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^{13}C NMR Study of Methanol in HY Zeolite

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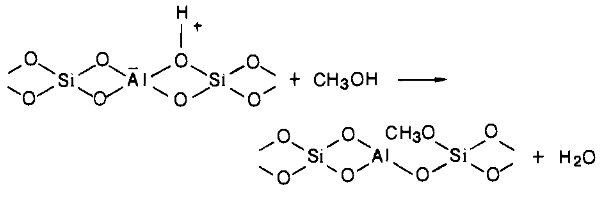
Abstract: ^{13}C CPMAS spectra of methanol adsorbed on HY zeolite contain two resonances with solid-sample characteristics and one resonance with liquid-sample characteristics. The resonances with solid-sample behavior are attributed to methoxylated silanol sites located in the supercages and β cages of the zeolite. Methanol species in the β cages are retained during evacuation of the sample at 140 °C, whereas those in the supercages are removed. Spectra of methanol adsorbed on zeolites activated at 500 and 600 °C do not contain the resonance associated with species in the β cage. Relaxation experiments are used to elucidate the spin dynamics, from which details of the molecular structure and dynamics are derived. Of particular interest for characterizing the species observed is the homogeneous vs. inhomogeneous character of the ^{13}C–^{1}H dipolar interaction, as manifested in the behaviors of rotational echoes in interrupted-decoupling experiments and in dipolar contributions to spinning sidebands.

Adsorption of methanol onto HY zeolite is to some extent irreversible. This has been attributed to the formation of methoxysilane groups within the zeolite.[1,2]



(1)

In samples of HX, HY, and other H zeolites loaded with methanol at room temperature and then evacuated at 150–200 °C, species identified as Si–O–CH_3 groups are observed in the infrared spectrum.[1-5] In the case of HY there is a reduction in the total intensity of two stretching absorptions, denoted as the HF and LF stretching absorptions, of supercage and β cage hydroxyl groups[1] compared to the infrared spectrum of the unloaded zeolite. This suggests that both supercage and β cage hydroxyl sites can participate in reactions with methanol. These reactions may occur to some extent during the evacuation.

In samples that are not evacuated, the analysis by infrared spectroscopy is complicated by an overlapping signal due to mobile methanol. Adsorption studies show an increased uptake of methanol in HY zeolite as opposed to NaY zeolite that suggests occupation of the β cages by methanol in the former. However, this does not appear to be consistent with infrared spectra of unevacuated samples.[1]

The CP (cross polarization) NMR experiment[6,7] with MAS (magic-angle spinning) favors signals arising from species that experience a static dipolar coupling, i.e., molecules for which molecular motion does not average dipolar coupling to zero. A CPMAS spectrum of a compound adsorbed onto HY zeolite should be selective toward signals from species that are immobilized by a strong interaction or chemical reaction with active (e.g., acid) sites. Thus, in the case of ^{13}C CPMAS spectra of methanol on HY, the direct observation of immobile species can be expected. In the present study, solid-state MAS ^{13}C NMR techniques, utilizing both cross-polarization and Bloch-decay methods, were used in the study of the methanol/HY system.

Experimental Section

The NH_4Y zeolite used in this work was obtained from Strem Chemical Co. Activation of the zeolite was carried out under normal bed conditions. A relatively thick bed (10 mm) was heated in stages under vacuum to the final temperature.

Alcohols were obtained from J. T. Baker Chemical Co. and Fischer Scientific Co. These were distilled and stored over molecular sieve under a nitrogen atmosphere. ^{13}C labeled methanol from Merck, Sharp and Dohme Canada, Limited, was diluted with unlabeled methanol to a 10% level of ^{13}C for $T_{1\rho}{}^{C}$ studies.

Prior to the adsorption on the zeolite, alcohols were subjected to 3 freeze–pump–thaw cycles. After exposure to the alcohol, the zeolite sample was evacuated for 10 minutes and the amount of adsorbed material determined gravimetrically.

^{13}C spectra were recorded on a modified Nicolet NT-200 spectrometer, utilizing low-speed bullet rotors operating at 2–2.5 kHz rotation rates. The $T_{1\rho}{}^{C}$ study reported here was carried out on a modified Nicolet NT-150 spectrometer, utilizing a prototype variable-temperature probe. This probe uses a "Windmill" spinner design[8] capable of 4–4.5 kHz rotation rates.

Samples were loaded into a spinner fitted with a silicone rubber plug and spun with dry nitrogen as the drive gas. The diameter of the cylindrical plug is slightly greater than the i.d. of the rotor. Its length is roughly 20% that of the insert. Shorter plugs fail under MAS conditions, pushing the insert up and exposing the sample. In several bench tests, samples of HY zeolite that had been activated at 400 °C were found to gain 15%–20% H_2O by weight over a 12-h period if spun under N_2 without sealing. The same sample when sealed with a silicone rubber plug did not show appreciable weight gain (<1 mg for a 300-mg sample) over the same 12-h spinning period. The silicon rubber yields a ^{13}C signal at 1.14 ppm relative to external Me_4Si; this signal was used as a secondary shift reference for this work, although the ^{13}C chemical shifts are reported with respect to Me_4Si by adding the 1.14 ppm shift difference. The experimental conditions for obtaining the CPMAS spectra reported here are the following: $H_{1C} = H_{1H} = 55$ kHz, contact time = 2 ms, and spinning rate = 2.5–4.0 kHz. For the variable-temperature $T_{1\rho}{}^{C}$ study, the radio frequency field strengths were maintained at 35.7 kHz at each temperature.

Results and Discussion

HY/Methanol. The 37.75-MHz ^{13}C CPMAS spectrum of 15% methanol (by weight) adsorbed into HY activated at 400 °C (we identify this sample as HY(400)/15% MeOH) is presented in Figure 1A. The spectrum contains a single peak at 50.1 ppm. The optimal contact time for observation of the spectrum is in the vicinity of 2 ms, a value that would be considered typical of a methyl group in an organic solid.

A variable-temperature study of $T_{1\rho}{}^{C}$ was performed on this sample at a ^{13}C resonance frequency of 35.75 MHz, using the $T_{1\rho}{}^{C}$

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[1] Salvador, P.; Fripiat, J. *J. Phys. Chem.* **1975**, *79*, 1842.

[2] Salvador, P.; Klading, W. *J. Chem. Soc., Faraday Trans.* **1973**, *1*, 73.

[3] Bosacek, V.; Traruzkova, Z. *Collect. Czech. Chem. Commun.* **1971**, *36*, 551.

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[6] Pines, A.; Gibbey, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

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[8] Wind, R. A.; Anthonio, F. E.; Duijvestijn, M. J.; Smidt, J.; Trommel, J.; deVette, G. M. C. *J. Magn. Reson.* **1983**, *52*, 424.

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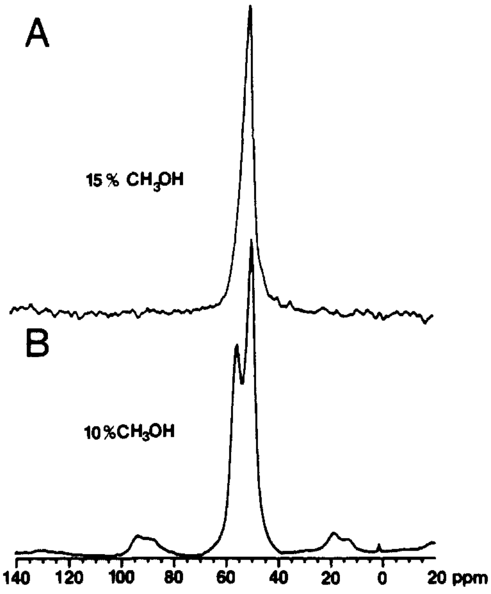

Figure 1. ^{13}C CPMAS spectrum of (A) 15% methyl alcohol by weight on HY(400) and (B) 10% methanol by weight on HY(400).

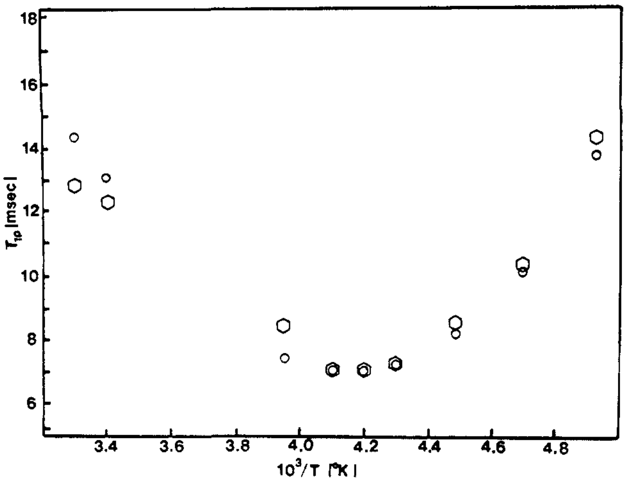

Figure 2. Plot of the $T_{1\rho}{}^{C}$ values measured on a sample of 15% methanol by weight on HY(400) vs. $10^3/T$. Hexagons represent experimental data and circles represent values calculated from eq 2.

procedure of Schaefer, Stejskal, and Buchdahl.[7] $T_{1\rho}{}^{C}$ data over the temperature range of 30 to −70 °C are presented in Figure 2. $T_{1\rho}{}^{C}$ is seen to pass through a minimum at −35 °C. In order to qualitatively assess the nature of the motion responsible for $T_{1\rho}{}^{C}$ relaxation, we attempted a fit of the data to a very simple model that assumes $T_{1\rho}{}^{C}$ relaxation is induced by isotropic fluctuations of the ^{13}C–^{1}H dipolar coupling. Only terms involving spectral density at $\omega_{1C} = \gamma_C H_{1C}$ are considered. With these assumptions one finds[9]

$$\frac{1}{T_{1\rho}{}^{C}} = \text{constant}\ \frac{\gamma_C{}^2\gamma_H{}^2}{r_{CH}{}^6}\ \frac{\tau_C}{1+\omega_{1C}{}^2\tau_C{}^2} \tag{2}$$

Equation 2 predicts the $T_{1\rho}{}^{C}$ minimum to occur for $\tau_C = 1/\omega_{1C}$. From the value of $T_{1\rho}{}^{C}$ at the minimum one can evaluate the proportionality constant and then use the constant and the measured value of $T_{1\rho}{}^{C}$ at each temperature to calculate a value of τ_C at each temperature. A plot of ln τ_C vs. $10^3/T$, shown in Figure 3, yields an activation energy of 3.0 kcal/mol. The $T_{1\rho}{}^{C}$ values predicted from eq 2 for a process with E_a = 3.0 kcal/mol are shown in Figure 3 as circles. Considering the crudeness of the model, the fit is surprisingly good. On the high-temperature side of the minimum, $T_{1\rho}{}^{C}$ is smaller than predicted by eq 2. T_1^C measurements (vide infra) indicate that higher frequency processes should not be neglected in a thorough analysis of $T_{1\rho}{}^{C}$. In any event, the values of τ_C and E_a obtained from our simple model are similar to those reported by Salvador and Fripiat in a liquid-state NMR study of $T_1{}^{H}$ relaxation of CD$_3$OH on HY (350).[1] It was concluded in that study that $T_1{}^{H}$ occurred via a proton exchange process of the sort indicated below.

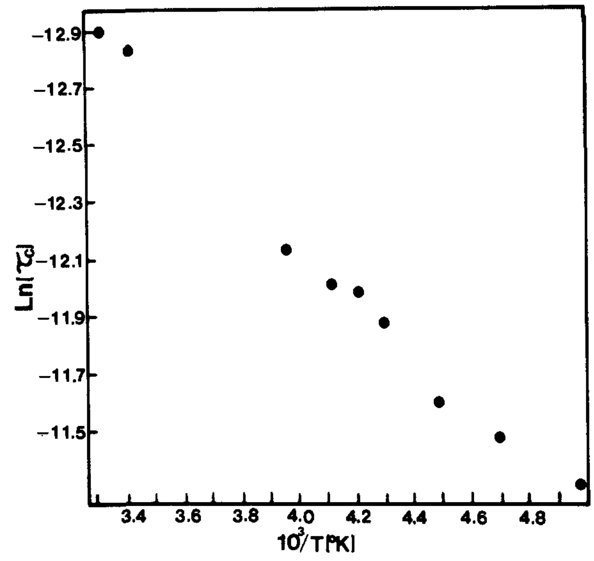

Figure 3. Plot of ln τ_c, obtained from eq 2, vs. $10^3/T$ for the sample HY(400)/15% MeOH.

$$\text{Me}'\text{OH}_A + \text{MeOH}_B\text{H}_C{}^+ \rightleftharpoons \text{Me}'\text{OH}_A\text{H}_C{}^+ + \text{MeOH}_B \tag{3}$$

Our results appear to be consistent with the notion that a similar mechanism is responsible for $T_{1\rho}{}^{C}$.

Thus, other than the implications of a static component of the ^{13}C–^{1}H dipolar coupling that allows cross polarization, there are no indications that the ^{13}C CPMAS spectrum of HY(400)/15% MeOH provides information not available by liquid-state techniques. The data indicate that a mobile, liquidlike species dominates the spectrum at this loading level. If there are species that are immobilized by stronger interaction with the zeolite, it is necessary to reduce the loading level in order to observe them. Accordingly, a sample containing 10% by weight methanol (HY(400)/10% MeOH) was prepared. The ^{13}C CPMAS spectrum of this sample is shown in Figure 1B. In addition to the peak at 50.1 ppm, the spectrum in Figure 1B contains a peak at 55.7 ppm. There are also now two sets of spinning sidebands of similar intensity, with the pair of maxima in each set spaced roughly 5 ppm from one another. These spinning sidebands are characteristic of species constrained from executing rapid, random motion within the zeolite, such as the constraint one would expect for the products of methoxylation of acid sites. There must be a distribution of time-averaged orientations of the methanol molecules or methanol-derived moieties that remains static for at least several spinner periods in order for a residual chemical shift anisotropy to be manifested as spinning sidebands. That is, if there is rapid motion of the CH$_3$O moieties, there must be highly anisotropic character to that motion. According to the double maxima of the sidebands, there are two immobile species, one corresponding to each maximum in a sideband.

A $T_1{}^{C}$ experiment clearly demonstrates differing mobilities in the sample. Relaxation data were obtained with Torchia's method.[10] The data are presented in Figure 4 as a plot of the logarithm of signal intensity vs. time. A fit of the data from the resonance at 55.7 ppm yields a $T_1{}^{C}$ value of 1.5 s. The corresponding plot for the line at 50.1 ppm shows a pronounced curvature that is inconsistent with single exponential relaxation. A

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[9] Mehring, M. *Principles of High Resolution NMR in Solids*; Springer-Verlag: New York, 1983.

[10] Torchia, D. *J. Magn. Reson.* **1978**, *30*, 613.

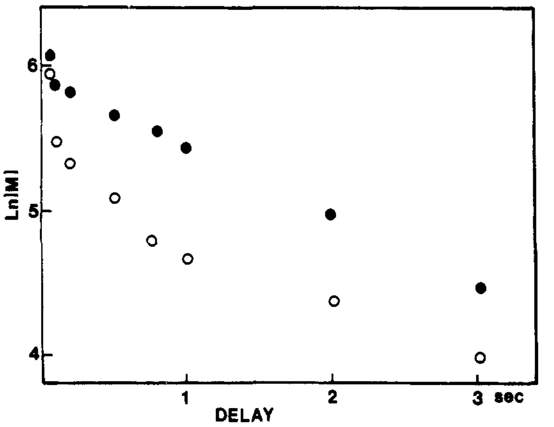

Figure 4. Results of a laboratory-frame ^{13}C relaxation measurement on the sample, HY(400)/15% MeOH. Open circles represent data from the signal at 50.1 ppm and filled circles represent data from the peak at 55.7 ppm.

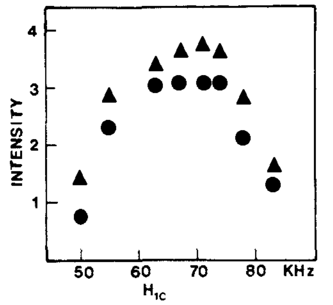

Figure 5. Plots of the peak heights of the lines at 55.7 and 50.1 ppm as a function of H_{1C} at constant H_{1H}. Circles represent the 55.7-ppm line and triangles represent the 50.1-ppm line.

fit to a two-component decay results in $T_1^C \approx 50$ ms for one component and an equal contribution from a component with $T_1^C = 1.7$ s.

Although the sample at the higher loading level of methanol (15% by weight) has a CPMAS spectrum which is dominated by a single broad peak at 50.1 ppm, at a loading level of 10% a second resonance, which appears at 55.7 ppm, is resolved and a third resonance remains unresolved from the 50.1-ppm line. The presence of the third resonance is manifested in the two-component T_1^C decay observed for the 50.1-ppm peak. The major component at higher loading levels could be due to "intercrystalline fluid" methanol of the sort one would expect to see in a liquid-state NMR experiment, i.e., relatively mobile, liquidlike material that resides in the supercages of the zeolite but which does not experience a strong, specific interaction with an acid site. The results of the $T_{1\rho}^C$ experiment on HY(400)/15% MeOH tend to support this idea, as does the relatively short T_1^C value measured for this species. However, the ease with which this species can be observed by cross polarization remains unexplained at this point.

It is possible to obtain a qualitative understanding of the dipolar processes involved in the cross polarization by determining the cross-polarization efficiency as a function of the radio frequency field strength. A spin system with weakly coupled protons will show greater sensitivity to changes in the proton and carbon radio frequency field strengths, H_{1H} and H_{1C}, respectively, than will a system with more strongly coupled protons.[11] Figure 5 shows a plot of the ^{13}C CPMAS peak height of both the 50.1- and 55.7-ppm resonances of HY(400)/10% MeOH as a function of H_{1C} at constant H_{1H}. It is evident that there is not an abrupt change in the height of either peak as H_{1C} is changed. It follows that the protons involved in the cross polarization of the species giving a ^{13}C CPMAS resonance at 50.1 ppm experience relatively strong dipolar coupling, even if part of the 50.1-ppm peak is due to a mobile species, for which the intramolecular ^{13}C–^1H dipolar coupling may be weak.

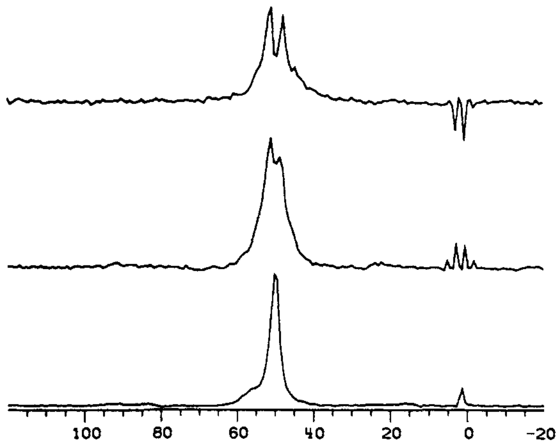

Figure 6. ^{13}C Bloch-decay MAS spectra of HY(400)/10% MeOH. Top: ^1H coupled with 1-ms preacquisition delay. Middle: ^1H coupled, acquired immediately after the ^{13}C 90° pulse. Bottom: ^1H decoupled.

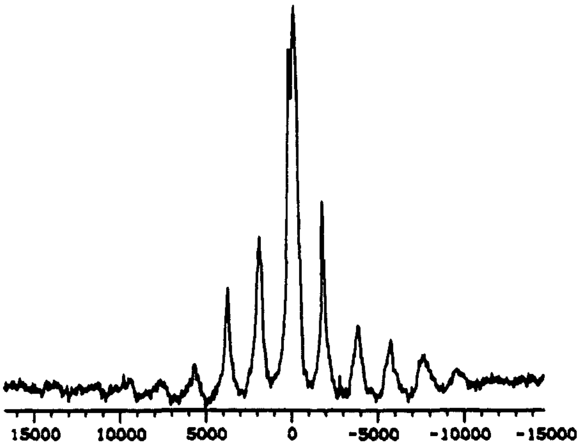

Figure 7. ^1H coupled ^{13}C CPMAS spectrum of HY(400)/10% MeOH.

A series of Bloch-decay ($\pi/2$ pulse, observe, delay) MAS spectra of HY(400)/10% MeOH are presented in Figure 6. The bottom spectrum is the routine Bloch-decay MAS spectrum, with high-power proton decoupling applied during acquisition of the free induction decay (FID). From the relative intensities it is clear that the resonance at 50.1 ppm is dominant, comprising roughly 90% of the total signal intensity. The middle spectrum is a Bloch-decay MAS spectrum recorded without proton decoupling. The resonance at 50.1 ppm has apparently split into a partially resolved *J* quartet, while the resonance at 56 ppm is no longer visible. The top spectrum in Figure 6 is the proton-coupled Bloch-decay MAS spectrum obtained with a delay of 1 ms imposed between the ^{13}C 90° pulse and acquisition of the FID. The resolution for the multiplet at 50.1 ppm is considerably better than that in the spectrum obtained with no delay, taking on the appearance of a broadened quartet. A broader component has decayed during the 1-ms preacquisition delay, indicating the presence of spins that are more strongly dipolar coupled in the sample. The central splitting in this apparent quartet is roughly 148 Hz, which is larger than that of pure CH_3OH (142 Hz), but not unreasonable for a related species of the CH_3–O–X type. This ability to resolve *J* coupling indicates that molecular motion averages ^{13}C–^1H and ^1H–^1H dipolar coupling nearly to zero. In this sense, the 50.1-ppm resonance coresponds to a species of nearly liquidlike mobility.

If the 50-ppm peaks in the cross polarization and Bloch-decay spectra are due to the same chemical species, then *J* coupling would be expected to appear in the proton-coupled CPMAS spectrum. Figure 7 shows the proton-coupled CPMAS spectrum of HY(400)/10% MeOH. This spectrum displays a sideband pattern extending roughly 10 kHz on each side of the 50-ppm

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Table I. ^{13}C Chemical Shifts (ppm from Me_4Si) of Several Alcohols on HY(400)

	C1	C2	C3	C4
methanol	55.7 (+6.4)[a] 50.1 (+0.8)			
ethanol	68.7 (+11.4) 60.1 (+2.8)	15.0 (−2.9)		
1-propanol	66.6 (+2.7)	24.9 (−1.20)	8.08 (−2.12)	
2-propanol	23.8 (−1.6)	67.3 (+3.6)		
2-butanol	19.67 (−3.23)	73.18 (+4.2)	30.49 (−1.8)	8.08 (−2.1)
2-methyl-2-propanol	71.67 (+2.5)	29.77 (−1.3)	19.77 (−0.6)	

[a] Difference in ppm from values for pure liquids given in parentheses.

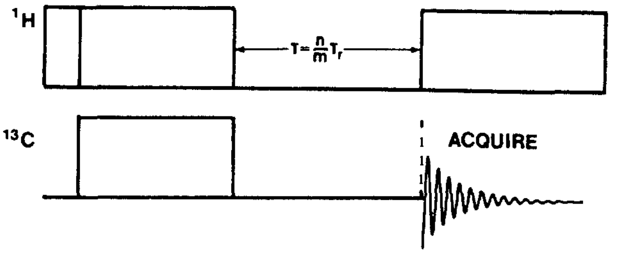


Figure 8. Pulse sequence for the rotationally synchronized interrupted-decoupling experiment.

region. The spinning sidebands in this spectrum are characteristic of an inhomogeneous interaction, which in this case points to an inhomogeneous ^{13}C–^{1}H dipolar coupling; i.e., the proton dipolar coupling experienced by ^{13}C is time-independent (apart from modulation under MAS) over the duration of one or more spinner periods. ^{13}C–^{1}H dipolar coupling within an isolated methyl group will be inhomogeneous as a result of rapid internal rotation of the methyl group. If the methyl protons within a specific methyl group are involved in rapid flip–flop processes with other protons, the ^{1}H–^{13}C dipolar coupling of the methyl carbons will be rendered homogeneous. Thus, Figure 7 shows that the methyl protons of one of the immobilized species must be removed from dipolar contact with other protons in the system.

The periodic refocussing of an inhomogeneous resonance can be seen clearly in a rotationally synchronized interrupted-decoupling experiment. The pulse sequence employed in this experiment is shown in Figure 8. In this experiment the ^{13}C magnetization is prepared by cross polarization and allowed to evolve without proton decoupling for an incremented time, T, which precedes the data acquisition period. High-power proton decoupling is employed during data acquisition. The value of T is chosen to be a fraction of the sample rotation period, so that $T = nt_{\mathrm{rot}}/m$, where n and m are integers. During the evolution period the ^{13}C magnetization evolves under both the chemical shift and dipole–dipole interactions, which are both modulated by magic-angle spinning. When the decoupler is turned on for accumulation of the signal, the dipolar coupling is removed and the magnetization retains the dephasing accumulated during the evolution under dipolar coupling. In this experiment a homogeneously broadened resonance will show a rapid decay as a function of T, and the signal intensity will not refocus at $T = nt_{\mathrm{rot}}$. In contrast, the intensity of an inhomogeneously broadened resonance will refocus at $T = nt_{\mathrm{rot}}$. The results of a series of rotationally synchronized interrupted-decoupling experiments with $T = nt_{\mathrm{rot}}/4$ are displayed in Figure 9. The 56-ppm resonance demonstrates the rotational dipolar echo expected of inhomogeneous dipolar coupling. There is clearly a two-phase pattern in the behavior of the 50-ppm peak. One component of this peak decays quickly over the first 100-μs delay, and a second component persists with only slight decay over the duration of that segment of the experiment (roughly 1 ms). The rapid decay of the first component is what one expects from a homogeneous interaction, as in a typical, strongly coupled organic solid. The second, persistent behavior is characteristic of a species with liquidlike mobility; i.e., the protons of this species are almost decoupled from each other and other protons by molecular motion.

Steric Restriction. The isolation of the species corresponding to the resonance at 55.7 ppm, as reflected by its inhomogeneous ^{1}H–^{13}C dipolar coupling, suggests adsorption into the β cages of HY. Species located in the β cage would be relatively remote from the bulk of the adsorbed material and thus might experience reduced ^{1}H–^{1}H dipolar coupling. The interaction of an alcohol with a β cage site will be limited to those alcohols that are sterically capable of accessing the sites. In order to pursue this idea, a set of experiments was carried out in which a series of alcohols, all of which are small enough to pass the 12-ring aperture of the supercage, were adsorbed onto HY(400), and the NMR spectra were recorded. Table I summarizes the ^{13}C chemical shift results of several alcohols adsorbed into HY(400). Only methyl and ethyl alcohols yield zeolite-adsorption ^{13}C spectra that contain an α-carbon "splitting" that is indicative of interaction with two distinct sites in HY. The α-carbon resonances of the remaining alcohols are slightly (but significantly) displaced from their corresponding liquid-state spectra. Displacements for carbons not at the α position are seen to be very small. The data clearly indicate that there is a steric restriction on the interaction with one of the sites in the zeolite. Interaction with this site, when allowed (i.e., with CH_3OH or CH_3CH_2OH), produces a relatively large perturbation of the ^{13}C chemical shift.

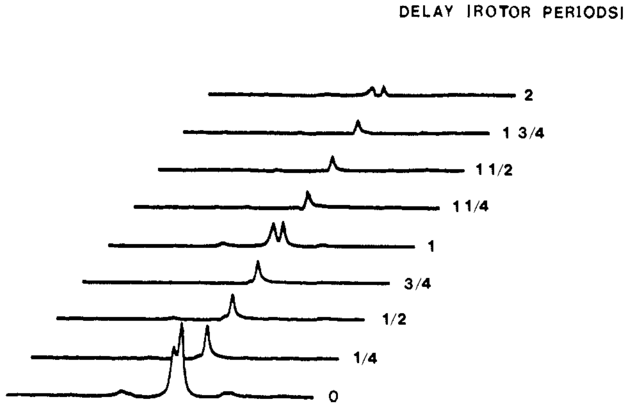


Figure 9. Evolution of the ^{13}C resonances of HY(400)/10% MeOH during the rotationally synchronized interrupted-decoupling experiment.

Effect of Activation Temperature. The ^{13}C CPMAS spectra of methanol adsorbed onto HY(300), HY(500), and HY(600) are shown in Figure 10. Perhaps the most noticeable feature of this series of spectra is the loss of intensity at 56 ppm from the spectra of the samples activated at 500 and 600 °C. In these latter two cases there are still spinning sidebands observed for the resonance in the 50-ppm region. Clearly the site associated with the 56-ppm resonance has been destroyed in the activation and/or the access of methanol to that site is denied as a result of structural changes within the zeolite. It has been reported that the heating of NH_4Y in vacuo to temperatures in the range of 500 °C results in the formation of cationic aluminum species that populate the β cages.[12] Adsorption of methanol into the β cage would presumably be blocked by the presence of such cationic aluminum species.

Desorption. In another set of experiments, rotationally synchronized interrupted-decoupling ^{13}C CPMAS experiments were performed on samples that were activated at progressively higher temperatures. The original sample containing 10% CH_3OH by weight was evacuated for 12 h at 40, 90, and 140 °C, and the NMR experiments were performed at each stage. Rotationally

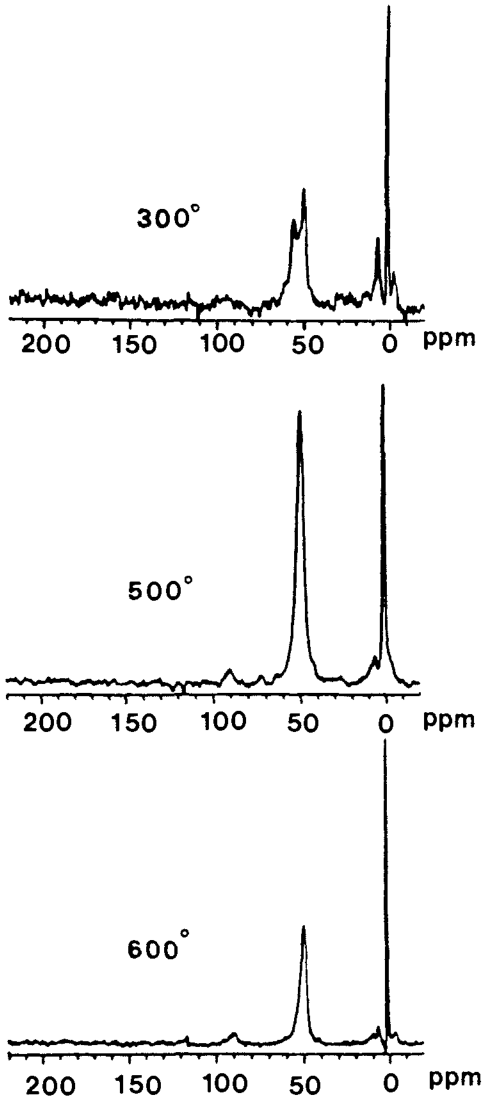


Figure 10. Effect of zeolite activation temperature (300, 500, 600 °C) on the ^{13}C CPMAS spectrum of methanol on HY. Methanol loading levels are 5%, 8%, and 7% by weight, respectively.

synchronized interrupted-decoupling results for the samples evacuated at 40 and 90 °C are shown in Figure 11. It can be seen that the 55.7-ppm resonance becomes relatively more intense as the sample is evacuated at higher temperatures. In the 40 °C sample a slight echo can be seen in the 50-ppm region, superimposed upon the unmodulated decay of the liquidlike resonance. The sample at 90 °C also shows an echo in the interrupted-decoupling experiment. The ^{13}C CPMAS spectrum of the sample evacuated at 140 °C (not shown) is dominated by the resonance at 55.7 ppm. The species in the 50.1-ppm region are detectable only as a small shoulder on the 55.7-ppm resonance.

Evacuation of the sample preferentially removes the species in the 50.1-ppm region and results in the damping of proton spin diffusion in the solidlike species in this region. An interpretation that is consistent with these results is that the solidlike species with its resonance in the 50-ppm region corresponds to species that are immobilized within the supercage. Spin diffusion between the protons in these species and those in mobile "intracrystalline" methanol is the source of the homogeneous ^{13}C–^{1}H dipolar coupling associated with this resonance. Cross polarization of the mobile species (50.1 ppm) also proceeds via dipolar coupling to the species bound in the supercage. Molecular motion of the mobile species is sufficient to average intramolecular ^{1}H–^{1}H dipolar coupling but will not remove ^{1}H–^{1}H dipolar coupling to molecules immobilized on the surface of the more-or-less spherical supercage cavity. The intermolecular ^{1}H–^{1}H coupling between mobile and bound methanol is weak enough to allow resolution of J coupling, but the protons of the immobilized methanol-derived species are strongly coupled to one another. Thus, cross-polarization efficiency of the mobile resonance will be relatively insensitive to misadjustments in the Hartmann–Hahn matching condition. It is the *width* of the proton resonance of immobilized protons, acting as the ^{1}H reservoir for cross polarization, not the mobility of the ^{13}C-containing species that is observed, that primarily determines the sensitivity to match, although that mobility will play a role in the cross-polarization dynamics.

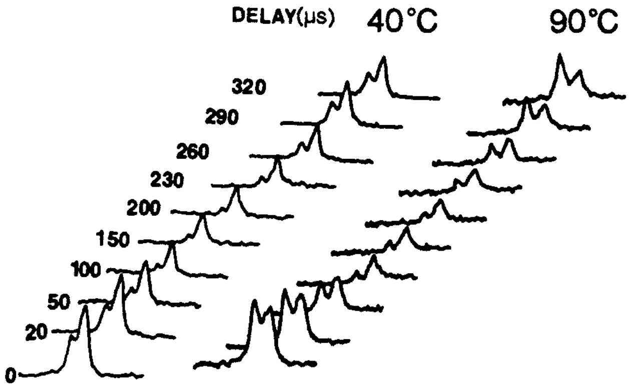
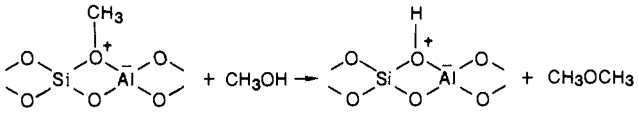


Figure 11. Evolution of the ^{13}C magnetization of HY(400)/10% MeOH under the rotationally synchronized interrupted-decoupling experiment, after evacuation at 0.1 μm for 12 h at 40 and 90 °C.

It is our interpretation that evacuation at 140 °C removes species in the supercage, but not those in the β cage. This is consistent with the proposed mechanism in which desorption of methoxysilane groups occurs by the formation of dimethyl ether and regeneration of the acid site.[1]



Methoxysilane groups located in β cages are retained during evacuation because of the unavailability of free methanol for participation in this reaction.

Summary

The ^{13}C NMR spectrum of 10% methanol adsorbed onto HY(400) contains two resolved peaks, one at 55.7 ppm and one at 50.1 ppm. At higher loading, the 50.1-ppm peak dominates the spectrum. The 50-ppm peak has contributions from two distinct species. This point was first brought out above by the biphasic T_1^{C} relaxation behavior of this peak and later confirmed in a rotationally synchronized interrupted-decoupling experiment, in which the two components exhibit completely different ^{13}C–^{1}H dipolar coupling behaviors.

The 50-ppm region of the Bloch-decay spectrum confirms the presence of mobile methanol molecules (50.1 ppm), which are seen to be the predominant species in the system. The comparatively weak intensity of this signal in the CPMAS experiment reflects a weak residual ^{13}C–^{1}H dipolar coupling that results in poor cross-polarization efficiency. This would lead one to expect that the cross-polarization rate for this species would be very sensitive to the accuracy of the Hartmann–Hahn match. However, it is not; it was demonstrated that one can move several kHz off the Hartmann–Hahn condition and still achieve cross polarization. Cross polarization of the mobile species must therefore occur via intermolecular dipolar contact to a reservoir of strongly coupled protons.

The second species in the 50-ppm region behaves in an NMR sense more like a solid. It displays chemical shift anisotropy, which means it is immobilized to some degree, and it displays homogeneous ^{13}C–^{1}H dipolar coupling. Evacuation of the sample results in partially inhomogeneous ^{13}C–^{1}H dipolar coupling in this species, as indicated by rotationally synchronized interrupted-decoupling experiments. Thus, we believe that this species acts as the proton reservoir for cross polarization of the mobile methanol species.

The third resonance, at 55.7 ppm, also behaves like the resonance of a bound species. The ^{13}C–^{1}H dipolar coupling corresponding to this resonance is inhomogeneous, which can be the case only if there is no appreciable ^{1}H spin diffusion from the methyl protons to other protons in the system. Each molecule of this species must therefore be in a region that is relatively isolated from protons not part of the molecule itself. Adsorption of a series of alcohols on HY indicates that there is a steric restriction associated with the site corresponding to the 55.7-ppm resonance in the methanol system. Access to this site is denied in zeolite samples activated at 500 and 600 °C, arguing against identifying the 55.7-ppm peak with a defect Al–O–CH_3 species. We interpret these data as indicating the adsorption of methanol and ethanol into the β cages of HY zeolite. Adsorption into the β cage probably requires a distortion of the 6-ring aperture, which has a diameter of approximately 2.2 Å,[12] to pass the alcohol. It is known that the framework of a zeolite can become distorted during the adsorption of a species with which it has a strong interaction.[12,13] The diameter of methanol, calculated from the Stockmayer potential,[12,14] is 2.4 Å; this compares to 2.6 Å for ammonia, which we know can exit the β cage.[12] We expect that the critical dimension perpendicular to the C–C bond axis of ethanol would be similar to the critical dimension of methanol. The higher alcohols, having bent C–C–C arrangements, will have substantially larger effective diameters. Methanol moieties interacting with the β-cage site are not desorbed by evacuation at 140 °C, a fact that also (1) argues for the isolation of the 55.7-ppm CH_3O species and (2) is consistent with the energetics one would expect for the 6-ring distortion that would be required for CH_3OH or CH_3OCH_3 desorption from a β cage, even if the 55.7-ppm CH_3O species were not mutually isolated.

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Mechanisms of Longitudinal ^{29}Si Nuclear Magnetic Relaxation in Aqueous Alkali-Metal Silicate Solutions

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Abstract: Silicon-29 longitudinal NMR relaxation times (T_1) have been measured by the inversion-recovery method over a range of solution compositions and temperatures (0 to +100 °C) for several of the silicate species which occur in solutions of silica in H_2O–D_2O alkali-metal hydroxide (MOH) solutions. At sufficiently high temperatures, Si–Si chemical exchange causes gross averaging of the apparent T_1 values so obtained, this becoming evident at ~20 °C for $[M^+]:[Si^{IV}] = 1.0:1$ and at higher temperatures for higher $[M^+]:[Si^{IV}]$ ratios. The predominant relaxation process evidently involves dipole–dipole interactions between ^{29}Si and M^+ nuclei (M = Na, K, Rb), with minor contributions from the ^{29}Si–^{1}H dipole–dipole mechanism. Contributions to T_1^{-1} from the spin-rotation mechanism are apparent for the smaller silicate species, but in general are of minor importance. These observations explain why previously reported T_1 values for ^{29}Si in aqueous alkali-metal silicates were much shorter than for other silicon compounds, such as organosilanes, and varied markedly from study to study because of differing experimental conditions.

An understanding of the dependence of the longitudinal nuclear magnetic relaxation time T_1 on sample composition and conditions is essential if quantitative NMR spectra are to be obtained, and can also provide useful information concerning molecular structure and dynamics. In the case of ^{29}Si NMR of $(HO)_3SiO^-$ and its polymers in aqueous alkaline solution, reported T_1 values are unusually short for silicon compounds[1,2] and range from about 0.5 s in a solution containing 2 mol kg^{-1} of Si^{IV} and 6 mol kg^{-1} of Na^+ [3] to 26 s in one containing <0.05 mol L^{-1} of Si^{IV} and 0.6 mol L^{-1} of Na^+ [4] for the dimer at 25 °C. This paper explores the reasons for this relative shortness of T_1 in aqueous silicates and for its variability.

Early on, it was suggested[3] that such efficient ^{29}Si relaxation could arise from rapid interchange between protonated and deprotonated silanol groups which, having different chemical shifts, should generate an appropriate fluctuating magnetic field. Harris and Newman,[5] however, noted that this field would be parallel to the external field B_0 and so could not cause longitudinal relaxation. Instead, they concluded from their observations of "aging" effects in silicate solutions contained in unlined glass NMR tubes that unidentified paramagnetic contaminants, introduced during sample preparation and/or by leaching from the NMR tubes, were probably the dominant factors controlling transverse (T_2) and longitudinal ^{29}Si relaxation.[2,5] Recently,[6] we demonstrated that temperature-dependent transverse relaxation of ^{29}Si in aqueous alkali-metal silicate solutions is due primarily to Si–Si chemical exchange mediated by $H_3SiO_4^-$. We now report evidence

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