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# Spatial Correlation of Charge Centers in the Tectosilicate Nonasil Determined by Multidimensional {$^1$H} → $^2$H CPMAS NMR Correlation Spectroscopy

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NMR spectroscopy has been a powerful tool in developing a fundamental understanding of zeolite synthesis.[1] It is well established in zeolite synthesis that the size and geometry of the organic structure-directing agent (SDA) strongly influence the structure of the final synthesis product.[1] However, the ionic interactions between the cationic SDA and the zeolite framework and their role in zeolite synthesis are poorly understood. We have previously shown that in as-made nonasil samples synthesized with trimethylalkylammonium compounds there are strong organic−inorganic forces that, for example, prevent isotropic reorientation of the SDA.[2] In contrast, electrically neutral molecules used to synthesize nonasil and other clathrasils reorient isotropically in the clathrasil cages.[3] An unresolved issue of our earlier study was whether the charges on the organic molecule and the nonasil framework are spatially ordered. Here we present compelling evidence in support of the spatial correlation of the charge centers using two-dimensional $^1$H−$^2$H CPMAS NMR correlation spectroscopy. While the possibility of $^1$H−$^2$H CPMAS NMR has been demonstrated previously in model systems[4] and a few theoretical investigations have been presented,[5] to the best of our knowledge this is the first time in which $^1$H−$^2$H CPMAS NMR is used to answer a pertinent question in zeolite materials chemistry. The results presented here clearly illustrate the importance of electrostatic interactions in structure direction and zeolite synthesis.

The synthesis, characterization, and dynamics of SDAs occluded in high-silica nonasil made with trimethylalkylammonium compounds have been presented elsewhere.[2] Figure 1 shows a tentative model developed for as-made nonasil based on previous work.[2,6] We present here the 2D $^1$H−$^2$H NMR correlation spectra for nonasil samples prepared with *N,N,N*-trimethylcyclopentylammonium-$d_9$ ($d_9$-TMC5) and *N,N,N*-trimethylcyclohexylammonium-$d_9$ ($d_9$-TMC6). Figure 2 shows the $^1$H−$^2$H CPMAS and the $^1$H MAS spectrum of $d_9$-TMC6 nonasil with a spin rate of 9 kHz. Samples with SDAs selectively deuterated at the methyl groups have relatively small deuterium quadrupole coupling constants (QCC) of approximately 15 kHz, due to fast rotations about the methyl group $C_3$ axis and the nitrogen N−R bond.[2] None of the SDAs used isotropically reorient on the $^2$H NMR time scale ($\sim 10^{-7}$ s), in contrast to nonasil samples made with electrically neutral amines.[3]

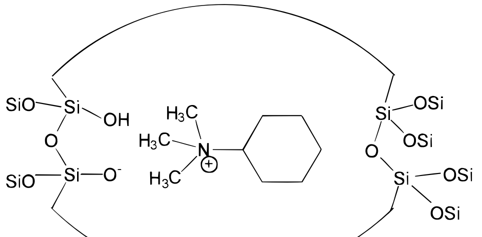

**Figure 1.** Tentative model for as-made nonasil based on previous work.

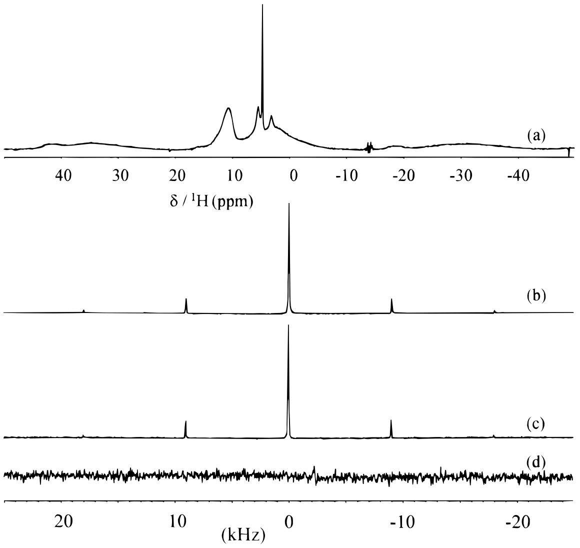

**Figure 2.** (a) $^1$H NMR spectrum of $d_9$-TMC6 nonasil. (b) Single pulse $^2$H MAS spectrum. (c) $^1$H−$^2$H CPMAS spectrum, 2 ms contact time. (d) $^1$H−$^2$H CPMAS spectrum, no $^1$H RF. For all spectra the rotor frequency is 9 kHz. Thirty-two scans were acquired for spectra b−d. All spectra were acquired on a Bruker MSL 300 spectrometer.

The $^1$H MAS NMR spectrum of high-silica nonasil synthesized with trimethylalkylammonium cations consists of a broad asymmetric line at ∼3 ppm due to the structure-directing agent fully resolved from a line at ∼10.5 ppm due to silanols hydrogen bonded to a siloxy group. There is also a Lorentzian line at 4.8 ppm due to water and a line at 5.5 ppm due either to water or additional silanol groups not engaged in strong hydrogen bonding. Previous investigations with several as-made all-silica zeolites showed that siloxy groups are present to balance the charge of cationic organic structure-directing agents.[6] Additionally, it was concluded that three silanol groups are present per siloxy group, two of which are strongly hydrogen bonded to the siloxy group with an average Si−OH···$^-$O−Si distance of ∼ 2.7 Å. Here, we want to determine whether these silanol groups are located near the methyl groups of the SDA.

Nonasil samples were prepared by using SDAs with perdeuterated methyl groups and $H_2O$ as the solvent. These were chosen due to their strong $^2$H signal and because the broad $^1$H NMR resonance at 3 ppm is now only due to the protons on the cyclic alkyl group.[7] If the methyl groups are in close proximity ($\leq 2$ Å) to the defect sites it should be possible to get *selective* magnetization transfer from the protons on the silanols to the deuterium-labeled methyl groups.

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[7] Solution $^1$H NMR was performed on the neat $d_9$-iodide salts in $D_2O$ to verify the methyl groups were fully deuterated (not shown).

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For the $^1H-^2H$ CPMAS experiments, the $^2H$ RF field was fixed at 50 kHz (5 $\mu$s, 90°), the $^1H$ RF field was varied to satisfy the Hartmann–Hahn match, and the rotor frequency was 9.0 kHz. To verify the presence of cross-polarization (CP), spectra were acquired with (1) a single-pulse ($^2H$) sequence, (2) the CP pulse sequence with the Hartmann–Hahn match satisfied, (3) the CP pulse sequence but with the Hartmann–Hahn match not satisfied, and (4) the CP pulse sequence with the $^1H$ RF turned off. In cases (3) and (4) no appreciable signal was observed, which verifies the inefficiency of the cross-polarization pulse sequence for $^2H$ when the Hartmann–Hahn match is not satisfied. In cases (1) and (2) a signal can be observed from a single scan. The integrated spectral intensity of (2) is approximately 60% of the intensity of (1). The theoretical maximum improvement in signal-to-noise is $S_{CP}/S_{\pi/2} = \gamma_{^1H}/\gamma_{^2H} = 6.5$, though the actual value for our samples is about 0.6. This is due to three factors: (1) the deuterons on the organic are undergoing two rapid rotations,[2] (2) in our samples the deuterons are not isolated and dilute relative to the proton reservoir ($N_{^2H} = 9$, $N_{^1H} \approx 16$), and (3) for spin $I = 1$ nuclei spin-locking and cross-polarization are in general not as efficient as in the spin $I = {}^1/_2$ case.[5b,8] For the nonasil samples studied in this work the $^2H$ RF field is much larger than the quadrupole coupling constant, which generally results in an improved efficiency of spin-locking. Efficient spin-locking of the protons in the sample was verified by performing $T_{1\rho}$ experiments using the $^1H$ RF field found to optimize the Hartmann–Hahn match.

The multidimensional correlation NMR pulse sequence consists of a $^1H$ 90° pulse followed by the $t_1$ increment, then the cross-polarization pulse sequence with the $^2H$ signal observed. Phase settings for the pulses are similar to those used by Vega in two-dimensional $^{29}Si-^1H$ correlation experiments.[9] The phase listings, optimization of the Hartmann–Hahn match, and other issues of the two-dimensional correlation experiments will be described elsewhere.[11]

The results of the 2D correlation experiment for $d_9$-TMC6 nonasil made in $H_2O$ are shown in Figure 3. The only signal observed is centered at 10.5 ppm in the $^1H$ (F1) dimension. This signal is a result of cross-polarization from the silanol protons to the methyl group deuterons. A cross section of the spectrum clearly shows that the line at 10.5 ppm has a much larger relative intensity in the 2D experiment than in the 1D proton spectrum (Figure 1). As has been shown previously, the proton resonance at 10.5 ppm is due to silanols hydrogen bonded to the charge-compensating siloxy group.[6] Molecular modeling performed with CERIUS$^2$2.0[10] shows that the average distance from the methine proton to the *closest* methyl deuteron is between 1.9 and 2.2 Å, and the closest methylene protons on the cyclohexyl ring are approximately 2.3 Å from the closest methyl deuterons. At a contact time of 200 $\mu$s no appreciable signal intensity is observed between 1 and 5 ppm, indicating that the silanol protons are closer to the methyl deuterons than the protons on the cyclohexyl ring. Experiments ran with a 600 $\mu$s contact time and a $^2H$ RF field of 42 kHz reveal a small signal centered at 3.2 ppm; this signal corresponds to the $^1H$ solution NMR resonance of the methine proton on the cyclohexyl ring. The same 2D NMR experiment was performed on the $d_9$-TMC5 nonasil sample in $H_2O$ (not shown), and similar results were obtained. The weak resonance at ~6 ppm will be discussed in detail elsewhere.

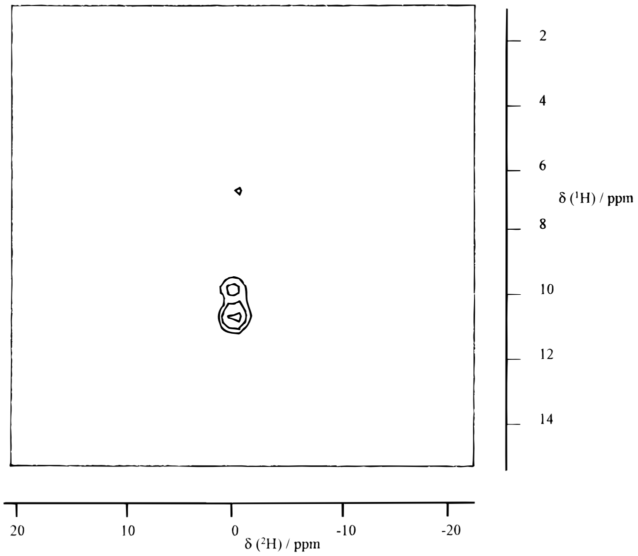

**Figure 3.** $^1H-^2H$ CPMAS 2D correlation spectrum for $d_9$-TMC6 nonasil (128 experiments, 200 $\mu$s contact time, 64 scans per experiment).

These results give the first evidence in support of a model that locates the charge center of the SDA spatially ordered toward the charge-compensating defect site in the zeolite framework. While extrapolation to synthesis conditions must be done with care, these results clearly show the importance of electrostatic interactions in as-made high-silica nonasil. These results suggest an additional role for the SDA, which is the control of the location of $T^{3+}$ atoms in the zeolite framework. These results also illustrate the utility of this experiment; the defect sites in these materials are in all likelihood not ordered in a crystallographic sense, but we can still determine the orientation of the SDAs relative to the defect sites. The defect sites in nonasil appear spectroscopically to be similar to defect sites in other high-silica materials,[6] so these results may apply generally to microporous silicates.

In summary, we have used a new variation of NMR multidimensional correlation spectroscopy to show the organic and inorganic charge centers in as-made nonasil are in close spatial proximity (near van der Waals contact). This experiment allows us to study spatial ordering at a length scale of ~2 Å in a material with defects that likely have no long-range order. These results clearly show the importance of electrostatic interactions in zeolite synthesis. This experiment should be of use in other areas such as studies of polymer interfaces, polymer liquid crystals, or ceramics where selective deuteration is possible.

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(11) The technical details of the 2D experiments as well as results for the $d_9$-TMC5-NON sample will be discussed in a future publication.