Multiple-Quantum ^{1}H MAS NMR Studies of Defect Sites in As-Made All-Silica ZSM-12 Zeolite

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Abstract: Multiple-quantum ^{1}H MAS NMR spectroscopy has been used to study defect sites in siliceous as-made ZSM-12 zeolite synthesized with perdeuterated benzyltrimethylammonium cations. The results of two-dimensional double-quantum and triple-quantum ^{1}H MAS NMR experiments show that three silanol (SiOH) protons of the defect site engage in hydrogen bonding with the charge-compensating siloxy (SiO^-) group. Simulations of the double-quantum sideband pattern were used to determine an average dipolar coupling between the protons of 4.0 (±0.5) kHz (an equilateral triangular geometry is assumed). This value corresponds to a maximum distance of 3.1 (±0.1) Å, if the protons are rigid. We believe that these results have important implications concerning the nucleation mechanism of high-silica zeolites, as they provide new information on the structure of charge-compensating units in the zeolite colloidal precursors reported by others.

Introduction

Zeolites are an important class of microporous solids which are used industrially in heterogeneous catalysis, the adsorption and separation of gases, and ion-exchange operations.[1] The catalytic and adsorption properties of zeolites are strongly affected by structural features such as the framework composition, topology, and identity of extraframework cations. Framework defects including stacking faults and tetrahedral vacancies are also known to affect the catalytic and adsorption properties of zeolites.[2] However, the structures of defects in zeolites are difficult to study because they are usually not ordered in the crystallographic sense, and therefore are not easily amenable to analysis by diffraction methods.

Solid-state NMR spectroscopy offers numerous powerful methods suitable to characterizing structural features which do not exhibit long-range order. Strong anisotropic couplings present in solids usually cause severe NMR line broadening in nonrotating powders. Magic-angle spinning (MAS) can be used to improve spectral resolution, as it averages out the anisotropic couplings that lead to broad lines. High-resolution spectra can be obtained under the conditions of MAS, which allows a straightforward and quantitative characterization based on the isotropic chemical shift of different sites. Although measurements of anisotropic interactions, such as the homonuclear dipolar coupling, contain structural information, these anisotropic couplings are eliminated under the conditions of fast MAS. The development of experiments which allow the measurement of the homonuclear dipolar interaction under the high-resolution conditions of MAS has been a major advance in solid-state NMR spectroscopy.[3,4] Using double-quantum (DQ) and triple-quantum (TQ) techniques it is now possible to extract structural details of homonuclear systems of spins.[4] In the two-dimensional double-quantum NMR experiment presented here the scale in the F2 dimension corresponds to the chemical shift. The F1 dimension contains the chemical shifts of the double quantum signals which depend on the chemical shift of the participating nuclei. For a two-spin system double-quantum intensity is observed at a chemical shift of $\delta_{DQ} = \delta_1 + \delta_2 - \delta_c + n(\nu_{MAS}/\nu_{ref})$, where δ_1 and δ_2 are the chemical shifts of the two nuclei, δ_c is the chemical shift of the carrier frequency, ν_{MAS} and ν_{ref} are the sample spinning frequency and the reference frequency, respectively, and n is an integer number representing the order of spinning sidebands observed in the DQ dimension. All chemical shifts given in the text of this report are in the F2 dimension.

The dipolar coupling is strongly dependent on the internuclear distance and can be used to determine the geometry of the coupled spins. Distances and bond angles can be determined from sideband patterns in the F1 dimension of nonrotor synchronized two-dimensional (2D) DQ NMR spectra or by measurement of multiple-quantum excitation curves. The experimental spectra and curves are then simulated for different geometries/interaction strengths, as has been demonstrated for a number of spin $I = {}^1/_2$ isotopes.[5] Two-dimensional MQ NMR spectroscopy offers the additional advantage that spectral

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artifacts are easily discerned because multiquantum resonances in the indirect dimension appear at frequencies that are different from those of single-quantum resonances.[6]

Here we report a double- and triple-quantum NMR spectroscopy investigation of as-made all-silica ZSM-12 zeolite synthesized with perdeuterated benzyltrimethylammonium cations as the structure directing agent. Previous studies of several as-made all-silica zeolites synthesized with a variety of quaternary ammonium compounds have shown the presence of a resonance in the one-dimensional ^{1}H MAS NMR spectra at approximately 10 ppm.[7] This resonance was assigned to internal defect silanol groups which are hydrogen bonded to the charge-compensating siloxy group. On the basis of empirical correlations,[8] the chemical shift of the resonance at 10 ppm corresponds to a Si−OH···$^-$O−Si oxygen−oxygen distance of 2.7 Å. This work[7] shows that there are two silicon−oxygen bonds broken per charge in the organic structure-directing agent, and thus the defect site consists of one charged SiO$^-$ group and three SiOH groups. On the basis of ^{1}H NMR spectra of all-silica ZSM-5 made with perdeuterated d_{28}-tetrapropylammonium cations (TPA), it was suggested that there are two strongly hydrogen-bonded silanol protons responsible for the resonance at 10 ppm. In addition, the third silanol was assigned to a resonance at 6.5 ppm in the ^{1}H MAS NMR spectrum. Since the first report on these defect sites,[7] substantial developments in NMR methods have taken place which now allow a more sophisticated study of homonuclear spin systems.

Here we investigate the structure of these defect sites using DQ and TQ ^{1}H MAS NMR. Our results show that in as-made ZSM-12 the resonance at 10 ppm is in fact due to three protons in close proximity, and not by two as was suggested previously. This was deduced from the sideband patterns observed in two-dimensional rotor-encoded double-quantum (DQ) MAS experiments, and independently verified using triple-quantum (TQ) MAS NMR by the observation of a triple-quantum signal at 10 ppm.

Experimental Section

All-silica ZSM-12 was synthesized with benzyltrimethylammonium (BTMA) hydroxide using a synthesis gel composition of 1 SiO$_2$:0.15 R$^+$OH$^-$:0.05 NaOH:40 H$_2$O. Perdeuterated benzyltrimethylammonium chloride was synthesized from d_9-trimethylamine (CIL, 99+%) and d_7-benzyl chloride (CIL, 99+%) in acetone. Details of the synthesis of benzyltrimethylammonium hydroxide can be found elsewhere.[9] Solution ^{1}H NMR verified there was no proton−deuteron exchange during the organic synthesis within detection limits of NMR. The synthesis of all-silica ZSM-12 was performed as follows: 25 mL of a 0.3 N d_{16}-benzyltrimethylammonium hydroxide solution was added to 3 g of Cab-O-Sil M5. Ground NaOH (0.1 g; 95% Aldrich) were added to this solution, followed by 7 mL of deionized water. The solution was allowed to mix for 2 h, until a translucent homogeneous liquid was obtained. The mixture was then charged into two 23 mL Teflon lined autoclaves and heated to 160 °C for 13 days under static conditions. The autoclaves were then quenched and the solids collected by filtration, washed several times with deionized water, and allowed to dry overnight at 80 °C. Samples were dried under vacuum (10^{-3} Torr) overnight at 100 °C prior to the NMR experiments to eliminate the presence of physisorbed water.

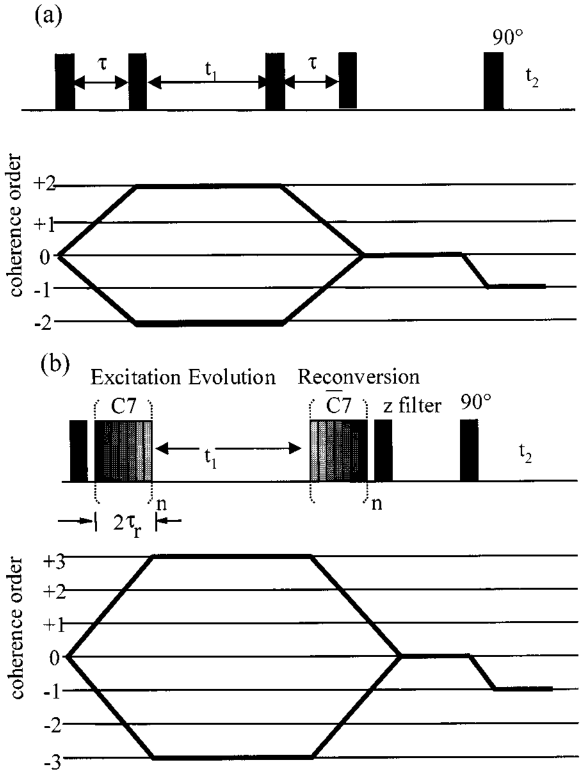

Figure 1. Pulse sequences used for double- and triple-quantum MAS experiments: (a) five-pulse sequence and (b) C7 sequence for TQ MAS.

Analytical. Powder X-ray diffraction (XRD) was performed using a Philips X'Pert System with Cu Kα radiation. The patterns were collected from 4−50° 2θ using the step scan mode, a 0.02° step size, and a 15 s count time per step. Analysis of the XRD patterns verified the materials are a pure and highly crystalline ZSM-12. Thermogravimetric (TGA) measurements were performed using a Cahn TG-121 microbalance with a heating rate of 2 °C/min from room temperature to 650 °C in air.

Solution ^{1}H NMR spectra were measured using a Bruker AC 250 spectrometer operating at 250 MHz with the chemical shifts referenced to tetramethylsilane. Solid-state ^{1}H NMR spectra were acquired on a Bruker Avance DSX 500 operating at 500.13 MHz. The ^{1}H MAS NMR spectrum was acquired using the DEPTH[10] sequence to remove the probe background. The DEPTH sequence consists of a 90° pulse (3.5 μs) followed by two 180° pulses. Two-dimensional double-quantum (DQ) and triple-quantum (TQ) NMR experiments were performed with the following general setup: excitation, evolution, reconversion, z-filter, read pulse, and detection. Rotor-encoded 2D DQ spectra were acquired with this setup using a simple two-pulse excitation and two-pulse reconversion, as found in ref 3b. Two-dimensional TQ NMR experiments were performed using a variation of the C7 sequence,[4a] where a 90° pulse is placed in front of the C7 sequence, thereby exciting triple-quantum (and higher odd order) coherences. The pulse sequences used are shown in Figure 1. The rotor-encoded 2D DQ MAS NMR experiments are performed with an increment time t_1 that is *not* a multiple of the rotor period (e.g., $t_1 = 7.58\ \mu\text{s} \neq Nt_R$). This leads to the observation of sidebands in the second spectral dimension, the number and relative intensities of which are directly related to the dipolar coupling between spins.[4d] The rotor-encoded 2D DQ MAS spectrum was acquired with a 90° pulse length of 3.5 μs, a recycle delay of 5 s, and a delay between the pulses of 30 μs, t_1 was changed in 7.58 μs increments, the rotor frequency was 11 kHz, 16 scans were acquired per FID, and 1024 experiments were performed. The delay between the reconversion pulses and the read-out pulse was 10 ms

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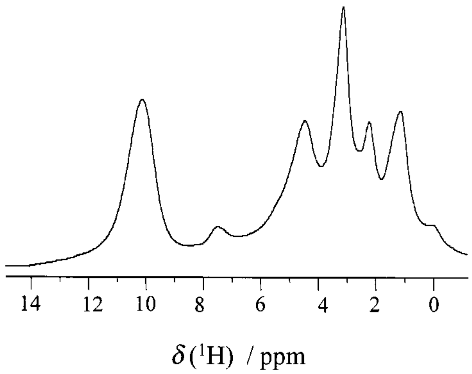

Figure 2. ^{1}H MAS NMR spectrum of as-made all-silica ZSM-12 zeolite synthesized with perdeuterated benzyltrimethylammonium cations.

for all experiments. The TQ C7 experiments were performed using a 3.57 μs 90° pulse and a rotor frequency of 10 kHz, thereby satisfying the necessary condition for C7 experiments that $\omega_{RF} = 7\omega_R$. The C7 experiments were performed using a 3 s recycle delay, t_1 was incremented in 100 μs intervals, an 800 μs excitation time was used, 64 scans were acquired per FID, and 64 experiments were performed. All 2D MQ spectra were rescaled in the MQ dimension such that autocorrelation signals have the same chemical shift in both dimensions.

The DQ rotor-encoded sideband patterns were numerically calculated with the SIMPSON software package.[11] Convergence of the simulated DQ spectra was satisfied with a powder average of 30 × 168 orientations and by approximating the time-dependent Hamiltonian by a product of piecewise constant Hamiltonians with a time step of 0.5 μs. Force field calculations were performed using the minimizer module in Cerius^2 3.8.[12] The force field derived by Hill and Sauer[13a] based on ab initio calculations was used, and was supplemented with the universal force field generator[13b] for terms not available in the force field, i.e., the bond and angle parameters for SiO$^-$ groups.[14]

Results and Discussion

^{1}H NMR. The ^{1}H NMR spectrum of as-made all-silica ZSM-12 is shown in Figure 2. The lines at 2.2 and 1.2 ppm are due to silanol protons on the surface of the crystals.[15] The narrow line at 3.3 ppm is due to the methyl protons, the broad asymmetric resonance at 4.5 ppm is assigned to the methylene protons of the BTMA cations, the signal at 7.5 ppm is due to the aromatic protons, and the line at 10.2 ppm is due to silanol protons hydrogen bonded in the charge-compensating defect sites in the framework.[7] ^{1}H NMR spectra of samples that have not been dehydrated (not shown) exhibit an additional resonance at approximately 5 ppm, which is assigned to a small amount of physisorbed water. The ^{1}H NMR spectrum of as-made Al-ZSM-12 synthesized with BTMA cations deuterated at the methyl and aromatic position also shows an asymmetric resonance between 5.2 and 4.5 ppm (see also ref 9). This asymmetric line and the signal at 4.5 ppm in the all-silica ZSM-12 sample studied here are both assigned to two structurally inequivalent protons within the same methylene group, based on the double-quantum NMR experiments described below. As discerned by the signals observed for the BTMA cations, substantial proton/deuteron exchange occurred during the zeolite synthesis period. The amount of proton/deuteron exchange was unexpected, and it has not been observed in other perdeuterated structure directing agents in zeolites before.

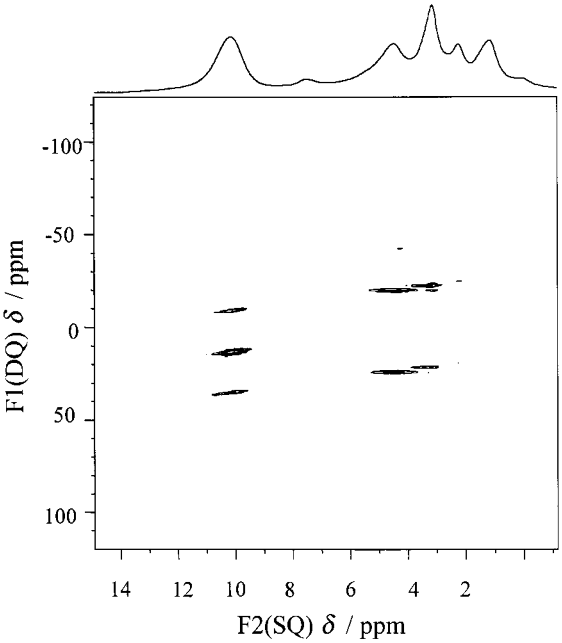

Figure 3. DQ rotor-encoded 2D ^{1}H MAS spectrum of as-made all-silica ZSM-12. The spectrum on top is the 1D SQ spectrum shown in Figure 2.

Multiple-Quantum NMR. Figure 3 shows the two-dimensional rotor-encoded DQ MAS NMR spectrum. The signal at 10 ppm in the SQ dimension is due to a double-quantum coherence generated by the cluster of silanol protons of the defect site. The other two signals are double-quantum coherences due to the methylene (4.5 ppm) and methyl (3.3 ppm) groups. Also, as expected, no DQ signals are observed at 1.2 or 2.2 ppm as the silanol protons on the surface of the crystals are isolated. The presence of a signal in the DQ spectrum indicates that two protons are in close proximity ($<$5 Å), as the DQ coherences observed are strongly dependent on the internuclear distance. Two important things can be discerned from the spectrum upon closer inspection. First, the resonance at 10 ppm has a central line in the DQ dimension but a central line is *not* observed for the signals at 4.5 and 3.3 ppm. The presence of a strong central line is consistent with the resonance at 10 ppm being due to more than two protons in close proximity. Spiess and co-workers have demonstrated when the sideband pattern is encoded in the second spectral dimension that a strong central line is not observed for isolated spin pairs.[4d] Second, the lines in Figure 3 have two different shapes. While the resonance at 10 ppm is broadened along the autocorrelation diagonal, the lines at 3.3 and 4.5 ppm are parallel to the F2 axis. This difference indicates that the two latter lines arise from protons in two inequivalent sites. DQ MAS NMR experiments performed on a sample of Al-ZSM-12 made with BTMA deuterated at the methyl and aromatic positions (not shown) exhibit a similar resonance at 4.5 ppm. This resonance in the Al-ZSM-12 sample is attributed to the double-quantum coherence generated by the methylene protons which are chemically inequivalent in the zeolite. Therefore, the signal at 4.5 ppm in Figure 3 is attributed to BTMA cations with both deuterons at the methylene position exchanged for protons. Obviously, some

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(11) SIMPSON, A general NMR simulation package. Written by M. Bak and J. T. Rasmussen, Department of Chemistry, University of Aarhus, Denmark.

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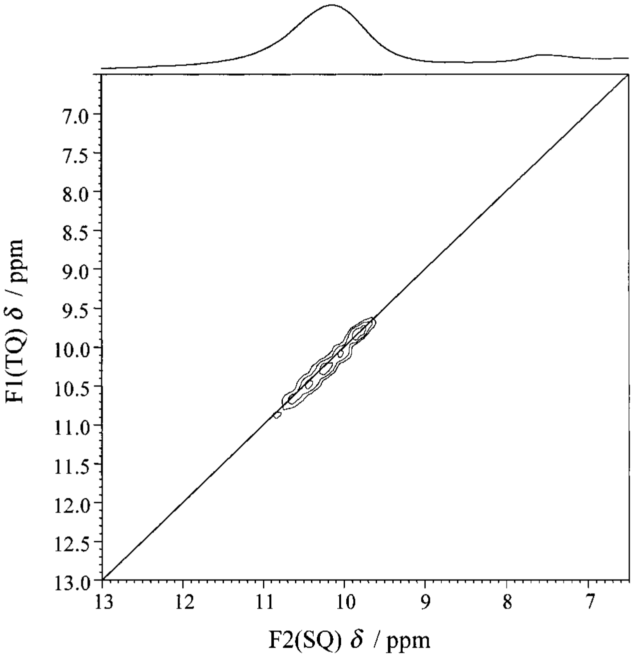

Figure 4. TQ 2D ^{1}H MAS spectrum of as-made all-silica ZSM-12. The spectrum at the top is the 1DSQ spectrum shown in Figure 2.

of the methyl groups are also proton-exchanged and give rise to the line at 3.3 ppm.

Triple-quantum NMR experiments were performed using the pulse sequence shown in Figure 1b to verify the interpretation of the DQ results (Figure 4). It should be noted that the chemical shift scale of the TQ dimension was rescaled by a factor of $^1/_3$ to make it easier to distinguish between real signals and artifacts. The only signal observed is at 10 ppm, due to the three silanol protons of the defect site. This result shows that the defect silanol groups have clusters of three protons in close proximity which are responsible for the resonance observed at 10 ppm. The inhomogeneously broadened line observed suggests that the cluster of three protons is isolated and is not part of a network of spins. The results of the TQ experiment and the rotor-encoded DQ MAS experiment can only be explained if more than two protons in close proximity are responsible for the resonance at 10 ppm. Quadruple-quantum MAS NMR experiments were not performed to verify that the proton cluster size is less than four. However, TGA and ^{29}Si NMR spectra for several as-made materials[7] show conclusively that there are four Q^3 groups (where Q^n stands for $X_{4-n}Si[OSi]_n$, X = OH or O^-)[16] per organic charge, i.e., $Q^3/N^+ = 4$. One of the Q^3 groups is the charge compensating siloxy (SiO^-) group, and thus the maximum number of silanol protons per defect site is three. The ^{29}Si NMR spectra, which determine the Q^3/Q^4 ratio, and the TGA experiments, which determine the organic content, show that there are four Q^3 groups per BTMA cation.

Line-Shape Simulations. The DQ and TQ MAS spectra show that the defect sites in this sample consist of three silanol protons which are strongly hydrogen bonded to the charge-compensating siloxy group. Numerical simulations of the MQ line shape may be used to extract more quantitative information from the experimental data.[5] Here we use numerical simulations to estimate the distance between the silanol protons of the defect site. Figure 5 shows the experimental and simulated sideband patterns (slices along the DQ dimension) of the silanol resonance from the 2D rotor-encoded DQ ^{1}H MAS spectrum. Integration of the experimental sideband pattern shows that the central line and two first-order sidebands combined have relative intensities of 1:1.1.

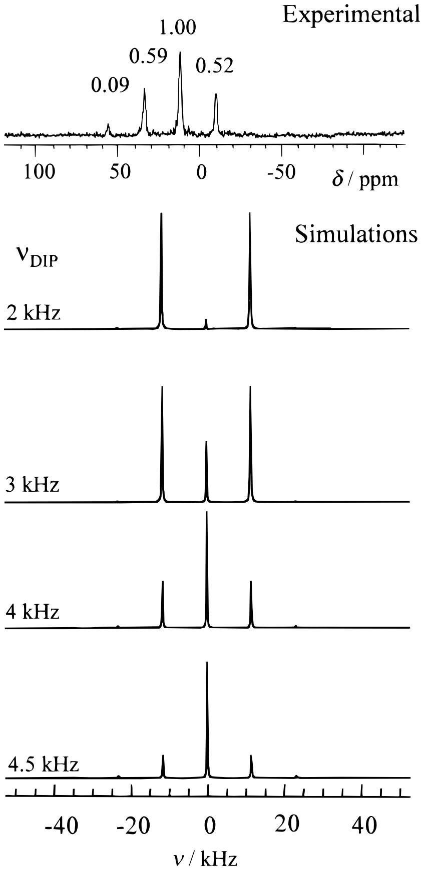

Figure 5. Sideband pattern of the resonance at 10 ppm from the 2D rotor-encoded DQ ^{1}H MAS spectrum (top). Simulations of the sideband pattern for a three-spin system with identical couplings. The dipolar coupling strengths are given in the figure. The numbers on top are integrated areas normalized to the biggest peak.

The three-spin system was modeled as an equilateral triangle (Figure 5) and as a linear equidistant arrangement of three protons (not shown). These two models are respectively the limiting cases with maximum and minimum dipole interactions for equivalent distances. Since the shape of the double-quantum excitation curve of a three-spin system is determined by a single parameter, the mean dipolar interaction,[17] we have used this simplification for the simulation of the double-quantum sideband pattern. We believe that the triangular model is a more reasonable assumption because the protons are likely *not* in a linear configuration. The best agreement between the simulated and experimental patterns is for a dipolar coupling strength, ν_{DIP}, of 4.0 ± 0.5 kHz for the triangular model and 10 kHz for the linear model. Given that the silanol protons are not completely rigid[18] the dipolar coupling will give an estimate of the maximum distance between protons, as the effective dipolar coupling would be reduced by motion. A dipolar coupling of 4.0 ± 0.5 kHz corresponds to a proton−proton distance of 3.1 ± 0.1 Å. The linear model would result in proton distances of 2.3 Å. We believe that the triangular model is a better model

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(18) ^{2}H NMR spectra of all-silica nonasil samples synthesized with deuterated silanol groups do not have a Pake doublet indicative of rigid deuterons, but rather a Gaussian line. This line suggests that the deuterons are not rigid. However, without knowing the geometry of the motion in detail, it is not possible to determine the effect of the motion on the dipolar coupling.

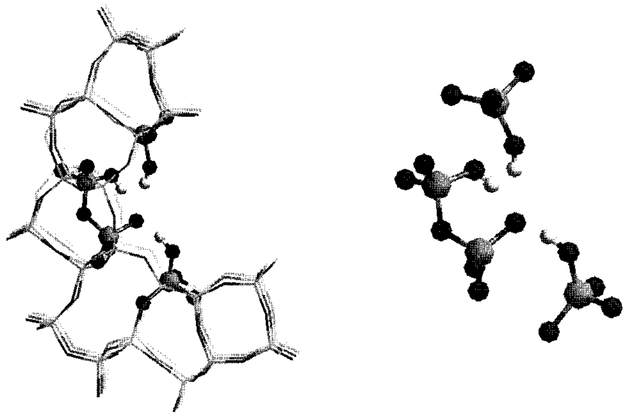

Figure 6. Model of the defect sites in as-made all-silica ZSM-12. A fragment of the zeolite pore was used to artificially create the defect site.

to represent the structural defect, because steric effects will prevent three protons from arranging in a linear fashion. It is worth noting that there are only certain pairs of silicon−oxygen bonds that could be broken which satisfy the experimental observation that the defects do not contain Q^2 groups (^{29}Si NMR spectroscopy).

The experimental data support the following conclusions. First, ^{1}H MAS NMR (1D) of the as-made ZSM-12 confirms that there are silanol protons engaged in hydrogen bonding with the charge-compensating siloxy group, forming Si−OH···$^-$O−Si groups with oxygen−oxygen distances of 2.7 Å. Second, DQ and TQ ^{1}H MAS NMR experiments show that all three silanol protons of the defect site contribute to this resonance. Third, assuming an equilateral triangular geometry for the three protons, simulations of the DQ NMR spectrum give a dipolar coupling which corresponds to a maximum internuclear distance of 3.1 (± 0.1) Å. Taking these facts into account, Figure 6 shows a plausible model for the defect sites in all-silica ZSM-12. On the basis of the modeling performed and steric arguments, to accommodate all three silanol protons, one of the silicon−oxygen bonds that is broken must be out of the plane of the siloxy group so that the two additional silanols are not prevented from hydrogen bonding.

It was noted in an earlier report[7] that the siloxy group is energetically unfavorable without stabilizing hydrogen bond interactions, and this work clearly shows that it is stabilized by the *three* hydrogen-bonded silanol protons, rather than by *two* as was suggested previously.[7] There is growing evidence that small amorphous colloidal aggregates containing tetrapropylammonium cations and silica form before the detection of the first crystals of ZSM-5 zeolite during synthesis.[19] Since the peak at 10 ppm in the ^{1}H NMR spectra is detected early during the zeolite synthesis,[7] it is reasonable to assume that structures, such as the defect model suggested here, are also present early on as charge-compensating groups for the organic cations. Consequently the determination of the defect site structure gives additional information about the structure of the silicate species that the organic structure-directing agent interacts with during zeolite nucleation and crystallization.

Conclusions

Double-quantum and triple-quantum ^{1}H MAS NMR have been used to study the defect sites in siliceous as-made ZSM-12 synthesized with deuterated benzyltrimethylammonium cations. The results are consistent with a structural model of the defect sites where all three silanol (SiOH) protons are engaged in hydrogen bonding with the charge-compensating siloxy (SiO$^-$) group. Based on simulations of the DQ ^{1}H NMR spectra, a maximum distance between the protons of 3.1 (± 0.1) Å is determined. The defect site cluster investigated here probably plays an important role in the nucleation process of high-silica zeolites.

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