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Supplementary Material Available: ^{1}H z-filtered 1D-COSY spectrum of **1**, two H,C-COSY spectra of **1** (aliphatic carbons or aromatic carbons are observed), two sections of the E.COSY spectrum of **1**, and table of general displacement parameter expressions for the orthorhombic modification and the monoclinic modifications of **7** (8 pages). Ordering information is given on any current masthead page.

Heteronuclear Chemical-Shift Correlations of Silanol Groups Studied by Two-Dimensional Cross-Polarization/Magic Angle Spinning NMR

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Abstract: A two-dimensional ^{1}H–^{29}Si magic-angle-spinning (MAS) NMR experiment is proposed as a method to characterize peaks in conventional proton MAS spectra of surface species on silicas and zeolites. Mixing is achieved by cross polarization. The 2D spectra identify the protons that are rigidly bound to silicon atoms in the substrate. The application of heteronuclear or homonuclear decoupling is not necessary, as sample spinning is sufficient to suppress the effects of dipolar interactions in the systems of interest. The criteria for proton line narrowing by MAS and for effective cross polarization are discussed. The assignment of proton signals is further aided by proton MAS spectra obtained following a spin-lock pulse and by ^{29}Si MAS spectra taken with varying cross-polarization periods. The method is demonstrated in anhydrous samples of H-rho and NH$_4$-rho zeolites. It is shown that the 2D method identifies the minor proton component which is the single source of cross polarization in a hydrated form of Ca,Na-A zeolite. In the fully hydrated form of H-rho, new proton and silicon species are revealed and the interconnectivity of the various sample components is brought out. Finally, a homonuclear 2D proton experiment was evaluated for the detection of proton spin exchange that could hinder the interpretation of heteronuclear correlations, but the results were inconclusive in the present application.

Proton magic angle spinning (MAS) has been used extensively in recent years to characterize surface hydroxyls on silicas,[1-4] aluminosilicates,[4,5] and zeolites.[2,6-16] With a few exceptions,[1,6] well-resolved chemical-shift spectra were routinely obtained without the simultaneous application of line-narrowing multiple pulse schemes which would suppress proton–proton dipolar interactions.[17,18] This is possible because the dipolar interactions in these samples are so weak that they can be averaged out by sample rotations with speeds of only a few kilohertz.[19]

The chemical information directly revealed by the proton resonance frequencies concerns in particular the acidity of hydroxyl groups.[4,11,12] Further structural identification of proton signals is generally based on an a priori knowledge of the sample chemistry or on the response of the spectrum to the adsorption of deuterated molecules.[1-4] Among the types of structural features that need to be distinguished are bridging and terminal hydroxyls, single and geminal hydroxyls, AlOH and SiOH, and hydrogen bonding, but the amount of information contained in the chemical shifts of the fairly wide proton MAS peaks is often insufficient to identify all the various proton species. On the other hand, additional spectroscopic information can sometimes be deduced from the spinning-sideband intensities, which indicate anisotropic dipolar interactions,[14,15] or from the extent to which the sidebands are affected by partial deuteration, which helps distinguish homonuclear from heteronuclear dipole interactions.[14,15] Furthermore, the ^{29}Si line shape obtained by ^{1}H–^{29}Si cross-polarization (CP/MAS)[20] with short contact times reveals the ^{29}Si subspectrum of the silicon sites that are in the proximity of a hydroxyl group.[3,14,15] The results presented in this paper suggest that an extension of the latter technique to two-dimensional (2D) spectroscopy can contribute significantly to the assignment of multiple proton MAS peaks, in that it allows the identification of the proton species that interact most strongly with the silica lattice.

In this paper we present 2D CP/MAS ^{1}H–^{29}Si results of some zeolite samples containing proton species with varying structural and dynamical properties. The anhydrous NH$_4$ and H forms of zeolite rho serve as examples to demonstrate the method, although actual spectra are only shown for the latter. The 2D spectrum

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of a hydrated sample of Ca,Na–A shows the ability of the technique to distinguish between the signals of protons with different structural properties. In the last example the method is used to reveal some novel information on the structure of the hydrated form of H-rho. Finally, a homonuclear 2D proton experiment is performed on the same samples and is evaluated as a tool for the characterization of proton spin exchange.

Background and Theory

The relative ease with which the dipolar broadening of the surface-species proton signals can be suppressed by magic angle spinning is a direct result of the weakness of the dipolar interactions.[19] In dehydrated samples this is mostly a consequence of the spatial dilution of the hydrogen atoms, while in hydrated or solvated samples it results from the mobility of the protonated species. A third possibility is the situation observed in the anhydrous ammonium form of zeolites where a sizable residual intramolecular dipolar interaction does exist, but gives rise to a wide pattern of narrow sidebands.[14] Although the four NH_4 protons exchange rapidly, this motion does not result in a vanishing dipole interaction because the tetrahedral symmetry of the ammonium ion is distorted by the zeolite framework. The fact that the MAS spectrum breaks up into narrow sidebands is unusual for a cluster of more than two interacting spins, because their dipolar Hamiltonian,

$$\sum_{i<j} D_{ij}(\phi)(3I_{zi}I_{zj} - \mathbf{I}_i\cdot\mathbf{I}_j) \quad (1)$$

does generally not commute with itself at different rotor orientations ϕ, so that no line narrowing is achieved unless the spinning rate exceeds the interaction strength D_{ij}. The case of NH_4 is special, because the exchange process makes all four protons equivalent and creates a dipolar Hamiltonian of the form

$$D(\phi)\sum_{i<j}(3I_{zi}I_{zj} - \mathbf{I}_i\cdot\mathbf{I}_j) \quad (2)$$

which does commute with itself at different rotor orientations. Isolated rotating CH_3 groups have the same property, as we have verified for anhydrous sodium acetate (7% CH_3COONa in CD_3COONa) where sample spinning at 2.5 kHz resulted in a proton spectrum with up to 20, about 0.6 kHz wide, sidebands. Likewise, we previously observed a narrow MAS peak with sidebands for a surface $Si(CH_3)_3$ group where the combined methyl and silyl rotations render all nine protons equivalent.[3]

The suppression of the weak dipolar interactions by magic angle sample spinning includes the heteronuclear ^1H–^{29}Si interaction, as well. Nevertheless, this interaction remains active in the magnetization-transfer process. This has been explained by Stejskal et al.[21] who pointed out that in an I–S spin system with weak I–I and S–S interactions, transfer takes place when the mismatch of the Hartmann–Hahn condition, $\Delta = \gamma_s H_{1s} - \gamma_I H_{1I}$, is a multiple of the MAS frequency, Ω. This is caused by the simultaneous modulation of the geometric coefficients,

$$D_{ik}(t) = D_{ik}^{(1)}\cos(\Omega t + \phi_1) + D_{ik}^{(2)}\cos(2\Omega t + \phi_2) \quad (3)$$

and the spin parts (provided $\gamma H_1 \gg \Omega$)

$$F_{ik}(t) = -(I_{zi}S_{zk} + I_{yi}S_{yk})\cos\Delta t + (I_{yi}S_{zk} - I_{zi}S_{yk})\sin\Delta t \quad (4)$$

of the effective heteronuclear dipole Hamiltonian,

$$\sum_{i<k} D_{ik}(t)F_{ik}(t) \quad (5)$$

Nonzero time averages of the products in eq 5 are thus obtained when Δ matches the frequency of a nonvanishing frequency component of the geometric coefficient. This implies that for an isolated I–S pair, CP matching is achieved at $\Delta = \pm\Omega$ and $\pm 2\Omega$, with relative transfer efficiencies of 1 and $2^{-1/2}$ in powders,[21] while no polarization can be transferred at the exact Hartmann–Hahn condition $\Delta = 0$. When the protons mutually interact, more sidebands, including the centerband, are activated by additional modulations of the spin system.[21] In all the samples used in this study we observed a CP behavior that agrees with the model of isolated ^1H–^{29}Si pairs. An example is shown in Figure 1 where the ^{29}Si signal intensity in hydrated zeolite Ca,Na-A resulting from a CP/MAS experiment with a short contact time is plotted as a function of the Hartmann–Hahn mismatch frequency Δ. Surprisingly, a similar curve with vanishing centerband amplitude was also measured for anhydrous NH_4-rho, where the intramolecular proton–proton interactions would be expected to create additional sidebands. The symmetric form of the dipolar Hamiltonian (eq 2) perhaps prevents the generation of the required spin-state modulations.[21] As Figure 1 indicates, the ranges of active transfer can be quite narrow, and appropriate care must be taken to ensure that the spin rates remain constant over the duration of the 2D experiments.

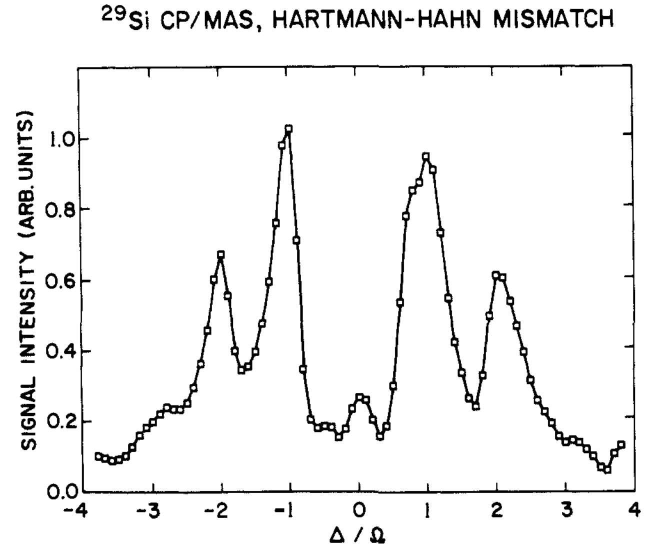

Figure 1. Signal intensity of the ^{29}Si CP/MAS spectrum of hydrated Ca,Na-A zeolite as a function of the ratio of the Hartmann–Hahn mismatch frequency, $\Delta = \gamma_s H_{1s} - \gamma_I H_{1I}$, and the spinning rate Ω. The proton rf amplitude is kept constant at 42 kHz, while the ^{29}Si rf field is varied: $\Omega/2\pi = 4.2$ kHz; contact time $\tau = 2$ ms.

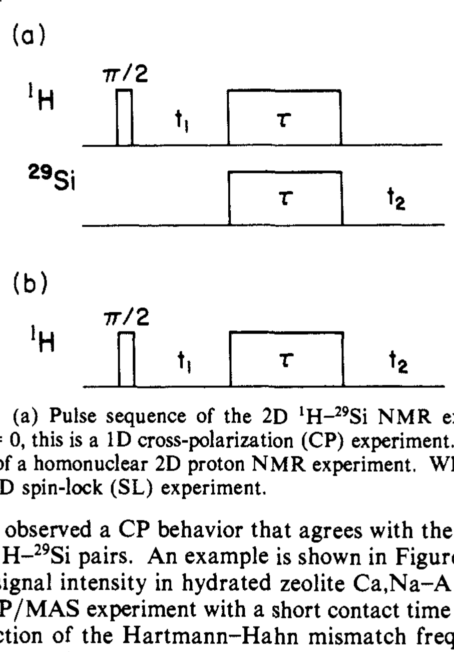

Figure 2. (a) Pulse sequence of the 2D ^1H–^{29}Si NMR experiment. When $t_1 = 0$, this is a 1D cross-polarization (CP) experiment. (b) Pulse sequence of a homonuclear 2D proton NMR experiment. When $t_1 = 0$, this is a 1D spin-lock (SL) experiment.

The 2D NMR pulse sequence is shown in Figure 2a. It differs somewhat from the ^1H–^{29}Si chemical shift correlation experiment in solutions,[22] where the mixing mechanism depends on scalar J coupling. In fact, it closely follows previously reported heteronuclear correlation experiments in solids for ^{13}C[23] and ^{29}Si[24] and consists of a $\pi/2$ proton preparation pulse, a proton evolution period t_1, a cross-polarization mixing period τ, and a ^{29}Si detection period t_2. Since magic-angle spinning is sufficient to suppress the effects of dipolar interactions in the samples we wish to study,

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neither heteronuclear[23,24] nor homonuclear[23] decoupling need to be invoked. Another difference with the previously reported 2D ^{1}H–^{29}Si results of a solid sample[24] is that the present data correlate the ^{29}Si spectra with the proton chemical shift rather than with the proton dipolar broadening.

If the results of a particular 2D experiment show that silicon atoms are coupled to one out of several distinct proton species, the obtained information is twofold. The proton–silicon connectivity has been revealed and the absence of spin exchange among the proton species during the cross-polarization time τ has been established. If, on the other hand, more than one proton signal shows correlation with the silicon spectrum, the extent of proton spin exchange should be investigated in order to distinguish between direct and indirect ^{1}H–^{29}Si correlations. This may be accomplished in the homonuclear proton 2D experiment shown in Figure 2b. Cross peaks in spectra obtained by this method indicate that spin exchange, either by spin diffusion or by chemical exchange, has taken place during τ.

Experimental Section

Two types of zeolites were used in this work. One was a Ca,Na form of zeolite A (Linde 5A) used in as-received, hydrated form. The second sample is a hydrogen form of zeolite rho, prepared by vacuum calcination of the ammonium form in a two-step procedure described elsewhere.[14] In this study we investigated the anhydrous and hydrated forms of H-rho, both of which have been subjects of previous multinuclear NMR investigations.[14,15]

The NMR measurements were performed on a Bruker CXP300 spectrometer operating at 300 and 59.6 MHz for ^{1}H and ^{29}Si, respectively. The MAS experiments were done with a Doty-Scientific probe, using sapphire rotors and Kel-F end caps to minimize proton background signals. Spinning rates were about 4 kHz. The ^{1}H–^{29}Si 2D spectra were taken with the pulse sequence shown in Figure 2a, employing simultaneous phase cycling of the proton $\pi/2$ pulse (x, y, $-x$, $-y$) and the ^{29}Si receiver (x, $-y$, $-x$, y) for quadrature detection in f_1.[25] The ^{1}H and ^{29}Si CP pulses had phases y and x, respectively. The radiofrequency field amplitude H_1 for the protons corresponded to 42 kHz and a $\pi/2$ pulse of 6 μs. The optimum CP matching condition was found empirically for each sample by adjustment of the ^{29}Si rf amplitude for maximum CP signal intensity. This adjustment is critical (see above), as in samples with more than one signal component one could within the same Hartmann–Hahn sideband establish matching for only a portion of the signals. For this experiment it is not necessary to synchronize the contact time τ with the sample rotation.

For each 2D spectrum a set of 64 or 128 FID's was obtained with t_1 increments of 60 μs and a dwell time of 80 μs. The 2D Fourier transforms were calculated in absolute-value mode and resulted in a matrix of 128(^{1}H) × 256(^{29}Si) spectral data points. A Gaussian line broadening of two to four data points was applied in both frequency domains. The number of transients per FID, the recycle time, and the contact time τ varied from spectrum to spectrum as indicated in the figure captions. The projected spectra are shown as skyline projections.

Two-dimensional proton MAS spectra were obtained with the pulse sequence shown in Figure 2b, applying phase cycling to the $\pi/2$ pulse (x, y, $-x$, $-y$) and the receiver (x, $-y$, $-x$, y). When the spectrum contains spinning sidebands, it is desirable to choose values for τ that are integer multiples of the rotor period,[26] but this was not necessary for the examples shown in this work. Finally, we took one-dimensional (1D) ^{29}Si CP/MAS and proton spin-lock (SL/MAS) spectra using the same pulse sequences as shown in Figure 2, but with $t_1 = 0$. Signal dependence on the contact or spin-lock time τ allowed the independent investigation of CP dynamics and proton $T_{1\rho}$'s.

Results and Discussion

Anhydrous H-rho. In an extensive NMR study of the anhydrous H form of zeolite rho,[14,15] we established that the main peak in the proton MAS spectrum occurs around 3.6 ppm and that the accompanying spinning sidebands arise from the heteronuclear interaction with the ^{27}Al spins. These protons do not move between different Al sites on the NMR time scale; thus magnetization transfer to the ^{29}Si is complete within a few milliseconds. Consequently, the 2D NMR spectrum could readily be obtained. The result, shown in Figure 3, displays proton and ^{29}Si projections that are essentially identical with the single-pulse-excitation MAS spectra. The 2D projections appear to be broader because they are shown in the absolute-value mode. Since the ^{29}Si signal intensity for each t_1 value is simply proportional to the amplitude of the proton FID at the end of the corresponding t_1 period, the contributions of the proton center- and sidebands to the 2D signal are essentially in proportion to their 1D amplitudes. As pointed out in the previous section, the proton MAS spectrum of anhydrous NH_4-rho is also accompanied by spinning sidebands, but in contrast to H-rho, the NH_4-rho sidebands are caused by homonuclear dipole interactions. Despite this difference, it was found that sideband intensities are similarly reproduced in a 2D ^{1}H–^{29}Si spectrum (not shown).

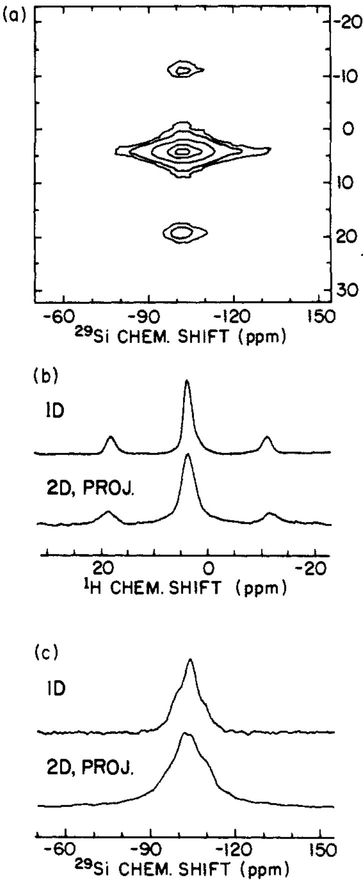

Figure 3. 2D and 1D ^{1}H, ^{29}Si MAS spectra of anhydrous H-rho zeolite. (a) Countour plot of 2D spectrum obtained with $\tau = 5$ ms. The vertical axis represents the proton chemical-shift scale, the horizontal axis the ^{29}Si chemical-shift scale. The spectrum was obtained from 64 FID's with 900 scans each: delay 1 s; t_1 increments 60 μs. (b) Proton spectra: single-pulse-excitation 1D spectrum and projection of the 2D spectrum shown in (a). (c) ^{29}Si spectra: single-pulse-excitation 1D spectrum and projection of the 2D spectrum shown in (a).

Zeolite Ca,Na-A. Figure 4 shows the combined 1D and 2D ^{1}H, ^{29}Si results obtained in zeolite Ca,Na–A. The 2D spectrum consists of a single cross peak, the projections of which are shown in the bottom traces of Figure 4, a and b. In Figure 4a the 2D proton projection is compared with 1D MAS spectra obtained with single-pulse excitation (top) and with a $\tau = 4$ ms SL experiment (center). There are two peaks in the 1D proton spectra arising from water (4.8 ppm) and structural hydroxyls (1.3 ppm). Neither peak is accompanied by spinning sidebands. The water and hydroxyl $T_{1\rho}$'s were found to be 1.9 and 4.9 ms, respectively, which explains why the 1.3-ppm peak is relatively higher in the spin-locked spectrum. The difference in proton $T_{1\rho}$'s does, however, not account for the gross underrepresentation of the water signal in the 2D spectrum which was obtained with a CP time of the same duration $\tau = 4$ ms. We therefore conclude that the cross-polarization of the ^{29}Si spins can only originate from the structural hydroxyl groups. The residence times of water molecules

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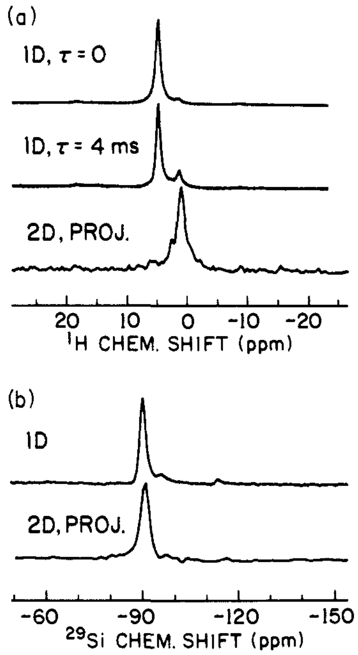

Figure 4. 1D and 2D ^{1}H, ^{29}Si MAS spectra of hydrated zeolite Ca,Na–A. The 2D data were obtained from 128 FID's with 240 scans each: τ = 4 ms; delay 2 s; t_1 increments 60 μs. (a) Proton spectra: single-pulse-excitation 1D spectrum; 1D spectrum following a 4-ms SL pulse and projection of the 2D spectrum. (b) ^{29}Si spectra: single-pulse excitation 1D spectrum and projection of the 2D spectrum.

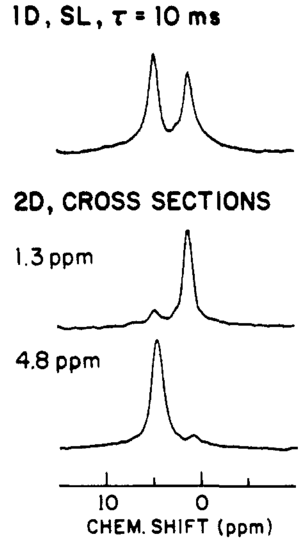

Figure 5. 1D and homonuclear 2D proton MAS spectra of hydrated zeolite Ca,Na–A: 1D spectrum following a 10-ms SL pulse; two cross sections through diagonal peaks of a 2D spectrum obtained from 64 FID's with 20 scans each: τ = 10 ms; delay 1 s; t_1 increments 60 μs; dwell time 30 μs.

on specific framework positions are thus much shorter than typical CP times (~1 ms).

The results shown in Figure 4 clearly demonstrate that there is no appreciable proton spin exchange between the two proton species during the τ = 4 ms mixing time. The unequal $T_{1\rho}$'s provide additional evidence, as do the following results of a homonuclear 2D proton experiment. The data, shown in Figure 5, are taken with the pulse sequence outlined in Figure 2b using a mixing time τ = 10 ms which is longer than the τ = 4 ms employed for the heteronuclear experiment. The difference between the two $T_{1\rho}$'s leads to a 1D SL/MAS spectrum with approximately equal peak intensities (Figure 5, top). The cross sections of the 2D spectrum (Figure 5, bottom traces) show only small cross peaks, which either originate from the onset of exchange, or from extended signal wings of the absolute-value spectrum.

As to the nature of the structural hydroxyls, it should be noted that the position of the ^{29}Si peak obtained by cross polarization coincides with the –90.5-ppm peak in a 1D single-pulse-excitation spectrum of Ca,Na–A (Figure 4b). This rules out the possibility that the 1.3-ppm proton peak represents terminal $(AlO)_3SiOH$ groups on the surface of the particles or at crystal imperfections, because their ^{29}Si chemical shift is expected to be some 5 ppm downfield from the $Si(OAl)_4$ peak at –90.5 ppm.[27] Moreover, the OH groups are not residing on or near framework Al atoms, because that would lead to strong spinning sidebands as in H-rho, unless the ^{1}H–^{27}Al interaction is reduced by molecular motion. In parallel 1D experiments in hydrated Na–A we did not observe a similar OH peak, nor could a ^{29}Si spectrum be obtained by CP/MAS. This suggests that the 1.3-ppm peak is related to one of the particular species that are formed during the calcination of zeolite A when it contains divalent ions. One possibility is the hydrolysis of divalent ions, which is assumed to take place in zeolites:[28]

$$Ca^{2+} + H_2O \rightarrow CaOH^+ + H^+$$

The details of this process and the exact nature of the two resulting protonated species remain, however, uncertain. Recent ^{27}Al NMR data indicated that the hydrolysis introduces a deformation of the immediate Al coordination.[29] If the OH group identified in the present work is, indeed, a result of such hydrolysis, we have now found that it is closely associated with the silicons in the framework and that its proton does not exchange rapidly with water sorbed in the pores. Another, maybe related, possibility is that the 1.3-ppm protons belong to the $Al(OH)_4^-$ ions that were found by MAS NMR.[29] The tumbling motion of these ions is then responsible for the suppression of ^{27}Al–^{1}H sidebands. On the other hand, the ^{1}H–^{29}Si interactions established by hydrogen bonding to the framework are not sufficiently quenched by the motion to suppress the CP mechanism as well. The aluminate ions are believed to be located at the centers of the sodalite cages,[29] which could explain why proton exchange with water in the α-cages is inhibited.

Hydrated H-rho. Before presenting the 2D results of hydrated H-rho, we recall the earlier proton MAS results[14,15] which showed a spectrum with a strong water peak at 4.6 ppm and a much weaker peak at 9.1 ppm. No appreciable spinning sidebands accompanied the signals. The nature of the protons giving rise to the smaller peak could not be determined, other than by stating that they are highly acidic,[4] that the proton exchange rate with the water is slow on the NMR scale ($<10^{-3}$ s^{-1}), and that they number about 12 per unit cell, i.e., ~1 per Al atom on the average.[15] One important unanswered question was whether the 9.1-ppm protons are associated with regular zeolitic structure or with structural impurities. The same study[14] also showed that, in contrast to hydrated NH_4-rho, hydrated H-rho allows magnetization transfer from the protons to the ^{29}Si nuclei in a CP/MAS experiment. This indicates that while intrazeolite water is too mobile to be a source of cross polarization, the hydrated form of H-rho contains nonexchanging hydroxyl protons which are rigidly bound to the zeolite framework. This may lead to the almost obvious speculation that the latter hydroxyls are to be identified with the protons that resonate at 9.1 ppm. The following 2D data demonstrate that this is not so.

The hydrated H-rho sample studied in the present work is not exactly identical with the one previously investigated.[14,15] As will be shown below, the 9.1-ppm proton MAS peak is now not as well resolved as in the previous sample. However, the ^{29}Si MAS spectra are essentially identical and the NMR features summarized in the foregoing paragraph apply to the present sample as well, so that the differences may be considered as being of minor importance.

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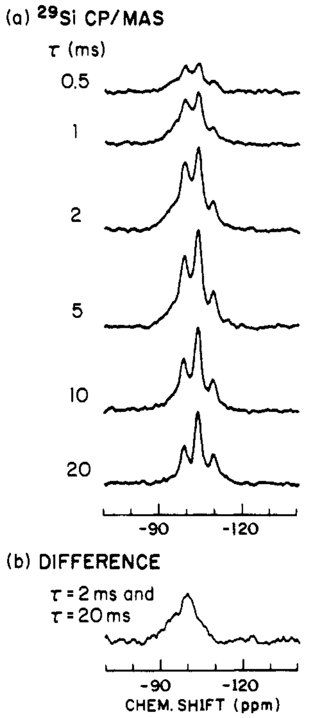

Figure 6. (a) 1D ^{29}Si CP/MAS spectra of hydrated H-rho obtained with different contact times τ, as indicated. (b) A linear combination of the 2- and 20-ms line shapes in (a), showing the probable line shape of a nonuniform inclusion.

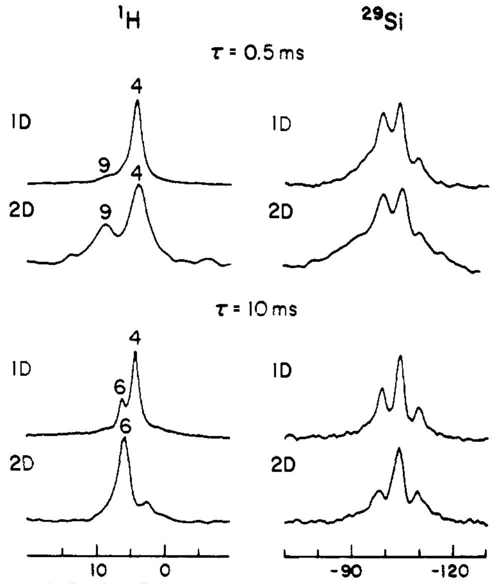

Figure 7. 1D and 2D ^1H (left) and ^{29}Si (right) MAS NMR spectra of hydrated H-rho obtained with τ = 0.5 ms (top) and 10 ms (bottom). The proton 1D spectra were obtained following an SL pulse, the ^{29}Si spectra with CP, and the 2D traces are projections of the 2D spectra. The latter were obtained from 64 FID's with 4200 and 2300 scans each, 0.2- and 0.5-s delay, for τ = 0.5 and 10 ms, respectively. t_1 increments were 60 μs. The numbers next to the proton peaks indicate the approximate chemical shifts.

The ^{29}Si spectra obtained by cross polarization from the protons depend on the contact time τ, as is shown in Figure 6a. While for long τ values the ^{29}Si line shape closely resembles the well-resolved spectrum obtained by single-pulse excitation,[14,15] short τ's lead to more complex spectra that appear to be composed of the resolved peaks and an additional broad peak. By linear combination of two of the traces in Figure 6a we can construct a line shape, shown in Figure 6b, that approximates this broad spectrum. These data indicate that in addition to the previously observed, highly uniform and symmetric framework, the zeolite contains a minor component with a structure that is less regular, or amorphous, because the Si(nAl) peaks are not as well resolved.[14,15] The dynamics of the CP experiment is not sufficiently understood to determine how large a fraction of the silicon atoms contributes to this signal.

Another hitherto-unnoticed component of fully hydrated H-rho was revealed in a proton SL/MAS experiment (Figure 2b, t_1 = 0). These measurements showed that the peaks at 4.6 and 9.1 ppm decrease in intensity upon increasing τ, with equal relaxation times, $T_{1\rho}$ = 2.2 ms. When τ exceeds 5 ms, the proton spectrum begins to exhibit a new peak around 6 ppm which has a longer $T_{1\rho}$ of ~4 ms and thus gains in relative intensity with longer τ's (see the 1D proton traces in Figure 7). This new peak, which was hidden between the two earlier identified signals in the single-pulse excitation spectrum, is estimated to represent 10% of the total proton content. As to its chemical identity, it could either be residual ammonium or a hydroxyl species of the type that has been observed around 6 ppm upon addition of small amounts of water to H-rho.[15] The following 2D data suggest that it is the latter.

The 2D results of hydrated H-rho are shown in Figure 6. The displayed spectra were taken with two τ durations, 0.5 ms (top) and 10 ms (bottom). For each τ value we show on the left the proton spectrum measured in a 1D spin-lock experiment and the proton projection of the 2D spectrum. On the right are shown the 1D ^{29}Si spectrum measured by CP and the ^{29}Si projection of the 2D spectrum. These results demonstrate that the broad ^{29}Si component generated with short contact times originates from the proton species that resonate at 4 and 9 ppm (τ = 0.5 ms), whereas the CP mechanism that creates the ^{29}Si signal of the regular framework involves the 6-ppm protons (τ = 10 ms). Hence, only the protons resonating at that frequency are attached to the regular aluminosilicate framework with sufficient rigidity to be a source of cross polarization. This rules out the possibility that they belong to NH_4^+ ions, as there cannot be cross polarization in hydrated NH_4-rho.[14] It may be estimated from the $T_{1\rho}$ data, mentioned above, that their number is of the same order as the number of Al atoms or acid sites, which suggest that the 6-ppm peak represents some hydrated form of bridging hydroxyls. However, there is no rapid proton exchange between these hydroxyls and the bulk water in the cavities, because the $T_{1\rho}$'s of the 6- and 4-ppm peaks differ substantially, and the 4-ppm peak is essentially absent in the 2D spectrum with τ = 10 ms.

The interaction of the 9-ppm proton species with water is less clear, because the two $T_{1\rho}$'s are equal and both contribute to the CP ^{29}Si signal of the nonuniform portion of the framework, as is evident from the τ = 0.5 ms data presented in Figure 7. This could mean that the water protons exchange with the 9-ppm hydroxyls, but there is also the unlikely possibility that the water is closely enough associated with the silicons of the nonuniform inclusions that direct cross polarization can occur. The representation of the 4-ppm peak in the 2D spectrum is relatively weak in proportion to its intensity in the 1D spectrum. The cause of this could be that only a fraction of the total water content exchanges with the 9-ppm hydroxyls or is in the vicinity of the nonuniform inclusions. We attempted to obtain more direct information on a possible exchange process by performing a homonuclear 2D proton experiment (Figure 2b) with the same SL time, τ = 0.5 ms. The cross sections of the resulting spectrum, shown in Figure 8, indeed contain the cross peaks that would be associated with spin exchange. Unfortunately, we cannot rule out the possibility that they are merely the dispersion wings of the absolute-value diagonal peaks, and the 2D proton data are thus inconclusive.

The ^{29}Si line shape of the nonuniform component (Figure 6b) is shifted downfield from the regular spectrum over ~4 ppm. This can be interpreted in two ways. One possibility is that the shift of the first moment may be the result of a changed chemical composition, i.e., higher Al content or added terminal hydroxyl groups. The alternate interpretation is that the shift is caused by the same kind of structural differences that have been observed

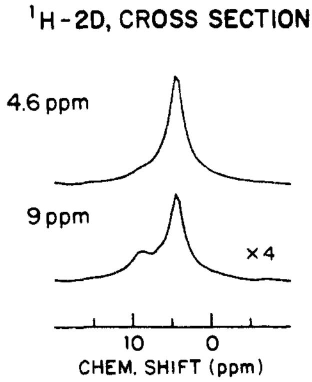

Figure 8. Homonuclear 2D proton MAS results in hydrated H-rho. Shown are two cross sections through the diagonal peaks of the 2D spectrum obtained from 64 FID's with 24 scans each: $\tau = 0.5$ ms; delay 0.5 s; t_1 increments 60 μs; dwell time 30 μs.

between hydrated H-rho and anhydrous NH_4-rho, where the ^{29}Si spectrum of the latter is also less resolved and shifted to lower field by 4 ppm.[14] This framework deformation is related to the exceptional flexibility of the rho lattice where the double eight-rings can be circular or elliptical.[13,30] Ellipticity is induced in anhydrous NH_4-rho by the ammonium ions that are located at the centers of the eight-rings.[30] We may, therefore, speculate that the "nonuniform" framework components in hydrated H-rho are substructures with strongly coordinating ligands in the eight-rings. These then carry the 9-ppm hydroxyl groups. Further speculation about their nature is obviously not warranted, although we may recall at this point that ^{27}Al NMR has shown the samples to contain nearly two aluminum atoms per unit cell in a highly symmetric octahedral coordination.[14] Two-dimensional ^1H–^{27}Al spectroscopy can perhaps contribute to a better understanding of this aspect of the zeolite structure.

Conclusions

The examples presented in this paper demonstrate that the interpretation of proton MAS spectra of surface species on siliceous substrates can be aided by ^1H–^{29}Si double-resonance experiments. The methodology includes CP/MAS ^{29}Si experiments with varying contact time and corresponding heteronuclear 2D spectroscopy. While the former may reveal ^{29}Si subspectra of sample components with different degrees of association with proton-containing groups, the later selectively identifies the chemical shifts of the protons that are rigidly bound to these substrate components.

The method was proved to be useful for the structural characterization of hydrated zeolites, where it was shown that the bulk water in the cavities is not a source for ^{29}Si cross polarization. This was found for the hydrated zeolites Na–A, Ca,Na–A, NH_4-rho, and with some uncertainty for H-rho. When cross polarization did occur, we could identify the MAS peak of the corresponding structural hydroxyl. In Ca,Na–A this hydroxyl group is evidently associated with the main zeolite framework, because the CP ^{29}Si spectrum is identical with the single-pulse-excitation spectrum. In hydrated H-rho the results revealed a newly observed nonuniform framework component, and the OH signal of each component was identified.

Since proton spin exchange during the CP contact time obscures the selectivity of the 2D experiment, a homonuclear 2D proton experiment could be valuable for the independent confirmation of exchange. An example is hydrated H-rho where water appears to contribute to cross polarization. The proton 2D data are, however, inconclusive in this case, because of the proximity and the intensity difference of the two peaks involved.

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The ^{31}P Chemical Shielding Tensor in Phospholipids[∥]

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Abstract: The ^{31}P chemical shielding tensor has been determined for single crystals of 1-hexadecyl-2-deoxyglycerophosphoric acid monohydrate, an analogue of the naturally occurring phosphatidic acid. The measured values for the principal components of the shielding tensor are −53, −2, and +58 ppm relative to 85% H_3PO_4. It is found that its principal axes coincide within 2° with a Cartesian coordinate system defining the symmetry of the phosphate group. The orientation of the chemical shielding tensor of 1-hexadecyl-2-deoxyglycerophosphoric acid is similar to that measured in single crystals of other phosphomonoesters, such as phosphoethanolamine, phosphoserine, 3′-cytidine monophosphate, and deoxy 5′-monophosphate. These compounds are water-soluble polar molecules and have no hydrocarbon chains, contrary to 1-hexadecyl-2-deoxyglycerophosphoric acid. The orientation of the chemical shielding tensor of 1-hexadecyl-2-deoxyglycerophosphoric acid differs only by 7–13° from that of the phosphodiester barium diethyl phosphate, which has been used as a model for the ^{31}P chemical shielding tensor of phospholipids.

1. Introduction

Phosphorus-31 NMR has been widely used in the structure elucidation of phospholipid bilayers and biological membranes. In particular, the anisotropy of the ^{31}P chemical shielding tensor allows one to deduce information on conformation and orientation of the phospholipid molecules in these anisotropic structures. In order to exploit this source of information, it is necessary to know the orientation of the shielding tensor within the molecular framework. Because computational approaches are unfeasible, it is necessary to determine the orientation of the shielding tensor experimentally on suitable model systems.

A principal problem in the experimental determination of the tensor orientation is the extreme difficulty to grow single crystals sufficiently large for NMR investigations. So far, single crystals

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[∥] This paper is dedicated to Professor Giorgio Semenza on the occasion of his 60th birthday.

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