istence of an "H-bonded" association between adsorbed O_2 and N_2 and the –OH groups of a silica surface; (iii), the recent suggestion[11–16] that a comparable HBB competitive complexation process controls the potency of fluorocarbon

anesthetics; and (iv), the observed effects[17] of H-bonds donors on the glass transition temperature of linear alcohols.

Further work is underway and a longer report will be issued shortly.

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Effect of Hydration on the Local Symmetry around Aluminum in ZSM-5 Zeolites Studied by Aluminum-27 Nuclear Magnetic Resonance

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The effect of hydration and dehydration on the electric field gradient at the ^{27}Al nucleus in ZSM-5 zeolites is investigated by magic angle spinning NMR at three different magnetic field strengths. The experiments show that dehydration causes an increase of the ^{27}Al NMR line width due to an increased quadrupole interaction. The dehydration therefore causes a redistribution of electric charges and/or a conformation change of the aluminum–oxygen tetrahedra. The latter possibility seems to be most important since the effect is cation dependent, as shown by results on Na–ZSM-5 and H–ZSM-5. Similar effects have been observed for faujasite H–Y and amorphous SiO_2/Al_2O_3.

Introduction

Zeolites are crystalline aluminosilicates composed of silicon–oxygen and aluminum–oxygen tetrahedra. The negative charge of the aluminum–oxygen tetrahedra is neutralized by cations like Na^+ or H^+. All zeolites display catalytic activity but especially the class of zeolites denoted by ZSM-5 has received much interest recently due to its unique catalytic properties.[1]

Magic angle spinning proton NMR of H–ZSM-5 showed that at low water content two resonances are present, arising from water molecules chemisorbed at the Bronsted acidic site (Si–OH–Al) and from water molecules adsorbed at silanol groups, the terminating Si–OH groups at the surface of the crystallites.[2] It is believed that water molecules adsorbed at the Bronsted sites form clusters with the acidic proton: $H^+(H_2O)_n$ where n is of the order of 2.[3] Hydration and dehydration of H–ZSM-5 therefore is expected to slightly alter the position of the H^+ proton and consequently change the conformation of and the charge distribution around the aluminum–oxygen tetrahedron.

Aluminum has a nuclear spin $^5/_2$ and therefore a nuclear quadrupole moment which can interact with an electric field gradient at the site of the nucleus caused by surrounding ions. For a perfect tetrahedral surrounding of

aluminum by four oxygens, the electric field gradient is zero. Any distortion of this tetrahedron, however, should cause a field gradient at aluminum and consequently a quadrupole interaction of the aluminum nuclear spin.

In this letter we report results from magic angle spinning NMR of aluminum in Na–ZSM-5 and H–ZSM-5 which show unambiguously that hydration and dehydration affect the conformation of the aluminum–oxygen tetrahedra. Similar experiments on amorphous SiO_2/Al_2O_3 and faujasite H–Y show the same phenomenon, except that for aluminum in octahedral sites, present in amorphous SiO_2/Al_2O_3, hydration or dehydration has no detectable effect on the field gradient at the aluminum nucleus.

Experimental Section

The Na–ZSM-5 (Si/Al ratio 40) and H–ZSM-5 (Si/Al ratio 15) were donated by DSM, Geleen; faujasite H–Y (Si/Al ratio 2.5) and the amorphous SiO_2/Al_2O_3 (HA HPV, Si/Al ratio 2.4) are commercial samples from Union Carbide and AKZO Nederland, respectively. Dehydration of the samples was achieved by vacuum drying (10^{-2} torr) at temperatures between 200 and 400 °C ("shallow-bed" treatment). To prevent rehydration, spinners are filled under an anhydrous nitrogen gas atmosphere in a glovebox. ^{1}H NMR measurements[2b] revealed that rehydration through the spinner walls during the experiment is negligible. Hydration was performed at room temperature by exposing the material in a closed system to a small container with water.

The magic angle spinning aluminum NMR experiments were carried out by straightforward 90°-pulse excitation in three different spectrometers: a Bruker CXP 300 (ν_{Al} = 78.2 MHz; 90° pulse duration, 5 μs; repetition time, 0.2

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s), a home-built 180-MHz spectrometer (ν_{Al} = 46.9 MHz; 90° pulse duration, 8 μs; repetition time, 0.5 s), and a home-built 60-MHz spectrometer (ν_{Al} = 15.6 MHz; 90° pulse duration, 8 μs; repetition time, 0.5 s). The repetition times give full relaxation because T_1 values are of the order of 10 ms. For all three spectrometers the same spinner was used, a cylindrical Delrin spinner supported by two air bearings.[4] A spinning frequency of ~3 kHz proved to be sufficient.

Magic Angle Spinning NMR of a Quadrupolar Nucleus

Aluminum nuclear spins in an aluminosilicate are subjected to three anisotropic inteactions: dipolar interactions with neighboring nuclei like ^{1}H and ^{29}Si, interaction of the nuclear quadrupole moment with electric field gradients, and the anisotropic chemical shift interaction. Of these three interactions the quadrupole interaction will prove to be the most important for our experiments. A discussion of the effect of magic angle spinning on the NMR spectra of quadrupolar nuclei can be found at several places in the literature.[5] Here we want to mention only the outcome of these theories.

For half-integer nuclear spins like ^{27}Al, the anisotropic quadrupole interaction causes a severe line broadening in solid-state NMR spectra, except for the $m = \frac{1}{2} \leftrightarrow m = -\frac{1}{2}$ transition if the quadrupole interaction is small compared to the Zeeman interaction of the nuclear spin. It is easy to show that for this $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition the quadrupole interaction contributes only in second- and higher-order perturbation theory.[6] In practice, therefore, only this transition is observed in solid samples, showing a characteristic powder pattern depending on the value of the asymmetry parameter η;[7] magic angle spinning reduces but does not eliminate the width of this powder pattern. A formula for the frequency of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition under fast magic angle spinning conditions has been derived by Kundla et al.[5b] and can be rewritten as

$$\nu_{1/2,-1/2} = \nu_z - \frac{1}{16}\frac{\nu_Q^2}{\nu_z}\left\{I(I+1) - \frac{3}{4}\right\}\{A(\alpha)\cos^4\beta + B(\alpha)\cos^2\beta + C(\alpha)\} \tag{1}$$

where

$$\nu_z = -\gamma B_0(1 - \sigma_i)/2\pi$$

$$\nu_Q = 3e^2qQ/\{2I(2I - 1)h\}$$

$$A(\alpha) = \frac{7}{2} - \frac{7}{3}\eta\cos 2\alpha + (7/18)\eta^2\cos^2 2\alpha$$

$$B(\alpha) = -3 + \frac{2}{9}\eta^2 + \frac{8}{3}\eta\cos 2\alpha - \frac{7}{9}\eta^2\cos^2 2\alpha$$

$$C(\alpha) = \frac{5}{6} - \frac{1}{3}\eta\cos 2\alpha + (7/18)\eta^2\cos^2 2\alpha$$

and α and β are the polar angles of the spinning axis with respect to the principal axes of the quadrupole tensor.

Singular points and discontinuities in the powder pattern are found when $\partial\nu_{1/2,-1/2}/\partial\alpha = \partial\nu_{1/2,-1/2}/\partial\beta = 0$. Figure
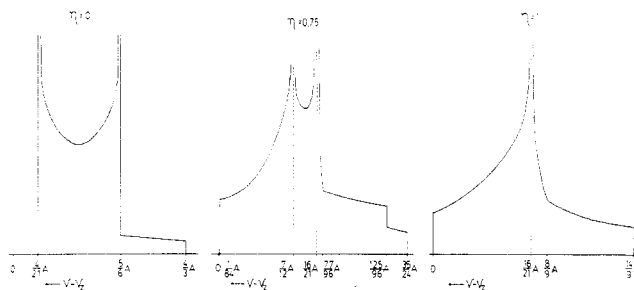
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Figure 1. Theoretical line shape of $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition of quadrupolar nuclear spin in a powder with fast magic angle spinning for different values of the asymmetry parameter η; $A = -(1/16)(\nu_Q^2/\nu_z)\{I(I + 1) - \frac{3}{4}\}$.
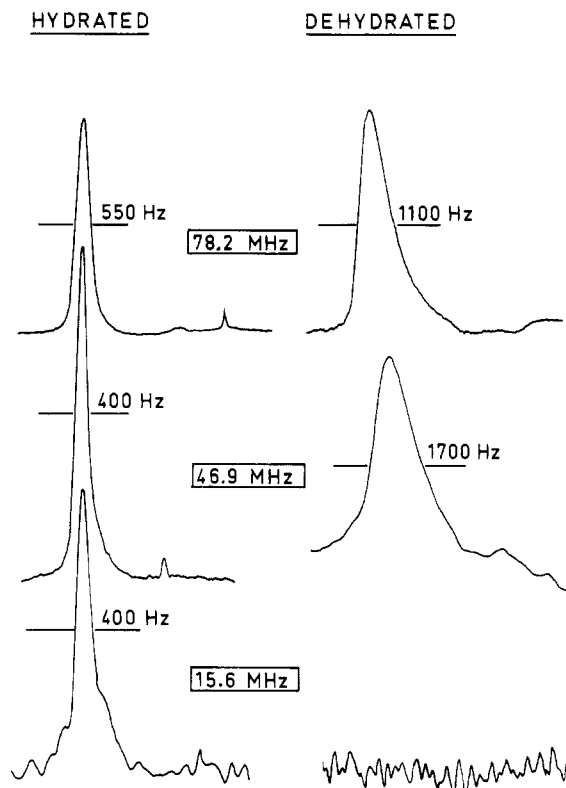

Figure 2. ^{27}Al spectra of H–ZSM-5 at three different magnetic fields at 78.2, 46.9, and 15.6 MHz with 3-kHz magic angle spinning. All spectra are obtained at room temperature. The hydrated spectra are the result of 10 000 (at 78.2 MHz), 130 000 (at 46.9 MHz), and 350 000 (at 15.6 MHz) fid's. The spectra of the dehydrated material needed 250 000 (at 78.2 MHz) and 180 000 (at 46.9 MHz) fid's. At 15.6 MHz no signal was obtained of the dehydrated material after 750 000 fid's.

1 shows the pattern for $\eta = 0$, $\eta = 0.75$, and $\eta = 1$. Equation 1 shows in addition that the width of powder pattern decreases with magnetic field. Therefore, when in an experimental situation it is found that the line width of a line decreases with field, then this points to the existence of quadrupole broadening. This is in contrast to a broadening due to a distribution of chemical shifts, a common source of line broadening in magic angle spinning NMR, which increases with field.
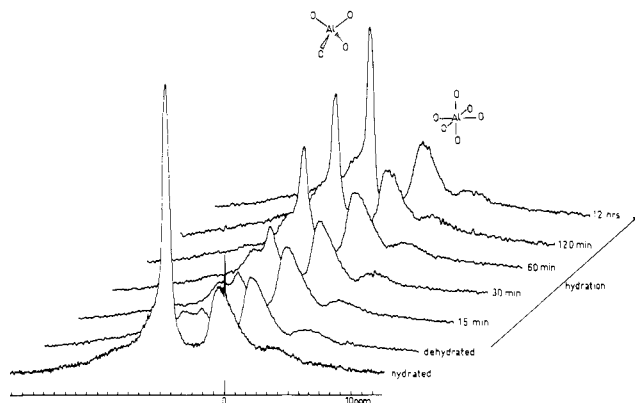
Results and Discussion

Figure 2 shows ^{27}Al spectra of H–ZSM-5 at three different frequencies for the hydrated and dehydrated form. For the hydrated samples the line width first decreases from 550 Hz at 78.2 MHz to 400 Hz at 46.9 MHz and then remains constant at 15.6 MHz. The initial decrease of this line width with field shows that for the hydrated samples quadrupole broadening is certainly not the most important factor determining the line width at 78.2 MHz. As the

Figure 3. ^{27}Al spectra of Na–ZSM-5 as a function of water content at 78.2 MHz. All spectra represent 25 000 fid's and are obtained with 3-kHz magic angle spinning.

Figure 4. ^{27}Al spectra of amorphous SiO_2/Al_2O_3 at 78.2 MHz with 3-kHz magic angle spinning. The spectrum of the hydrated form represents 25 000 fid's, and that of the dehydrated form 50 000 fid's.

chemical shift anisotropy is eliminated by magic angle spinning, the initial decrease of the line width has to be due to the fact that the line width is caused by a distribution of ^{27}Al chemical shifts. Only at the lowest fields, where the chemical shift distribution in frequency units is small, does the quadrupole broadening become important. At frequencies below 15 MHz the line width is expected to increase again.

For the dehydrated samples, however, the situation is very different. Figure 2 shows that the line width increases from 1100 Hz at 78.2 MHz to 1700 Hz at 46.9 MHz to undetectably broad at 15.6 MHz. Dehydration clearly makes the ^{27}Al line broader, by a factor 2 at 78.2 MHz, by a factor 4 at 46.9 MHz, and by a much larger factor at 15.6 MHz. The field dependence of the line width shows that quadrupole interaction is the dominant factor determining the line width in the dehydrated samples. Clearly, dehydration causes a strong increase of the quadrupole interaction.

By comparing the experimental line shapes to the theoretical shapes of Figure 1, one can conclude that the resulting electric field gradient at aluminum is highly asymmetric (no separate quadrupole pairs are observed). At this point we should mention that proton decoupling during acquisition of the Al free induction decay does not affect the Al NMR line width, not in the hydrated case nor in the dehydrated situation. Dipolar interaction between protons and Al apparently is so weak that it can be eliminated by magic angle spinning alone.

Figure 3 displays ^{27}Al spectra of Na–ZSM-5 as a function of the water content. These spectra show not only a line at 53 ppm but in addition lines at 65, 5, and –1 ppm (relative to $Al(H_2O)_6^{3+}$). The aluminum coordination can be determined on the basis of these chemical shift data.[8] The line at 53 ppm of four-coordinated Al is attributed to Al in the ZSM-5 lattice. The narrow line at –1 ppm originates from six-coordinated Al, presumably $Al(H_2O)_6^{3+}$ in the pores. The broader lines at 65 and 5 ppm, from four- and six-coordinated aluminum, must be due to an impurity or lattice defects. Because of the resemblance of these lines with spectra of Al_2O_3[9] this might be an aluminum oxide impurity. X-ray analysis of this sample, however, did not reveal any impurity, presumably because the disordered regions are very small. Recently the existence of Al-rich non-zeolite material, which could not be detected by X-ray
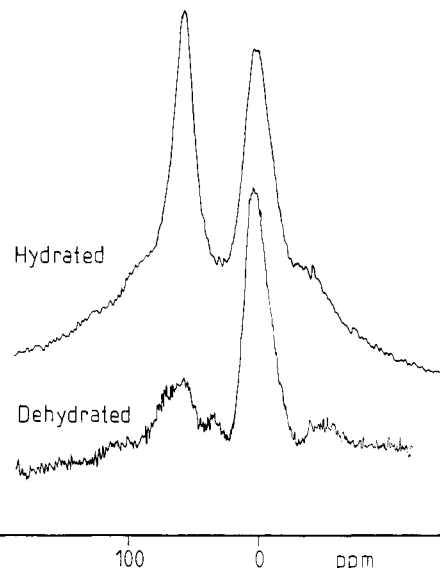
diffraction, is also reported by Hughes et al.[10]

When the sample is dried at 250 °C, the tetrahedral Al line at 53 ppm collapses; hydration for a variable length of time makes this line slowly appear again. In the dehydrated sample, evidently, the quadrupole interaction becomes so strong that the tetrahedral Al line of the genuine ZSM-5 aluminum becomes too broad to be detectable, even at 78.2 MHz. Apparently, the increase of quadrupole interaction on dehydration is much stronger for Na–ZSM-5 than for H–ZSM-5. Dehydration of the Na–ZSM-5 sample has no effect on the broad lines at 5 and 65 ppm; the narrow line at –1 ppm disappears and does not come back at hydration.

The same experiments were carried out on faujasite H–Y and amorphous SiO_2/Al_2O_3. For faujasite H–Y the situation is just the reverse of that for ZSM-5: the Al line width of the hydrated sample *increases* on going to the lower frequency (750 Hz at 78.2 MHz, 1350 Hz at 46.9 MHz). Apparently, even in the hydrated form there is already a considerable broadening due to quadrupole interaction, showing the existence of distorted tetrahedra. This distortion may be inherent to the structure which is different from H–ZSM-5, and possibly due to the presence of aluminum in higher coordination spheres (faujasite H–Y has a Si–Al ratio of 2.5!). On dehydration the faujasite H–Y Al line width at 78.2 MHz increases to 1800 Hz, showing a considerable extra distortion around aluminum.

Figure 4 shows the ^{27}Al spectrum of amorphous SiO_2/Al_2O_3 at 78.2 MHz for hydrated and dehydrated material. Only the peak at ~52 ppm from tetrahedrally surrounded aluminum broadens on dehydration, indicating that strong chemisorption of water takes place only at the tetrahedral sites, not at octahedrally coordinated aluminum.

As a conclusion of this work we can then state that in both Na–ZSM-5 and H–ZSM-5 dehydration causes a lowering of local symmetry around aluminum as evidenced by the increase in quadrupole interaction of aluminum. This increase is cation dependent. Similar effects are observed in faujasite H–Y and amorphous SiO_2/Al_2O_3. On the crucial question of what precisely causes this lowering of local symmetry, we can at this moment only speculate. As mentioned in the Introduction it is believed that in

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hydrated material the cation forms a cluster with water molecules. On dehydration the cation presumably comes nearer to aluminum. This causes a change in the distribution of charges around aluminum and possibly a distortion of the aluminum–oxygen tetrahedra. Both effects, the change in charge distribution and distortion of the tetrahedron, can give rise to an increase electric field gradient at the aluminum nucleus. However, from the observation that the increase in quadrupole interaction on dehydration is stronger for Na–ZSM-5 than for H–ZSM-5, we tend to believe that the distortion of the tetrahedra is more important for the increased electric field gradient than the redistribution of charges, although of course the latter effect may induce the local distortions.

In the case of dehydrated H–ZSM-5 it is often indicated that the H$^+$ ion exists in a Al–O$^-$H$^+$ band. For a perfect tetrahedron with an Al–O distance of 1.59 Å and an O–H distance of 1 Å, the dipolar interaction between Al and H would give rise to a broadening of the Al NMR line of 2300 Hz. Such a broadening, however, is not observed, suggesting either that the Al–H$^+$ distance is much larger or that the H$^+$ ion is mobile.

Finally, we want to comment on the statement made earlier in this paragraph that in hydrated H–ZSM-5 the ^{27}Al line width is caused by a distribution of ^{27}Al chemical shifts. Preliminary ^{27}Al spin–lattice relaxation (T_1) experiments clearly reveal several species with distinct T_1 values and distinct chemical shift. Further investigations are needed to establish the origin of these different ^{27}Al sites which together form the line shapes discussed in this paper.

Exponential Fluorescence Decay from Single Rovibrational Levels of S₁ Acetaldehyde

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Single rotational level S$_1$ emission has been observed for jet-cooled acetaldehyde and α-monodeuterated acetaldehyde. All the levels studied (up to E_{vib} = 1760 cm^{-1}) yielded single exponential decays, the vibronic origin being the longest-lived levels (CH$_3$CHO, 220 ns; CH$_3$CDO, 1.52 μs). The data are correlated with previous room temperature studies.

Introduction

Acetaldehyde is a molecule of atmospheric significance[1] as well as a possible model for the photochemical and kinetic behavior of larger aldehydes.[2] Because it is a seven-atom molecule with 15 vibrational degrees of freedom and small rotational constants ($A'' = 1.8870$, $B'' = 0.3387$, $C'' = 0.3033$ cm^{-1}),[3] the room temperature electronic spectrum is too congested to obtain detailed rovibrational information. In spite of this congestion, the weak nature of the S$_1$ ← S$_0$ transition, and the less than unity quantum yield for fluorescence, several attempts have been made to study its S$_1$ dynamics by absorption and emission spectroscopic measurements.[2,4,5]

A recently reported experiment by Speiser et al. is the closest to a single vibrational level collision-free study.[6] In this experiment an unnarrowed frequency doubled dye laser (fwhm > 1 cm^{-1}) was used to excite low-pressure (≥ 25 mtorr) acetaldehyde vapor at 320 nm. This wavelength was arbitrarily chosen to lie below the predissociative threshold (≥31 250 cm^{-1}).[7] These authors reported the first observance of biexponential decay for S$_1$ acetaldehyde

(at 25 mtorr: $\tau_{fast} \sim 29$ ns, τ_{slow} 94 ns) and estimated the fluorescence quantum yield as 7.5×10^{-2}, whereas a prior study[2] in our laboratory found the longest lifetime at 10 torr to be 3.7 ns at 325 nm. The biexponential decay observed by Speiser et al. was found to be pressure dependent: the slow component was preferentially quenched upto 400 mtorr (self-quenching rate coefficient: 6.7×10^7 torr^{-1} s^{-1}) at which pressure the decay appeared single exponential. Above 400 mtorr the decay continued to be self-quenched at the same rate. The authors attributed this overall behavior to the process of rapid reversible intersystem crossing followed by internal conversion. This is a model which has been introduced and used to explain the same behavior in α-dicarbonyls by Kommandeur and co-workers.[8]

As part of our overall studies into the dynamics of small molecules in electronically excited states, we have observed the laser-induced fluorescence decay from single rovibrational levels of S$_1$ acetaldehyde and α-monodeuterated acetaldehyde. The assignment of these levels was known from our acetaldehyde (CH$_3$CDO) rovibronic analysis of the π* ← n transition of acetaldehyde and its deuterated derivatives.[9,10] The fluorescence lifetimes of these levels show interesting mode specificity and energy dependence which will be reported in detail elsewhere.[10] We report

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