Direct Observation of Brønsted Acidic Sites in Dehydrated Zeolite H-ZSM5 Using DFS-Enhanced ^{27}Al MQMAS NMR Spectroscopy

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Zeolites are a unique class of porous solid aluminosilicates which are highly popular as heterogeneous acid catalysts. The active acidic site consists of an aluminum atom in a tetrahedral framework position with a proton in an OH group forming a bridge to a tetrahedral silicon neighbor. Due to charge-balance requirements the aluminum and the proton belong together. Much IR and NMR spectroscopic research has been invested in the characterization of the Brønsted-acidic proton in different zeolites.[1] Thus far, solid-state NMR investigations of the local structure of the aluminum in the activated dehydrated state were much less successful. This is attributed to the large electric field gradient at the framework aluminum site, induced by the highly asymmetric charge distribution resulting from the fact that one of the coordinating oxygens has a proton attached to it. As a result, the aluminum will experience a very large quadrupole interaction leading to a strong broadening of the corresponding ^{27}Al NMR line. This resulted in terms such as "NMR-invisible aluminum" being frequently used in the literature. The first observation of these sites came with static ^{27}Al spin–echo NMR experiments with which it was possible to detect broad lines indicating the presence of quadrupole coupling constants in the range of 11–18 MHz.[2]

Na-ZSM5 (Degussa, Si/Al = 14) was ion-exchanged with NH$_4^+$ and then evacuated overnight at room temperature. Then the sample was heated at a rate of 2 K/min to a final temperature of 723 K, and activated for 12 h. During the heating process, two stops were made for 2 h each at 353 and 433 K. The obtained H-ZSM5 sample was sealed under vacuum and reopened in a drybox under argon gas to fill the rotors. The efficiency of this treatment was checked in a ^{1}H MAS NMR experiment yielding three lines at 1.8, 4.0, and 6.4 ppm, without any indication of the presence of water. During MAS NMR experiments the rotors were spun using dry nitrogen gas, and static experiments were performed under a dry gas stream.

Figure 1 shows the Hahn echo ($\pi/2 - \tau - \pi$, $\nu_1 = 180$ kHz) spectrum of dehydrated H-ZSM5 obtained at 14.1 T. The full width of the spectrum amounts to 80 kHz assigned to an Al resonance with a $C_{qcc} \approx 16$ MHz and a low asymmetry parameter. On top of the broad line, a narrower component is visible, indicating the presence of aluminum in a less-distorted environ-
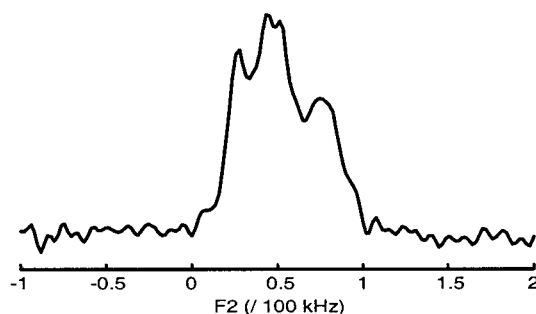

Figure 1. ^{27}Al static Hahn-echo spectrum of dehydrated H-ZSM5 obtained at 14.1 T.

ment. This component can originate from partially rehydrated sites, extraframework aluminum, or from sites charge-compensated by residual Na$^+$ or extraframework Al-species. These observations are in line with those of Freude et al. and Hunger and Horvath[2]

Combining the latest technical developments in solid-state NMR spectroscopy with recently developed pulse techniques, the awaited breakthrough in high-resolution solid-state ^{27}Al NMR of zeolitic acid sites can be achieved. This work utilizes a sufficiently high magnetic field strength ($B_0 = 14.1$ T) and fast magic-angle spinning (27 kHz) in combination with the multiple-quantum (MQ) MAS experiment that allows the separation of isotropic and anisotropic quadrupolar information in two-dimensional spectra of half-integer quadrupolar nuclei.[3] Unfortunately, the efficiency of the pulsed MQMAS experiment depends strongly on the ratio of the quadrupolar frequency and the rf-field strength (ν_Q/ν_1).[3] Using an rf-field strength of 270 kHz, Alemany et al.[4] could observe the Al-resonance with $C_{qcc} = 15.3$ MHz in the mineral andalusite, albeit with very weak intensity and distorted line shape. The recently developed double-frequency sweep (DFS) method improves the multiple- to single-quantum conversion substantially.[5] Using this method the andalusite could readily be detected with an undistorted line shape using significantly less rf power.[5b] Figure 2 clearly demonstrates that different aluminum environments in activated zeolite catalysts, such as dehydrated H-ZSM5, can be studied using DFS-enhanced ^{27}Al MQMAS spectroscopy at high field and fast spinning. A well-resolved spectrum is obtained, allowing the distinction of three different Al resonances with a hint of a fourth one.

In MQMAS spectra, after appropriate shearing, the F_1 projection consists of isotropic lines, with their respective anisotropic quadrupolar features in the F_2-dimension. The position of the center of gravity of these F_2 slices is identical to the position of the center of gravity in a normal MAS spectrum, given by the sum of the isotropic chemical shift and the quadrupolar induced shift, $\delta = \delta_{iso} + \delta_{qis}$. Scaling the F_1 sweep width by a factor $^{12}/_{17}$ (for $I = {}^5/_2$) after shearing, the position of the lines in the F_1 dimension is given by $\delta = \delta_{iso} - ({}^{10}/_{17})\delta_{qis}$.[6] This allows us to extract δ_{iso} and the quadrupolar interaction product $P_Q = C_{qcc}(1 + (\eta_Q^2)/3)^{1/2}$ from the spectra and assign the lines. The

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(1) (a) Pfeifer, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3777. (b) Flanigen, E. M. In *Zeolite Chemistry and Catalysis*; American Chemical Society Monograph 171; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1976.
(2) (a) Ernst, H.; Freude, D.; Wolf, I. *Chem. Phys. Lett.* **1993**, *212*, 588. (b) Freude, D.; Ernst, H.; Wolf, I. *Solid State Nucl. Magn. Reson.* **1994**, *3*, 271. (c) Hunger, M.; Horvath, T. *J. Am. Chem. Soc.* **1996**, *118*, 12302.
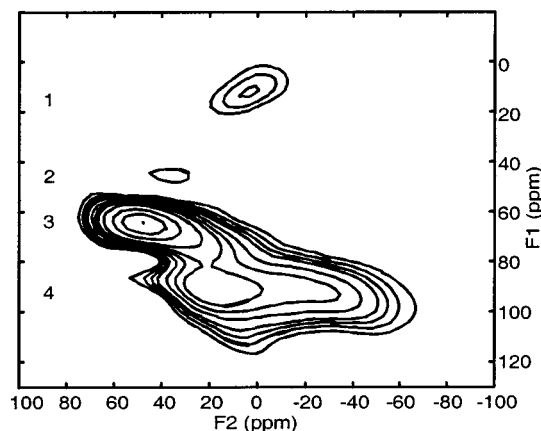(3) (a) Frydman, L.; Harwood, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5367. (b) Medek, A.; Harwood, J. S.; Frydman, L. *J. Am. Chem. Soc.* **1995**, *117*, 12779.
(4) Alemany, L. B.; Steuernagel, S.; Amoureux, J.-P.; Callender, R. L.; Barron, A. R. *Solid State Nucl. Magn. Reson.* **1999**, *14*, 1.
(5) (a) Kentgens, A. P. M.; Verhagen, R. *Chem. Phys. Lett.* **1999**, *300*, 435. (b) Iuga, D.; Schäfer, H.; Verhagen, R.; Kentgens, A. P. M. *J. Magn. Reson.* **2000**, *147*, 192. (c) Schäfer, H.; Iuga, D.; Verhagen, R.; Kentgens, A. P. M. *J. Chem. Phys.* **2001**, *114*, 3073.
(6) (a) Sarv, P.; Wichterlová, B.; Cejka, J. *J. Phys. Chem. B* **1998**, *102*, 1372. (b) Amoureux, J.-P.; Fernandez, C. *Solid State Nucl. Magn. Reson.* **1998**, *10*, 211. (c) Engelhardt, G.; Kentgens, A. P. M.; Koller, H.; Samoson, A. *Solid State Nucl. Magn. Reson.* **1999**, *15*, 171.

Figure 2. ^{27}Al DFS-enhanced 3QMAS spectrum of dehydrated H-ZSM5 obtained at 14.1 T and 27 kHz MAS. An octahedral (1) and two tetrahedral (3,4) lines can clearly be distinguished. There is an indication of a tiny amount of pentacoordinated Al (2). The NMR parameters of the lines are summarized in Table 1.

Table 1. *Average* Isotropic Chemical Shift and Quadrupole Interaction Product and Relative Line Intensities Extracted from the MQMAS Spectrum of Figure 2

line	δ_{iso} (ppm)	P_Q (MHz)	rel. intensity[a] (%)
1	9	4.5	4
2	41	5	<2
3	57	7.3	15
4	55	16.4	79

[a] Corrected for the 3Q excitation and 3Q→1Q DFS-conversion efficiency as calculated with the SIMPSON simulation package.[7]

data determined from the 3QMAS spectrum of Figure 2 are summarized in Table 1.

With the analysis of the spectrum an unambiguous assignment of the resonances is possible. Line 1 clearly belongs to an octahedrally coordinated aluminum, indicating that some dealumination has taken place during the preparation or dehydration process. This would also explain the presence of line 2, attributed to a tiny amount of pentacoordinated aluminum. Although this line is only just above the noise, it was reproduced in two consecutive experiments. The spectrum is dominated by the resonances of two tetrahedral sites with similar chemical shifts but experiencing different quadrupolar interactions. Line 4, experiencing an average $P_Q = 16.4$ MHz and η close to 0, is attributed to the Brønsted acidic site. By taking the 3Q-excitation and the 3Q→1Q conversion efficiency into account, this line represents about 80% of the aluminum. The second tetrahedral line (line 3) with an average $P_Q = 7.3$ MHz is attributed to framework aluminum charge compensated by ions other than H$^+$. Considering the observed dealumination, these ions can be extralattice alumina species, in line with observations in zeolite H-USY,[8] or residual Na$^+$ ions. Finally, H$_3$O$^+$ ions formed due to rehydration can play a role. That, despite precautions, some rehydration takes place becomes clear from inspecting the F_1-projection of the tetrahedral region of two subsequent MQMAS experiments (Figure 3). The intensity of line 3 has increased with respect to the intensity of line 4. This was confirmed by static echo experiments. It should be mentioned that the "narrow" line 3 is still much broader than the tetrahedral resonance in a fully
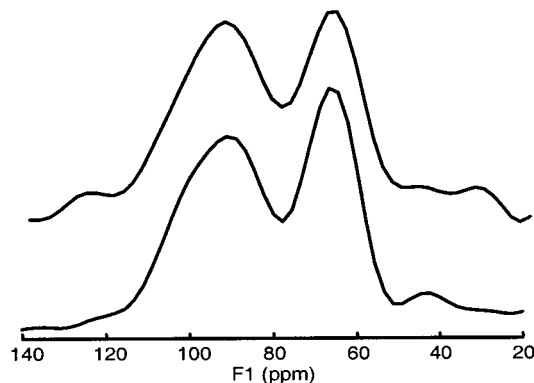

Figure 3. F_1-projection of the tetrahedral region of two subsequent MQMAS spectra of dehydrated H-ZSM5. In the bottom spectrum the effect of rehydration is visible as a relative increase of the narrow (right) line with respect to the broad line attributed to the Brønsted sites.

hydrated H-ZSM5 where the isotropic line width is dominated by a distribution in chemical shift attributed to a variation of the T−O−T angles for the different crystallographic T-sites.[9] As was confirmed by our own observations, this total shift distribution covers a range of approximately 8 ppm. The P_Q-value in hydrated H-ZSM5 amounts to only 1.7 MHz.[9]

The isotropic line width of both tetrahedral resonances is rather broad, a full width at half-height (fwhh) of 14 and 27 ppm is found for line 3 and 4, respectively. An analysis of the individual F_2-slices of the spectrum reveals that this broadening is dominated by a distribution in quadrupolar interaction. For both sites the P_Q-value covers a range of about 4 MHz. For line 3 this distribution is probably due to a variation in counterions, whereas for line 4 it is attributed to the variation in the geometry of the charge distribution for the different crystallographic sites. In fact the analysis of the spectrum hints at a correlation between P_Q and isotropic shift which would support this explanation. Despite the large distribution in quadrupole coupling constant for line 4, its asymmetry parameter is close to zero ($\sim$0.1), without large distribution. This implies a close to cylindrical symmetry for all sites.

The range of isotropic chemical shifts encountered for both sites is of the same magnitude as that found in a fully hydrated sample. It is remarkable to observe that dehydration does not significantly affect the isotropic chemical shift. Apparently, the expected distortions[10] of the Al−O bonds do not affect the isotropic shift. Possibly, the chemical shift anisotropy is affected by these changes.

High-field, DFS-enhanced MQMAS NMR spectroscopy of dehydrated zeolites makes it possible to resolve different framework, including the Brønsted acidic sites, and nonframework aluminum species. It makes detailed information about their chemical shift and local symmetry available. This opens the possibility to study structure−function relationships of activated zeolites which deserve further investigations.

(7) Baks, M.; Rasmussen, T.; Nielsen, N. Chr. *J. Magn. Reson* **2000**, *147*, 296.
(8) van Bokhoven, J. A.; Roest, A. L.; Koningsberger, D. C.; Miller, J. T.; Nachtegaal J. H.; Kentgens, A. P. M. *J. Phys. Chem. B* **2000**, *104*, 6743.

(9) Sarv, P.; Fernandez, C.; Amoureux, J.-P.; Keskinen, K. *J. Phys. Chem.* **1996**, *100*, 19223.
(10) Koller, H.; Meijer, E. L.; van Santen, R. A. *Solid State Nucl. Magn. Reson.* **1997**, *9*, 165.