuminated and weakly rehydrated zeolites H-Y are known to give rise to $^1$H NMR signals at ca. 6–7 ppm [7,8]. While it is generally agreed that these signals are evidence for the presence of Lewis acid sites in the zeolite, their nature is still discussed controversially. Also, the terms extra-framework or non-framework aluminium do not necessarily stand for aluminium being completely removed from the zeolite framework. Zeolite dealumination can produce aluminium still partially bonded to the framework [9], and as early as 1968 it was suggested by Hopkins [10] and Lunsford [11] that enhanced catalytic activity may be not due to pure Lewis acidity but rather to a synergism between Bronsted and Lewis acid sites. Hunger et al. [7] proposed a model of water adsorption on three-coordinated silicon atoms which occur as an intermediate state in the com-
combined dehydroxylation and dealumination process of the zeolite framework. In contrast to this, Batamack et al. [8], who investigated a zeolite H-Y that was dealuminated chemically instead of hydrothermally, attributed the signals to water adsorbed on aluminium atoms still partially bonded to the framework. From a recent study [5], we know that the considered signals are, in fact, two peaks at 6.7 and 7.3 ppm, and these have been assigned to water species that are locally mobile but "locked" at their position in the zeolite. New results concerning the 6.7- and 7.3-ppm 1H NMR signals in zeolites H-Y are reported in this paper. They were obtained by low-temperature 1H MAS NMR and a variety of echo 1H MAS NMR experiments including additional 27Al irradiation.

2. Experimental

The zeolite H-Y used in this study was prepared by Dr. J. Meusinger (Leipzig, Germany) from the original sodium form (Si/Al=2.6) by repeated exchange in a 0.5 N aqueous solution of NH4NO3 followed by calcination at 450°C. This procedure left a residual sodium cation concentration in the zeolite of 8% and caused a partial dealumination of the zeolite framework (final framework Si/Al = 3.1).

All samples went through the same activation procedure: 8-mm-deep layers of zeolite powder in glass tubes of 3 mm diameter were heated under vacuum at a rate of 10 K h⁻¹ up to 400°C and kept at this temperature and a pressure of less than 10⁻² Pa for 24 h. After the activation, the zeolites were loaded at room temperature with a small amount of water (one H₂O molecule per supercage) and alternatively with O₂ at 13 kPa or with deuterated pyridine (three NC₅D₅ molecules per supercage). Finally the glass ampoules were sealed off.

The oxygen adsorption was applied in order to effectively shorten the 1H NMR spin–lattice relaxation times T₁ of the weakly rehydrated samples. It could be skipped in the case of pyridine loaded samples.

All 1H MAS NMR experiments were performed on a Bruker MSL 500 spectrometer using a MAS probehead with sample containers of 4 mm diameter. The MAS rate was kept at 12.5 kHz. Room-temperature 1H MAS NMR spectra were acquired after a single-pulse excitation with a 80-μs ring-down delay corresponding to exactly one MAS period (see Fig. 1A). Low-temperature 1H MAS NMR experiments at 160 K allowed spinning rates of 6–8 kHz only. Here, a short ring-down delay of 20 μs and both zero- and first-order phase correction of the data had to be applied. Spin echo 1H MAS NMR experiments were carried out using a Hahn echo sequence (Fig. 1B) and implying a sixteen-step phase cycle [12]. The delay t₁ was varied in multiples of the MAS period (80 μs).

In addition, a Carr–Purcell–Meiboom–Gill (CPMG) spin echo sequence [13,14] with rotor-synchronized pulse delays and phase alternation between successive 180° pulses was applied in a 1H MAS NMR experiment on a pyridine-loaded sample (see Fig. 1D). Data acquisition in this experiment was initiated at the echo maximum after the first 180° pulse. The dwell time of 20 μs proved short enough to cover the spectral width including the first spinning sidebands on either

Fig. 1. Schematic representation of the pulse sequences applied in this study. (A) Single pulse experiment with data acquisition after ring-down delay. (B) Spin echo sequence. For rotor-synchronization the pulse delay t₁ was adjusted to an integer multiple of the MAS period. (C) Additional 27Al radiofrequency irradiation during the t₁ delays of (B) as used in dipolar dephasing experiments. (D) Carr–Purcell–Meiboom–Gill spin echo sequence with 180° pulses of alternating phase. Data acquisition was initiated at the maximum of the first echo.
side and long enough to filter ring-down effects due to the 180° pulse train.

We also performed spin echo 1H MAS NMR experiments with irradiation of 27Al resonance radiofrequency before and after the 180° pulse (Fig. 1B and C). As the 27Al NMR spectra of dehydrated zeolites are known to be extremely broad due to quadrupolar interaction (central transition ca. 70 kHz, satellite transitions up to 10 MHz) [4], we can by no means achieve 27Al radiofrequency power that would be strong enough for 27Al decoupling. Instead, the aluminium resonance irradiation during the echo MAS experiment results in a dephasing of the heteronuclear dipolar coupling between protons and aluminium nuclei, thus destroying the averaging effect of the MAS for those protons that are coupled to aluminium. This allows for a discrimination between aluminium-connected and aluminium-unconnected hydroxyl species in the zeolites. The basic idea of this effect has been used before by Van Eck et al. [15] in 31P and 29Si MAS NMR studies of AlPOs and zeolites and by Fyfe et al. [16] for 31P MAS NMR of VPI-5. It was introduced to 1H MAS NMR of zeolites by Beck et al. [17].

3. Results and discussion

The room-temperature and low-temperature 1H MAS NMR spectra of the zeolites H-Y are given in Fig. 2. The different proton signals are denoted by a–f, cf. Ref. [1]. Line a at ca. 2.0 ppm is caused by non-acidic silanol (SiOH) groups at framework defects and in amorphous parts of the sample. Lines b at 4.1 ppm and c at 4.7 ppm are due to bridging hydroxyl groups (Si–OH–Al) pointing into the supercages and the sodalite cages, respectively. Line e at 2.7 ppm is assigned to hydroxyl groups associated with non-framework aluminium species and bonded to framework oxygen atoms. Line f occurs after water adsorption at Lewis acid sites. Obviously line f splits up into two signals at 6.7 and 7.3 ppm. Except for a slightly increased linewidth at the lower temperature, there is no significant difference to be seen between the spectra at room temperature and at 160 K. The spinning sidebands in the low-temperature spectrum are due to the lower spinning rate of ca. 8 kHz.

If isolated water molecules (line f) are immobilized, they should be expected to give rise to spinning sidebands like in the MAS NMR spectrum of crystalline water in nearly anhydrous CaSO4 [18]. This is not observed down to 160 K. We can thus conclude that the water molecules undergo stochastic reorientation during one sample rotation period even at 160 K.

When loaded with three pyridine molecules per supercage, the spectra of the zeolites show additional broad signals at 17.1, 9.9 and 8.3 ppm. They can be interpreted to be signals resulting from the interaction of one pyridine molecule with one, two or three bridging hydroxyl groups, respectively. The values 9.9 and 8.3 ppm can be approximately obtained, if a fast chemical exchange of the protons is considered between resonance positions at 17.1 ppm (pyridinium ion) and 4.5 ppm (mean value for bridging hydroxyl groups). It is worth noting that unlike in zeolite H-ZSM-5, where a
sizeable pyridinium signal at ca. 19 ppm and a second signal at 16 ppm were resolved [19], we detected only one pyridinium line at 17.1 ppm of ca. 4 ppm linewidth at half maximum (FWHM) and much lower relative intensity.

Fig. 3 shows stacked plots of echo $^1$H MAS NMR spectra of weakly rehydrated zeolites H-Y without (A) and with (B) pyridine loading. The echo delays $t_1$ have been increased, respectively, from 0.8 to 23.2 ms and from 0.16 to 4.64 ms. The echo decay times $T^2_{\text{Hahn}}$ for the different proton species in the pyridine-free sample were determined from the corresponding $^1$H NMR signal intensities. The $T^2_{\text{Hahn}}$ values obtained in this way are: 40 ± 8 ms (line a), 20 ± 4 ms (lines b and c), 25 ± 5 ms (line e), 18 ± 4 ms (line f₁) and 12 ± 3 ms (line f₉). The echo intensities of the signals due to pyridine and pyridinium ions decay faster than 1 ms. The errors reported for the given values are not due to experimental limitations but rather to the assumption of a simple exponential decay. Numerical analysis shows that the superposition of two exponentials fits the data more accurately. The one-pulse $^1$H MAS NMR spectra of the two samples (Fig. 2, top and bottom) do not allow for a characterization of the accessibility of the line f species to pyridine. Echo MAS experiments reveal that the sample loaded with pyridine and water features a signal of approximately the same width and echo decay time as line f, but with slightly increased chemical shift of ca. 7.8 ppm. Therefore, we claimed in our former interpretation [5] that line f is not removed upon pyridine adsorption. However, this signal can be observed also in zeolite H-Y loaded with pyridine only, i.e. in the absence of any water. It means that the signal at 7.8 ppm cannot be identical with line (f) and we must take into consideration that the species giving rise to line f are accessible to pyridine molecules in contrast to our previous interpretation [5]. The echo decay time of the signal at 7.8 ppm is of the order of 10 ms. This value is in the same order of magnitude as the values for lines a-f, but long compared to $T^2_{\text{Hahn}}$ values for the signals due to pyridinium ions.

Fig. 4 shows the Fourier-transformed CPMG spin echo $^1$H MAS NMR train of weakly rehydrated zeolite H-Y loaded with pyridine. The delay between successive 180° pulses was adjusted to 6 ms, corresponding to sixty MAS periods at the spinning rate of 10 kHz. In analogy to the effect of sample spinning, the sequence of 180° pulses gives rise to an echo train in the time domain signal which after Fourier transformation turns

![Fig. 3. Stacked plots of spin echo $^1$H MAS NMR spectra of zeolite H-Y loaded with one H₂O molecule per supercage (A) and additionally with three NC₂D₅ molecules per supercage (B). Note that the pulse delay times $t_1$ of the two series differ by a factor of 5. The dotted line marks the $t_1 = 4.0$ ms spectra on either side.](image-url)
into an extremely narrow line with equally spaced sidebands. In order to avoid confusion with MAS sidebands we will label them “Carr–Purcell sidebands”. The space between the Carr–Purcell sidebands is given by the reciprocal value of the delay between the 180° pulses. The residual linewidth is indicative of the mobility of the observed proton species. In the frequency range of the various hydroxyl groups (0–5 ppm) we registered linewidths of FWHM ≤ 14 Hz, whereas in the range 5–15 ppm there are two very broad peaks (FWHM > 1 kHz) topped by a couple of narrow Carr–Purcell sidebands (FWHM ≈ 30 Hz). The broad components can be easily identified as the signals due to pyridine molecules which are highly mobile, and the narrow sidebands are due to the species giving rise to the 7.8-ppm signal in the Hahn echo spectra. The signal of pyridinium ions appears to be almost completely suppressed in this spectrum, mainly because the echo decay of pyridinium is too fast compared to the pulse delay.

Fig. 5 shows spectra obtained by rotor-synchronous spin echo 1H MAS NMR without (top) and with (centre and bottom) irradiation of 27Al resonant radiofrequency according to Fig. 1B and C. The pulse delay in the proton channel was 2 ms, corresponding to sixteen MAS periods at the spinning rate of 8 kHz (left) and eight MAS periods at the spinning rate of 4 kHz (right). Two different 27Al radiofrequency amplitudes of 25 and 50 kHz have been chosen. Obviously, the spectra are influenced by both MAS rate and 27Al radiofrequency amplitude. The change in relative intensity of the single lines as a function of the 27Al radiofrequency is given in Table 1. It appears that all signals are decreased upon 27Al radiofrequency irradiation. Even for the silanol groups, line a, there is found a weak dipolar coupling to aluminium nuclei in the neighbourhood. Their signal intensity decreases to 75% for $v_{rot}=50$ kHz and $v_{rot}=8$ kHz. This result differs from a study of zeolite H-ZSM-5 [19], where the signal intensity of the silanol groups remained unchanged even for higher $v_{rot}$ values of 100 kHz. This allowed a subtraction of the 27Al-dephased echo spectra from the “regular” echo spectra, where only the signals of aluminium-connected hydroxyl species remained. As the aluminium content of our zeolite H-Y is almost one order of magnitude higher than that of the H-ZSM-5 zeolites studied in Ref. [19], all protons in zeolite H-Y should be expected to...
feel a non-negligible dipolar coupling to aluminium.

The signal intensities of the other hydroxyl species, lines b, c and e, which are known to be connected to framework and extraframework aluminium, respectively, are drastically decreased upon $^{27}$Al radiofrequency irradiation. While the signal of extraframework $\text{AlOH}$ groups, line e, has completely vanished already at weak $^{27}$Al radiofrequency irradiation, the signals of the bridging hydroxyls, lines b and c, decrease to 10% for $v_{\text{Al}} = 50 \, \text{kHz}$ and $v_{\text{rot}} = 8 \, \text{kHz}$ and to 5% for $v_{\text{Al}} = 50 \, \text{kHz}$ and $v_{\text{rot}} = 4 \, \text{kHz}$. Even without forming difference spectra, which in our case did not work satisfactorily, the results obtained allow one to differentiate Al-connected from Al-unconnected hydroxyl species.

Returning to line f, we find that the signal intensity also decreases considerably to 25% for $v_{\text{Al}} = 50 \, \text{kHz}$ and $v_{\text{rot}} = 8 \, \text{kHz}$ and to 10% for $v_{\text{Al}} = 50 \, \text{kHz}$ and $v_{\text{rot}} = 4 \, \text{kHz}$. This means that the dipolar coupling to aluminium nuclei of the species giving rise to line f must be weaker than for bridging hydroxyl groups and for extraframework $\text{AlOH}$ groups, but clearly stronger than for silanol groups. Considering also the fact that these species are allowed to reorient rapidly, though remaining locked at their position, we can assume that their dipolar coupling to aluminium is to some extent reduced by motion. The interpretation of line f given by Hunger et al. [7], proposing water adsorption on three-coordinated $\text{Si}^+$ species, was based on the fact that spinning sidebands did not reveal a proton–aluminium interaction. The model discussed by Batamack et al. [8] of water adsorption on aluminium partially bonded to the zeolite framework and on bridging hydroxyls enabling additional hydrogen bonding between the two oxyhydrogenated sites is therefore to be favoured from our point of view. Still, both interpretations do not account for the existence of a two-fold signal at 6.7 and 7.3 ppm. Further investigations will be necessary to assign the two lines.

4. Conclusions

Adsorption of deuterated pyridine gives rise to additional proton signals at 8.3 and 9.9 ppm assigned to hydroxyl groups shifted by pyridine adsorption and a small, broad line at 17.1 ppm due to pyridinium ions. The interaction of pyridine molecules with the zeolite H-Y framework appears to be weaker than in zeolite H-ZSM-5. Comparison of $^1$H MAS NMR spectra of dealuminated and weakly rehydrated zeolites H-Y acquired at room temperature and at 160 K does not reveal any significant changes of line shapes and signal intensities of the various hydroxyl species and the signals caused by adsorbed water molecules.

Spin echo $^1$H MAS NMR experiments with rotor-synchronous pulsing allow to selectively determine the $T_2^\text{Hahn}$ values of the different proton species. Also, the application of the CPMG spin echo pulse train during data acquisition produces highly resolved $^1$H MAS NMR spectra that are very sensitive to the dynamics of the observed protons. Freely mobile or rapidly exchanging species appear as signals with the same linewidth as in the regular spin echo MAS experiment but decreased in relative intensity, whereas those species that are fixed or subject to restricted mobility only produce a spectrum of narrow equidistant Carr–Purcell sidebands with increased relative intensity.

Irradiation of high-power $^{27}$Al resonance radiofrequency during the spin echo $^1$H MAS NMR experiment generates a dephasing of the heteronuclear dipole coupling of protons and aluminium nuclei. Thus, the resulting spectra of protons located close to aluminium are decreased considerably. From these experiments we can conclude that the water molecules in the dealuminated zeolite H-Y are adsorbed in the neighborhood of aluminium atoms. The existence of two $^1$H MAS NMR signals attributed to the adsorbed water species remains to be explained.

References