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Adsorption of water by H-ZSM-5 zeolite studied by magic angle spinning proton n.m.r.

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It is shown that magic angle spinning considerably narrows the ^1H n.m.r. lines in zeolite H-ZSM-5. With this technique two n.m.r. lines are observed due to protons in either H_2O molecules around silanol groups and Brønsted acidic sites or structural $-\text{OH}$ groups at these sites. The desorption and adsorption behaviour of water at these sites are studied for samples with different Si/Al ratios and ion-exchange treatments.

Keywords: Adsorption; H-ZSM-5; MAS n.m.r.; solid state n.m.r.; proton n.m.r.

INTRODUCTION

Protons play an important role in the catalytic activity of crystalline zeolites, both in the structural hydroxyl groups and in physically or chemically adsorbed water¹. Due to their nuclear spin $I = 1/2$, protons can be conveniently detected by n.m.r. Chemically different protons give rise to separate n.m.r. lines if the chemical shift differences exceed the linewidth of the individual lines. In solids, usually, the line broadening by anisotropic interactions like dipolar interaction and chemical shift anisotropy, is so severe that a single, broad proton n.m.r. line is observed.

Here we want to report that magic angle spinning² of H-ZSM-5 samples reduces the proton n.m.r. line so much that two separate proton lines can be observed. The intensity of the two proton lines then is measured as a function of dehydration and hydration of H-ZSM-5 at different temperatures.

METHODS

Preparation of samples

Synthesis of zeolites normally takes place from strongly alkaline silicate and aluminate containing solutions. As described in the patent literature³ use of tetrapropylammoniumhydroxide as the main basic compound will lead to the formation of ZSM-5 type zeolites. We used this method to prepare three zeolite ZSM-5 samples with different Si/Al ratios, indicated as: EX3(Si/Al = 11), DX2- (Si/Al = 29) and KY(Si/Al = 75).

The hydrogen form of these samples was obtained either by a direct ion-exchange method, using a 1 M HCl solution (sample DX) or by an indirect method consisting of ion-exchange with a 1 M NH_4NO_3 solution followed by a thermal decomposition of the NH_4^+ ions into H^+ and $\text{NH}_3(\text{g})$ (samples EX and KY). X-ray diffraction showed that all zeolite samples are highly crystalline and exhibit the typical diffraction pattern of zeolite ZSM-5.

Chemical analyses of Na (and K), Si and Al were performed by conventional methods and lead to the following chemical formulae of a unit cell of the different samples, assuming that there are 96 (Al + Si) atoms per unit cell (*Table 1*). The magic angle spinners are filled under an anhydrous nitrogen gas atmosphere in a glove box.

Procedures of dehydration and hydration

Dehydration of the powdered samples was effected by means of vacuum pumping at 200°C or by a helium flow at 350°C in a pyrex tube. Hydration of the samples was performed at room temperature in an evacuated pyrex tube having a constant water

Table 1 Composition of samples

Sample	Si/Al ratio	Chemical formulae of unit cell			
		H	Na/K	AlO_2	SiO_2
EX3	11	6	2	8	88
DX2	29	1.6	1.6	3.2	92.8
KY	75	1.3		1.3	94.7

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vapour pressure because of an ampoule with water connected to the tube.

N.m.r. technique

The n.m.r. spectra are taken on a home-built 180 MHz FT spectrometer. The samples can be spun around the magic angle at frequencies up to 4 kHz in a cylindrical, double air-bearing KEL-F spinner⁴. Straightforward 90° pulse excitation is used while the receiver functions in the quadrature detection mode.

RESULTS AND DISCUSSION

Figures 1-3 show the proton MAS n.m.r. spectra for three H-ZSM-5 samples, denoted: EX3(Si/Al = 11), DX2(Si/Al = 29) and KY(Si/Al = 75), as a function of dehydration and subsequent hydration.

Figure 1 The ¹H MAS n.m.r. spectra of sample EX3 at different stages of hydration. Spectrum 1, untreated, gain = 1. Spectrum 2, vacuum dried at 200°C for 18½ h, gain = 8. Spectrum 3, idem for 33 h, gain = 10. Spectrum 4, material of spectrum 3 contacted for 15 min to water vapour at room temperature, gain = 9. Spectrum 5, idem for 30 min, gain = 7. Spectrum 6, idem for 90 min, gain = 4. Spectrum 7, idem for 210 min, gain = 3

Figure 2 The ¹H MAS n.m.r. spectra of sample DX2 at different stages of hydration. Spectrum 1, untreated, gain = 1. Spectrum 2, vacuum dried at 200°C for 66 h, gain = 5.5. Spectrum 3, idem for 83 h, gain = 6. Spectrum 4, material of spectrum 3 into contact with water vapour for 15 min, gain = 3. Spectrum 5, idem for 45 min, gain = 1.5. Spectrum 6, idem for 20 h, gain = 0.5

Figure 3 The ¹H MAS n.m.r. spectra of sample KY at different stages of hydration. Spectrum 1, untreated, gain = 1. Spectrum 2, dried with He at 350°C for 19 h, gain = 20. Spectrum 3, idem for 23½ h, gain = 23. Spectrum 4, material of spectrum 3 left in magic angle spinner for 2 days at room temperature, gain = 13. Spectrum 5, idem for 21 days, gain = 6

For all untreated samples, which were supposed to be saturated with water, only one line is found, right at the position of the proton resonance of free H₂O. This line clearly is due to physisorbed water, because drying the sample at 200° or 350°C causes this line to disappear and two, much weaker lines remain, one at lower field (high ppm value) and the other at a higher field than the free H₂O resonance. Infrared studies⁵ also have shown that dehydration starts with a rapid initial loss of physisorbed water, already at 150°C. Further dehydration of our samples always results in the same two line n.m.r. spectrum except that the relative line intensities change.

Before discussing these line intensity changes, let us first look into the assignment of the spectra. With a 310 Dupont Curve Resolver the spectra were decomposed into component Lorentzian lines. It appeared that a much better fit was found when simulating the spectra with three lines instead of two lines. The third line is much broader than the other two and its presence can be inferred directly from most of the spectra in Figures 1-3.

The two relatively narrow components have unequal intensity. For the maximally dried samples the low field component in the spectrum of EX3 (Si/Al = 11) is much stronger than the high field line, while they have about the same intensity for the samples with the higher Si/Al ratios. This seems to suggest that the low-field n.m.r. lines are due to protons around Al sites (Brønsted-acidic sites), either in water molecules or in OH groups. The high field lines must then belong to silanol groups, ≡SiOH, and/or water molecules around them. Also, protons at the Brønsted sites are expected to be more acidic than at Si sites and therefore should resonate at a lower field.

We tried to confirm this conclusion by determining the spectrum of Silicalite, a material with a similar structure to H-ZSM-5 but without aluminium. Figure 4 shows the MAS proton spectrum of Silicalite, untreated and after extensive drying. For comparison, Figure 4 also shows the corresponding spectrum of KY H-ZSM-5. In the spectrum of the untreated Silicalite a relatively broad line is found at about the free H₂O resonance which disappears on drying. Further, the untreated sample shows a high-field line at the same position as the high-field line in KY. Upon drying, this high-field line in Silicalite does not disappear but doubles. Also the dehydrated Silicalite shows a broad line centred at around -4 ppm. Apparently, the situation in Silicalite is much more complicated than in H-ZSM-5. However, for the present discussion it is important to note that in Silicalite no low-field line like that in the H-ZSM-5 samples is found. So, at least the assignment of this low-field line to protons at the Al sites is not contradicted by the Silicalite experiment.

The assignment of the third, very broad component in the H-ZSM-5 spectra is more difficult. Several causes for the existence of such a broad line can be mentioned. The presence of unpaired electron spins in the H-ZSM-5 samples (*vide infra*) may cause a broadening of the n.m.r. line of some of the proton spins. Also the dipolar interaction

Figure 4 The ¹H MAS n.m.r. spectra of untreated silicalite (relative spectrometer gain = 1), dried silicalite (80 h at 350°C, gain = 9.5) and dried KY (23½ h)

Figure 5 The integrated relative intensities of the low field, (○), high field (●), and broad line, (△), of sample EX3 as a function of drying and wetting time

between some of the nuclear spins (¹H-¹H, ¹H-²⁷Al) may not be averaged out completely by magic angle spinning.

On the other hand, magic angle spinning is essential for revealing the two-line spectrum, a stationary sample shows a broad (~3 kHz) structureless line. However, also for the two relatively narrow component lines magic angle spinning has not been as effective as one could have hoped for. A very trivial cause for the rather large linewidth may be the distribution of chemical shifts for clusters of molecules around the silanol groups and Brønsted acidic sites.

Another possible explanation which has to be mentioned, is the existence of unpaired electrons in our samples, as evidenced by e.s.r. signals, both at room temperature and at helium temperatures. These unpaired electrons seem to be responsible for the very fast, non-exponential proton spin-lattice relaxation (*T*₁ ~ 5 ms for the untreated sample and ~ 30 ms for the dehydrated sample).

Unpaired electrons are very efficient relaxation sources for proton spins surrounding the electrons. Proton spin and/or H₂O molecular diffusion takes care of the contact with proton spins farther removed from the unpaired electrons spins⁶. On dehydration H₂O molecules are removed and spin and/or molecular diffusion becomes less effective, making the average proton T_1 longer. Further experimental work has to be done to discriminate between the above-mentioned inhomogeneous or homogeneous sources for the line broadening.

On returning to Figures 1-3, we see that for all samples the relative intensities of the two n.m.r. lines are different at different stages in the dehydration or hydration process. A careful quantitative study therefore can clarify the kinetics of the water adsorption at these two sites in the H-ZSM-5 zeolite. Here we want to present a qualitative study only.

Figures 5-7 show the dependence of the integrated intensity of the above-mentioned three com-

Figure 6 The integrated relative intensities of the low field, (○), high field, (●), and broad line, (△), of sample DX2 as a function of drying and wetting time

Figure 7 The integrated relative intensities of the low field, (○), high field, (●), and broad line, (△), of sample KY as a function of drying and wetting time

ponents on dehydration and hydration. The broad component is denoted by a triangle, the low-field line by open circles and the high-field line by filled circles. The intensities are expressed as percentages of the integrated line intensity of the single line of the untreated, fully hydrated samples. So, after dehydration only a few percent of the protons are left. On bringing the samples into contact with water vapour at room temperature, all three components increase again in intensity. We never reached the point, however, where only one line was found again. This in spite of the fact that in the DX2 sample after 20 h of contact to the water vapour, the sum of the integrated intensity of the three components far exceeds 100%, i.e. more water is present than in the untreated sample.

The treatment of the KY sample during hydration was different from that of the DX2 and EX3 samples. The sample was kept in the KEL-F spinner all the time and water could only enter

through the spinner walls. The KY sample therefore did not absorb as much water as the two other samples.

It appears from *Figures 5–7* that upon drying the samples the integrated intensity of the silanol groups is lower than the intensity of the Brønsted acidic sites and that upon hydration the silanol group intensity of the samples EX3 and KY approaches an equilibrium value; in contrast to the Brønsted acidic sites and the silanol groups in DX2 which still seem to increase.

A possible explanation for this phenomena is the fact that in the EX3 and KY samples silanol groups are present only at the outer surface of the crystal and that in DX2 as caused by the HCl treatment silanol groups (apart from those at the surface) are generated in the pores⁷.

CONCLUSIONS

Magic angle spinning proton n.m.r. is a useful technique for the study of water adsorption by zeolites. In H-ZSM-5 two adsorbing sites can be observed by their difference in proton chemical shift. The low-field resonance is assigned to protons at Si-OH-Al sites, the high-field resonance

at $\equiv\text{SiOH}$ sites. By monitoring the line intensities as a function of dehydration or hydration the kinetics of water adsorption at these two sites can be followed. H-ZSM-5 samples with different Si/Al ratios and ion-exchange treatment behave differently on adsorption of water at Brønsted acidic sites and silanol groups.

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