

$^1\text{H}\{^{27}\text{Al}\}$ Double-Resonance Experiments in Solids: An Unexpected Observation in the ^1H MAS Spectrum of Zeolite HZSM-5,

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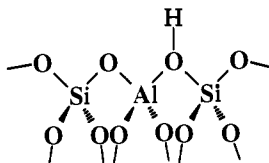
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Abstract: We report the existence of a previously unsuspected peak in the ^1H magic angle spinning spectrum of commercially available HZSM-5 samples. At 298 K, this resonance is a broad shoulder on the downfield side of the Brønsted acid signal at 4.3 ppm. Cooling the sample caused the line to narrow, and a clear peak at 6.9 ppm was visible at 123 K. As a first step in the assignment of this resonance, we report the results of several $^1\text{H}\{^{27}\text{Al}\}$ double-resonance experiments in the context of the broad ^{27}Al resonance of the dehydrated zeolite. Reverse cross polarization ($^{27}\text{Al} \rightarrow ^1\text{H}$) failed as an assignment technique, but a related indirect detection experiment in which ^1H transverse magnetization was drained to ^{27}Al performed marginally better. A more successful experiment resembled ^1H observation with ^{27}Al decoupling; we call this experiment "quadrupole tickling", because the ^{27}Al irradiation was insufficient for true decoupling. This technique resulted in selective broadening of the 4.3 and 6.9 ppm resonances as a result of conflicting averaging of the $^1\text{H}\text{-}^{27}\text{Al}$ dipolar coupling. The silanol resonance was unaffected by this procedure, as expected for a proton environment remote from ^{27}Al . Quadrupole tickling is shown to be related to a previously described spin-echo double resonance experiment. ^1H 2D experiments were carried out on HZSM-5 with a variety of temperatures and mixing times. These show that site exchange between the 6.9 and 4.3 ppm resonances is negligible on the time scale of the double resonance experiments, but exchange occurs to a measurable extent at 250 ms. We conclude that the 6.9 ppm resonance corresponds to a novel aluminum-containing site in zeolite HZSM-5 and is not an artifact due to exchange with the Brønsted site or an aluminum-rich impurity phase. A possible interpretation of these results is a second Brønsted site for the zeolite.

Introduction

The structure and function of Brønsted sites in zeolites and other solid acids are of great interest. These sites are generally believed to be best understood for zeolite HZSM-5, for which the low site density and crystallinity generate a narrower range of structures than might be found for other materials. The overall evidence from a number of experimental^{1,2} and theoretical studies³⁻⁵ is that the local structure of the site is a hydroxyl bridging aluminum and silicon atoms in the zeolite framework (1).



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One of the spectroscopic techniques most commonly applied to the study of $1^6\text{-}8$ and its interaction with adsorbates^{9,10} is ^1H

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NMR with magic angle spinning (MAS). The ^1H MAS spectrum of HZSM-5 is usually reported to have two peaks: a resonance at 4.3 ppm attributed to the acid site, 1, and a peak at 2.0 ppm due to silanol groups terminating crystallite surfaces or at defects.¹¹⁻¹⁴ ^1H MAS spectra of all solid acids are characterized by narrow chemical shift ranges and relatively broad lines. The assignment of solid acid spectra is challenging for materials with nonequivalent Brønsted sites,¹⁵ extra-framework Al-OH groups,^{16,17} or residual NH_4^+ ,¹⁸ templates, or adsorbates.¹⁰

We report the existence of a third peak in the ^1H spectrum of commercially available HZSM-5 samples. This resonance is visible as a poorly resolved shoulder in many previously published ^1H MAS spectra of the zeolite.¹¹⁻¹⁴ This shoulder sharpens into a clearly resolved peak at 6.9 ppm when the temperature is reduced to 123 K.

Since aluminum is associated with most of the chemically active sites imaginable in a zeolite, the single most important piece of assignment information in a ^1H MAS spectrum is establishing correlation with ^{27}Al . The secondary focus of this paper is to develop and compare various $^1\text{H}\{^{27}\text{Al}\}$ double-resonance experi-

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ments for this purpose. Cross polarization¹⁹ and reverse cross polarization²⁰ are shown to fail due to the difficulty of maintaining an effective spin lock of the very broad ²⁷Al resonance typical of dehydrated zeolites. Slightly better performance was achieved with use of a Hartmann–Hahn match to drain magnetization from the ¹H reservoir followed by ¹H observation in a difference mode. Far better results were obtained by weak irradiation of the ²⁷Al transitions during ¹H observation. This “quadrupole tickling” experiment selectively broadens the ¹H resonances of spins dipolar coupled to ²⁷Al ($I = 5/2$) as a result of conflicting averaging mechanisms. This broadening is homogeneous as shown by extending it to spin–echo experiments analogous to those used by Veeman²¹ and Fyfe²² in previous investigations of dipolar couplings.

The 6.9 ppm resonance is shown to be due to a proton in close proximity to an aluminum, so it appears likely that this feature is chemically significant. The observation of weak cross peaks due to magnetic site exchange in 2D ¹H spectra of HZSM-5 at 123 K suggests that this feature does not arise from a separate, macroscopic phase, but rather sites close to some of the 4.3 ppm acid sites. The detailed characterization of this site is deferred to a future investigation, but the most likely assignment based on indirect evidence is a second type of Brønsted site.

Experimental Section

Sample Preparation. The ZSM-5 sample used in this study was obtained from UOP Corp. It was received in the protonated form and had been previously calcined. Residual carbon and nitrogen analysis showed only trace amounts of both, proving most of the templating agent had been removed. Elemental analysis gave a silicon-to-aluminum ratio of 19; this result was confirmed by ²⁹Si MAS experiments in our laboratory (results not shown).

All zeolite samples were rigorously dehydrated under vacuum by a standard heating protocol over a period of 12 h²³ to an ultimate temperature of 673 K and a nominal pressure reading of 10⁻⁵ Torr in the vacuum line. After the samples were activated they were transferred to a drybox and packed into glass rotor inserts that were returned to the vacuum line and flame sealed by a procedure reported earlier.²⁴

NMR Spectroscopy. All the NMR spectra shown were obtained at 7.05 T on a Chemagnetics CMX-300 spectrometer, although spectra were also acquired at other fields to rule out any dramatic effect on the ¹H line shape.²⁵ Active spin speed control was used for all spin–echo and 2D experiments. ¹H MAS spectra were typically acquired with a spatially selective composite pulse that suppressed low intensity signals from the spinning module.²⁶ The proton T_1 of the zeolite materials is about 2 s at room temperature; thus a 10 s recycle delay ensured quantitative intensities. Typically 32 scans were averaged with quadrature phase cycling. ²⁷Al MAS spectra were obtained with a non-selective 10° pulse (as calibrated on a dilute aluminum nitrate solution) and with a sweep width of 400 kHz.

The 2D exchange spectra were obtained by the pulse sequence proposed by Jeener²⁷ and implemented by Ernst and others.^{28,29} For these spectra 256 points were acquired in the second dimension for 128 values of the

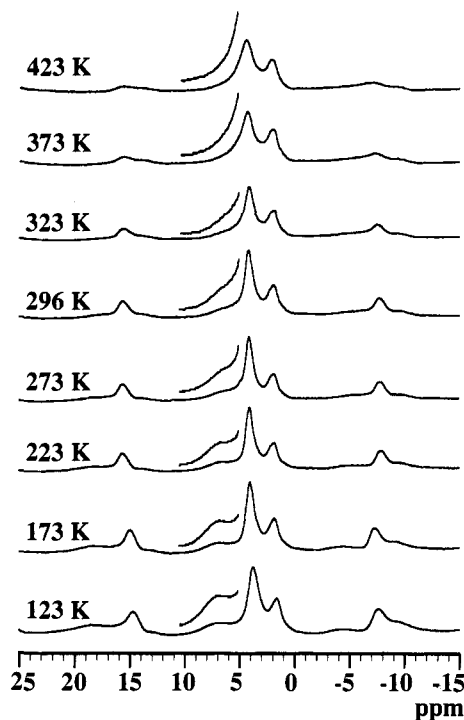


Figure 1. 300 MHz ¹H MAS spectra of zeolite HZSM-5 over a range of temperatures. In addition to the well-known Brønsted sites (4.3 ppm) and external silanols (2.0 ppm), a broad shoulder at 296 K sharpened to a third peak at 6.9 ppm when the sample temperature was reduced to 123 K. The spinning speed was 3.5 kHz, and spinning sidebands can also be seen in these spectra.

evolution period. This matrix was zero filled to 512 by 512 points followed by a complex Fourier transform in both dimensions. The spectra are displayed in the absolute value mode.

Results

Figure 1 shows ¹H MAS spectra of zeolite HZSM-5 obtained at moderate spinning speeds and over a range of temperatures. The well resolved isotropic signals at 296 K are the familiar silanol peak at 2.0 ppm and the acid site peak at 4.3 ppm; the broad shoulder on the low-field edge of the latter peak is visible in ¹H spectra of a number of HZSM-5 samples published by this and other laboratories. When the sample was cooled, this shoulder sharpened up into a well-defined peak at 6.9 ppm in the spectrum acquired at 123 K. The line shape seemed to be field independent over the narrow range examined (4.70–8.46 Tesla). When care was taken to include the contribution from the respective sidebands, the intensity of the 6.9 ppm peak was 40% of the 4.3 ppm resonance—this feature is clearly not a negligible contributor to the overall spectral intensity. (The downfield signal was also characterized for a number of other HZSM-5 samples of diverse origin; for simplicity, all of the results reported are from a single source.) As the temperature was increased (Figure 1), the 6.9 ppm signal broadened, and its intensity decreased with an apparent increase in the signal at 4.3–4.5 ppm. The effects of cycling the sample temperature were completely reversible over the range reported.

The observation of the 6.9 ppm signal motivated the investigation of ¹H{²⁷Al} double-resonance experiments for establishing spatial correlation between proton and aluminum. Proton is a chemically dilute nucleus in zeolite HZSM-5, so the problem can be cast as an isolated, two-spin system. In recent years, a number of increasingly elegant experiments have been devised for studying such systems, but the application of many is restricted by the appreciable quadrupolar coupling (e^2qQ_{zz}/h) of dehydrated HZSM-5 samples. Figure 2 suggests the nature of this problem

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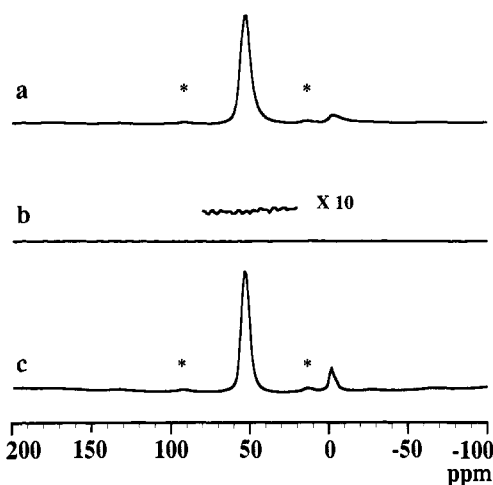


Figure 2. 78.1 MHz ^{27}Al MAS spectra of zeolite HZSM-5 showing the reversible effect of dehydration: (a) wet, as-received sample; (b) the same sample activated to 673 K to remove water; and (c) after rehydration in a desiccator.

by reporting ^{27}Al MAS spectra of a sample of the zeolite as a function of water loading. Figure 2a shows the spectrum of an as-received sample—framework aluminum resonates at 54.5 ppm and a small amount of octahedrally coordinated aluminum at -1.0 ppm. This sample was dehydrated by “activating” the sample at 673 K, and the ^{27}Al MAS resonances (Figure 2b) broaden so that no signal was detectable. This effect, which is well known, is the result of a distortion in the lattice upon removal of water.³⁰ Distortion of the electric field symmetry around aluminum increases the quadrupole coupling constant from ca. 1.5 MHz³¹ to ca. 10 MHz,³² and even the central transition of the ^{27}Al ($I = 5/2$) resonance was broadened beyond detection in an MAS experiment. Furthermore, the breadth of this resonance precludes the application of effective π or $\pi/2$ pulses for refocusing dipolar coupling³³ or coherence transfer. Figure 2c shows that the effect of dehydration to 673 K was reversible by rehydration. Since the proton spectra of hydrated samples are overwhelmed by the water signal and complicated by exchange, and the activated sample is, in any event, the material of interest, assignment techniques must deal with the very large ^{27}Al quadrupole coupling constant of the dehydrated zeolite.

The simplest way to transfer magnetization between two heteronuclear spins in a solid is a matched spin lock condition. For selective irradiation of the central transition of a quadrupolar nucleus, this condition is as follows:

$$\left(I + \frac{1}{2}\right)\gamma_{\text{Al}}B_{1\text{Al}} = \gamma_{\text{H}}B_{1\text{H}}$$

Ellis,^{34,35} Fyfe,²² and Klinowski³⁶ have previously demonstrated $\text{X} \rightarrow ^{27}\text{Al}$ cross polarization for more symmetrical sites in aluminas, clays, and other hydrated zeolites, but the difficulty of direct observation of aluminum in the present case precludes that possibility. Reverse cross polarization ($\text{X} \rightarrow ^1\text{H}$) has previously been used to assign proton spectra of phosphates²⁰ and to establish a correlation between a Brønsted site and the ^{13}C of an organic adsorbate.⁹ Repeated attempts were made to observe an ^{27}Al to ^1H cross polarization signal for activated HZSM-5;

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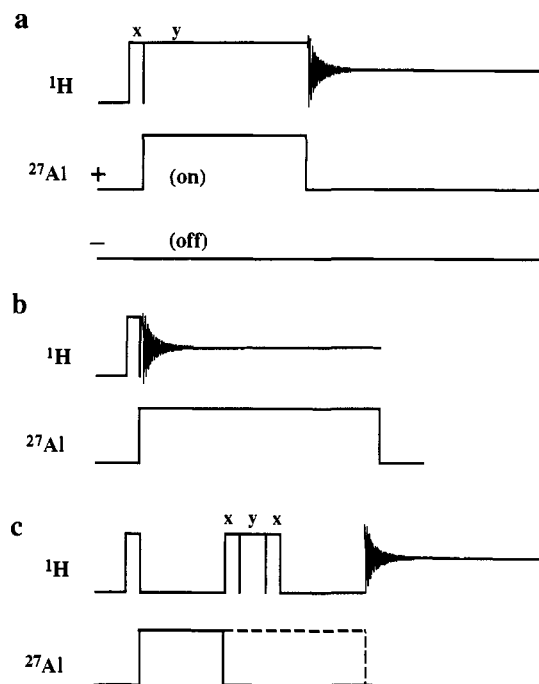


Figure 3. Diagram of the double-resonance pulse sequences: (a) the indirect detection or drain experiment—as indicated by the + and – signs, alternate scans have the aluminum field turned on, and the FID intensity is either added or subtracted from the data buffer to obtain a difference spectrum; (b) quadrupole ticking experiment—the aluminum spins are weakly irradiated during the acquisition of the proton signal; (c) spin-echo double-resonance experiment similar to the one previously demonstrated by Veeman—aluminum pulses may be applied during either or both of the delay periods, which equalled one rotor period.

those attempts failed totally, and we attribute this negative result to the difficulty of maintaining a finite amount of ^{27}Al magnetization in an effective spin lock with a field much smaller than the spectral width. The case of spin locking ^{23}Na with a smaller quadrupole coupling constant was treated theoretically and experimentally by Vega.³⁷

Figure 3 outlines the three experiments that were useful in ^1H spectral assignments for HZSM-5. Figure 3a is a variation of the standard cross polarization experiment with indirect detection of the low- γ spin through its draining of magnetization from the high- γ spin. This experiment was acquired in a difference mode where alternate scans having the aluminum pulse turned on or off were added or subtracted, respectively. As normally conceived, the indirect-detected experiment^{38,39} does not provide site resolution due to homonuclear broadening, but this zeolite system is more closely approximated as an isolated, two-spin system than typical organic solids. The drain experiment is less demanding than the reverse CP experiment in that a finite ^{27}Al magnetization need not be maintained in a spin lock for any period of time in order to transfer magnetization from the protons; however, the effect of off-resonant ^{27}Al irradiation was still detrimental in that it reduced the rate of polarization transfer.

Figure 4 reports the result of applying the drain experiment to activated HZSM-5. The control experiment in Figure 4a shows that the single resonance ^1H MAS spectrum was not unduly affected by the 0.8 ms ^1H spin lock; indeed, the ^1H $T_{1\rho}$ at 296 K was measured to be several orders of magnitude longer than this value. Otherwise identical experiments with a matched spin lock of ^{27}Al resulted in a very small decrease in the 4.3 ppm resonance. A difference experiment was performed in which ^{27}Al irradiation was applied on alternate scans, and the FIDs were subtracted. As shown in Figure 4b, a weak negative peak

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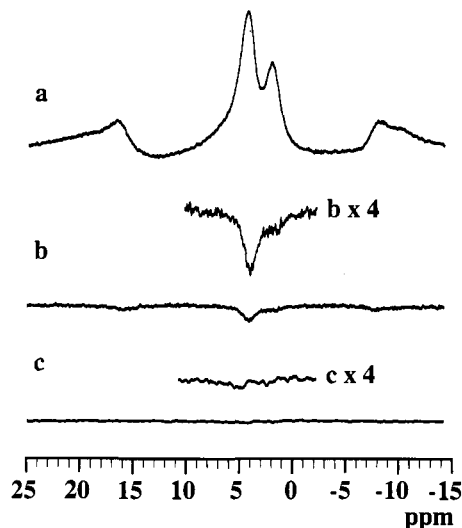


Figure 4. ^1H MAS spectra (296 K) of zeolite HZSM-5 demonstrating the inverse detection or drain experiment: (a) control experiment with 0.8 ms ^1H spin lock but no ^{27}Al irradiation; (b) difference spectrum with a matched spin lock of ^{27}Al ; (c) difference spectrum with a mismatch of the ^{27}Al field. The drain experiment was selective for the 4.3 ppm peak, but it was too inefficient to assign the weaker 6.9 ppm peak.

at 4.3 ppm indicated an inefficient but real drain of ^1H magnetization that occurred selectively for the Brønsted peak and not the silanol. The efficiency of this approach was too low for the assignment of the low-field signal. Figure 4c shows a similar experiment with an intentional mismatch of the Hartmann–Hahn condition; the difference spectrum in this case was uniformly null.

Figure 3b shows the second double-resonance experiment—direct excitation of proton with ^{27}Al irradiation during observation. If the irradiation field strength was greater than the ^{27}Al spectral width, this would be a decoupling experiment, but it is not. In solution NMR spin tickling⁴⁰ denotes an experiment in which weak irradiation of one spin is used to probe scalar coupling to other spins. Invoking an analogy, we call the experiment depicted in Figure 3b quadrupole tickling. Consider a single aluminum nucleus in a zeolite crystallite. The nuclear spin energy levels are greatly perturbed by the quadrupolar interaction, and that is strongly dependent on the orientation of the electric field gradient with respect to the applied magnetic field. The resonance frequencies of the five transitions are strongly modulated by sample rotation. If a 50 kHz radio frequency field is applied at the nominal ^{27}Al resonance frequency, each transition will experience a very rapid passage of rf through resonance as the rotor momentarily carries the quadrupolar interaction through its zero-crossing. Because the ^{27}Al line width is so broad for dehydrated HZSM-5, any given spin will be near resonance for a very small fraction of a rotor period, and the actual transition rate will be far less than 50 kHz.

Figure 5 shows the application of quadrupole tickling to activated HZSM-5 at 296 and 123 K. The 4.3 ppm isotropic ^1H signal and its associated spinning sidebands were greatly broadened by tickling the ^{27}Al transitions. From the 123 K spectrum, it is clear that the 6.9 ppm resonance was similarly affected; this strongly supports the assignment of the “new” resonance to a proton environment closely associated with aluminum. The silanol line was unaffected by ^{27}Al irradiation.

Broadening of resonances in MAS experiments can arise through conflicting averaging mechanisms operating on similar time scales.^{41,42} Figure 6 shows the effect of maintaining a 50

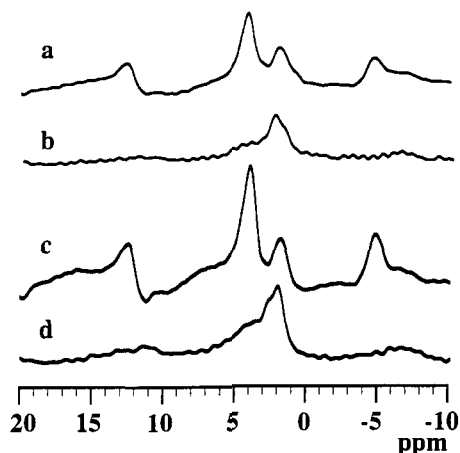


Figure 5. ^1H MAS spectra of HZSM-5 demonstrating the use of quadrupole tickling to assign protons dipolar coupled to ^{27}Al : (a) 296 K without ^{27}Al irradiation; (b) 296 K with 50 kHz (nominal) ^{27}Al irradiation; (c) 123 K without ^{27}Al irradiation; (d) 123 K with 50 kHz ^{27}Al irradiation. Irradiation of ^{27}Al selectively broadens the 4.3 and 6.9 ppm resonances.

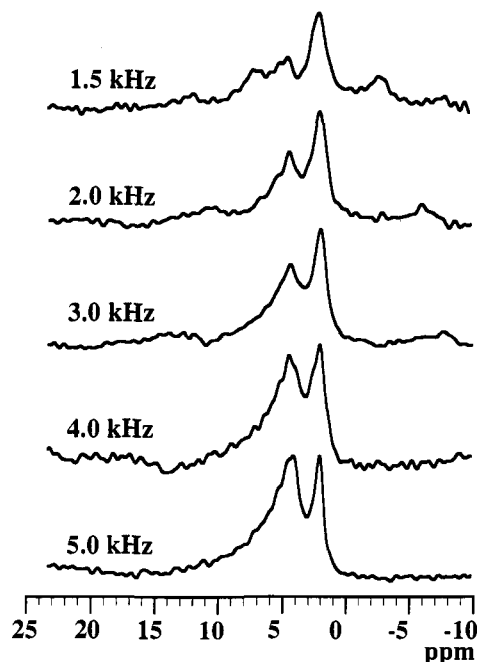


Figure 6. ^1H MAS spectra of HZSM-5 showing the effect of different spinning speeds during irradiation with a nominal 50 kHz ^{27}Al field. The broadening of the 4.3 ppm signal seems to maximize at 1–2 kHz, suggesting that the actual ^{27}Al transition rate is near this range.

kHz ^{27}Al field and varying the spinning rate between 5.0 and 1.5 kHz—lower rates were precluded by sideband overlap. Broadening of the 4.3 ppm signal seemed to level off at the lower spinning rates. Conflicting averaging mechanisms produce homogeneous (T_2 -like) broadening, and this can be exploited in suitable spin-echo experiments²¹ to achieve complete suppression rather than broadening of selected resonances. Figure 3c shows the pulse sequences used for this experiment. Each τ period conformed to one rotor period; there was little difference between application of ^{27}Al irradiation during one or both periods. Figure 7 reports representative results for 296 and 123 K—the suppression of the 4.3 and 6.9 ppm resonances is remarkable.

Discussion

Double-Resonance Experiments. The failure of reverse cross polarization for this system is hardly surprising in view of the near impossibility of maintaining a spin lock on such a broad

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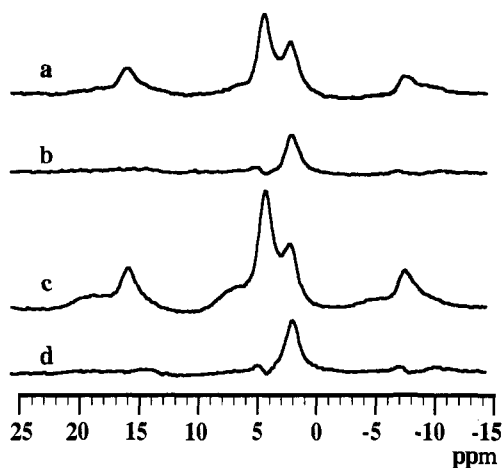


Figure 7. Proton spin-echo experiments on zeolite HZSM-5: (a) 296 K without ^{27}Al irradiation; (b) 296 K with ^{27}Al irradiation; (c) 123 K without ^{27}Al irradiation; (d) 123 K with ^{27}Al irradiation. Both the 4.3 and 6.9 ppm signals were eliminated in the double-resonance experiment. The rotor period was 286 μs .

resonance. The indirect detection or drain experiment gave marginal results in the present case, but it might be very useful for spin systems for which greater cross relaxation rates can be achieved by a matched spin lock.

Broadening of resonances due to conflicting averaging mechanisms is very common in solid state NMR. Some examples include incoherent averaging by molecular motion on the time scale of sample rotation⁴² or multiple pulse cycles⁴³ and motion on the time scale of decoupling.⁴¹ The ^1H - ^{27}Al dipolar coupling in HZSM-5 has previously been measured to be 19–20 kHz, and this has been used to estimate a 0.248 nm internuclear distance. The inhomogeneous broadening due to this coupling in powder samples is averaged by MAS. As stated previously, ^{27}Al irradiation was very inefficient due to the large quadrupole coupling and sample rotation. If the effective ^{27}Al transition rate is comparable to the sample rotation rate, a conflict of averaging mechanisms will occur. From the observed effect of spinning speed on peak intensity (Figure 6), we estimate that the actual transition rate achieved with a nominal 50 kHz field was only 1–2 kHz, and this is roughly consistent with what one would expect for a transition that was “on resonance” for only a few percent of the time.

Veeman and co-workers²¹ and others²² have reported the use of spin-echo double-resonance experiments to identify dipolar coupling to quadrupolar nuclei. The reader is referred to those papers for discussion of spin-echo methods.

The 6.9 ppm Peak. Variable-temperature experiments show that the familiar two-peak ^1H MAS spectrum of HZSM-5 is “deceptively simple”. The fact that this feature (seen as a broad shoulder on the downfield side of the 4.3 ppm signal) is present in many published spectra from various laboratories argues against this being an artifact of sample preparation. The evidence presented above for close association with aluminum seems very strong, but one alternate hypothesis must be considered. If magnetic site exchange between the 4.3 and 6.9 ppm resonances occurred on the time scale of the relevant experiment, the response of the 6.9 ppm peak could mimic that of a site in close proximity to aluminum. In the case of the spin-echo double-resonance experiment, the relevant time scale is one or two rotor periods, or less than 1 ms. A number of 2D ^1H exchange experiments were carried out at various temperatures and mixing times, and selected results are shown in Figure 8. Although small cross peaks were observed between the 6.9 and 4.3 ppm resonances at

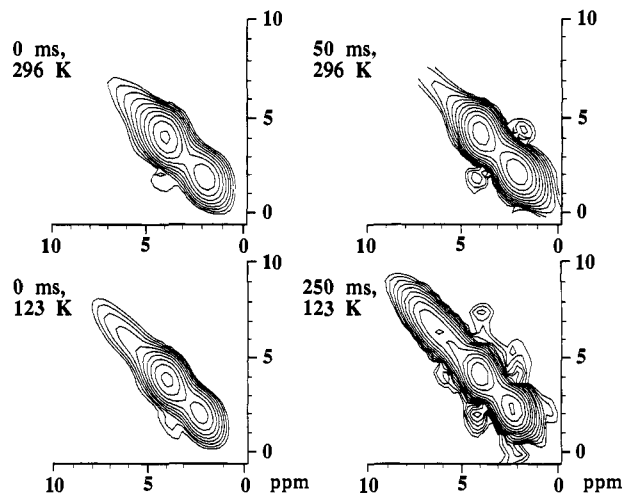


Figure 8. 2D ^1H MAS exchange plots for HZSM-5 are shown at 296 and 123 K for two mixing times each as indicated. The sample spinning rate was controlled to $3.0 \text{ kHz} \pm 1 \text{ Hz}$. The observation of weak cross peaks at 123 K indicates magnetic site exchange between the 4.3 and 6.9 ppm peaks on a time scale of 250 ms as a result of spin diffusion.

123 K with a mixing time of 250 ms, no site exchange was observed with much smaller mixing times. We rule out the possibility that magnetic site exchange accounts for the response of the 6.9 ppm signal to ^{27}Al irradiation. Figure 8 does provide evidence for some magnetic site exchange on a longer time scale, possibly due to spin diffusion. This result suggests that the 6.9 ppm signal is due to a site in the zeolite crystallite as opposed to a separate, aluminum-rich impurity phase. Cross peaks due to spin diffusion would not be observed if all spins of one type were more than several tens of nanometers from spins of other types.

Highly siliceous ZSM-5 is known to undergo a phase transition slightly above room temperature.^{44–46} The phase behavior of aluminum-rich materials is more poorly understood, but aluminum substitution apparently increases the transition temperature.⁴⁷ Thus, a phase transition does not appear to explain the formation of the 6.9 ppm peak. Another possible explanation, protons associated with extra-framework aluminum, can be discounted on the basis of the large discrepancy in ^1H chemical shift.

The most probable assignment of the 6.9 ppm proton signal is a second and previously unsuspected type of Brønsted site. This assignment is supported by previous titrations of the same material by a variety of reactive adsorbates. In situ NMR experiments revealed good agreement between moles of reactant titrated—indirectly providing the number of acid sites—and moles of framework aluminum.^{48,49} The observation of a significant new feature in the ^1H MAS spectrum of the “simplest” zeolite suggests a reexamination of the spectra of other solid acids using variable-temperature and double-resonance methods.

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