

^{29}Si NMR Studies of Zeolite Precursor Solutions

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Solution ^{29}Si NMR spectroscopy results of zeolite precursor solutions of composition $1 \text{ SiO}_2:4 \text{ C}_2\text{H}_5\text{OH}:0.36/n \text{ R}^{+n}[\text{OH}^-]_n:20 \text{ H}_2\text{O}$ are reported. This work employs isotopically enriched ^{29}Si materials to aid in spectral interpretation. Using both 1D and 2D methods, spectra of solutions containing tetrapropylammonium hydroxide are wholly consistent with the existing silicate chemistry literature and indicate that the majority of the species are high-symmetry silicate clusters previously observed in aqueous solutions. The results are inconsistent with the nanoblock or nanoslab model proposed by Kirschhock and co-workers. Mixtures containing the 4,4'-trimethylene-bis(1,1'-dimethylpiperidinium) dihydroxide cation were also studied. These mixtures have similar speciation to the TPA solutions, although the relative populations of the species are different. Preliminary variable temperature ^{29}Si NMR of these mixtures shows that the exchange properties of the high-symmetry silicate species, most notably the tetrahedral tetramer, depend on the organocation identity.

Introduction

Developing a molecular-level description of high-silica zeolite nucleation and crystallization is one of the most significant unresolved problems in zeolite science.^{1,2} This description will have implications both for understanding how to rationally control properties of existing zeolites and how to synthesize new phases. These outcomes are important beyond the basic research performed in academia as zeolites are used extensively in heterogeneous catalysis, separations, and ion-exchange operations.^{1,2} Reinforcing this point, numerous groups have intensely studied this problem over the last 20 years. Methods including small-angle scattering,^{3–11} microscopy, calorimetry,^{10,12–15} and NMR spectroscopy^{16,17} have yielded numerous insights into the growth of zeolitic materials. One area that by contrast has been sparingly studied is silicate speciation in these systems. While numerous works have extensively studied aqueous silicate solutions,^{18–44} relatively few studies have been performed on zeolite synthesis mixtures. This is in part due to the complexity of the mixtures, the high synthesis temperature, the low natural abundance of silicon-29 (4.9%), and the potential difficulties of assigning resonances in one-dimensional spectra.

Silicalite-1 syntheses from clear solutions at low temperatures (<368 K) open the possibility of bringing ^{29}Si NMR spectroscopy to bear on this problem in a meaningful way. The solutions are optically transparent and contain only four components, silica, tetrapropylammonium hydroxide, water, and ethanol; the initial mixtures likely contain small/oligomeric silicates, and the synthesis conditions are relatively mild. All these points should make determining the speciation in this system tractable. Of the numerous studies of this system, in the late 1990s a series of papers by Kirschhock and co-workers sparked intense interest.^{45–48} Among the reported results were ^{29}Si NMR spectra that the authors claimed proved the presence of silicate species that are components of the silicalite-1 structure after room-temperature aging.^{48–50} The authors assigned the resonances

observed to several silicate species not previously observed by the silicate chemistry community including double-five-membered silicate rings, a pentacyclic octamer, a tetracyclic undecamer, and its trimer. These reports, including both the NMR results and other aspects, have led to controversy in the zeolite community.^{51–55}

Our lab has been active in studying the growth of silicalite-1 in these clear solutions using small-angle X-ray scattering (SAXS).^{56–58} These studies have provided fundamental information about the kinetics of silicalite-1 formation and about how modification of the TPA moiety and the presence/content of alcohol in the synthesis mixture influence silicalite-1 formation. The SAXS studies, while providing useful information about kinetics, provide no information about the chemical species involved in the nucleation/growth processes. This motivates the work reported here, ^{29}Si NMR studies of silica/ethanol/organocation/water mixtures of similar composition to the silicalite-1 “clear solution” synthesis, prepared with isotopically enriched ^{29}Si . The use of isotopically enriched materials has several advantages including improved signal/noise ratios, the immediate determination of symmetric versus nonsymmetric species via the presence of multiplets because of J -coupling, and the ability to map connectivity of spins using 2D measurements. The spectra and their implications for zeolite nucleation are described below.

Experimental Section

Tetrapropylammonium hydroxide (Alfa Aesar, 40 wt % in water) was used as received. 4,4'-Trimethylene-bis(1,1'-dimethylpiperidinium) diiodide (TMBDMP₂) was synthesized and ion-exchanged to the hydroxide form using published procedures.⁵⁹ Isotopically enriched $^{29}\text{SiO}_2$ (96%+) was purchased from Cambridge Isotopes Labs. Zeolite synthesis mixtures were of the composition $1 \text{ SiO}_2:4 \text{ EtOH}:0.36/n \text{ R}^{+n}[\text{OH}^-]_n:20 \text{ H}_2\text{O}$. The mixtures were prepared by addition of the appropriate amounts of organocation solution, water, and ethanol to the enriched silica. The mixtures were aged at room temperature, typically for 48 h, and were stirred either using a shake plate

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or a Vortex mixer. An appropriate amount of the solution (0.6–0.8 mL) was then loaded into a 5-mm PTFE-FEP NMR tube liner (Wilmad) anchored in a 5-mm NMR quartz tube (Wilmad), and a small amount of D₂O (99+%-d, CIL) was added in the outer quartz tube for a lock signal. Any residual undissolved silica was removed before the NMR measurements via mild centrifugation (~500 rpm, 1 min) and results in optically transparent mixtures. As has been reported previously, the enriched silica contains appreciable amounts of dense crystalline phases, and complete dissolution is problematic. For samples made using the original material purchased from CIL, only about 60% of the silica was soluble on the basis of TGA analysis of the residual solids. Samples were also prepared using enriched silica that had been recovered using a procedure similar to that reported by de Freitas and co-workers.⁶⁰ The solubility of the silica in that case is improved with between 85 and 90% of the silica dissolving into solution. However, no differences were observed in the NMR spectra whether the as-provided or recovered enriched silica was used. The effect of room-temperature aging was also studied by remeasuring the same sample after several days or a week; no differences were observed in the spectra. Finally, a TPA/silica/ethanol/water mixture was prepared that was heated overnight at 333 K to facilitate silica dissolution. The spectrum of this sample was also identical to the samples that were mixed at room temperature.

Analytical. All NMR spectra were obtained on a Varian Unity Inova 400 MHz spectrometer hosted by a Sun Ultra 5 computer. A Varian 5-mm autoswitchable broad-band probe tuned to ²⁹Si (79.38 MHz) was used. The 90 degree pulse calibration (typically 12 μs) was done on the actual sample. A solution of TMS in CDCl₃ as an external reference showed that the monomer resonance was at −71 ppm relative to TMS. That was then used as an internal reference. The variable temperature work was performed in 20 °C increments from room temperature. The samples were heated to the desired temperature, were held there for 30 min, and then were measured (typical acquisition time 60 min). The homonuclear ²⁹Si COSY was performed at room temperature with a 10-s delay between the pulses and 128 scans. 2D spectra were recorded with a spectral width from −120 ppm to −60 ppm and 128 increments in *t*₁. The recycle delay was chosen given that 1D spectra with 10- and 60-s recycle delays appeared identical. The spectra were not background-subtracted to remove the probe background. All spectra shown are of samples 96+% enriched in ²⁹Si. Small-angle X-ray scattering measurements were also performed on the solutions studied by NMR as reported previously.⁵⁸

Results

Figure 1 shows the ²⁹Si NMR spectrum of 1 SiO₂:4 C₂H₅OH:0.36 TPAOH:20 H₂O aged at room temperature. There are several sharp singlets in the spectrum because of species that contain chemically equivalent sites. These include the monomer (**1**, −71 ppm), the monoethoxy substituted monomer (**2**, −72.2 ppm), dimer (**4**, −79.8 ppm), cyclic trimer (**6**, −81.2 ppm), cyclic tetramer (**8**, −87.7 ppm), prismatic hexamer (**9**, −89.0 ppm), tetrahedral tetramer (**11**, −97.7 ppm), and the cubic octamer (**12**, −98.3 ppm). These assignments are all consistent with the body of existing literature on silicate speciation.^{25,26,28,29,34,35,40} The lack of splitting in these resonances, given the level of isotopic enrichment, is strong evidence in support of the assignments. The strongest resonance is for the tetrahedral tetramer, whereas in TAAOH–silica mixture with high TAAOH:silica mixtures, typically the cubic octamer is the

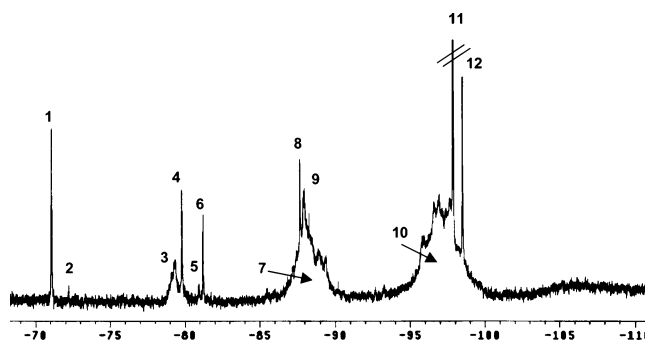


Figure 1. ²⁹Si NMR spectrum of 1 SiO₂:4 C₂H₅OH:0.36 TPAOH:20 H₂O after aging at room temperature. The broad peak feature from −105 ppm to the edge of the spectrum is the probe background.

dominant resonance.²⁸ Additionally, alcohol addition has also been shown to drive the speciation to the cubic octamer.³⁵

In addition to the sharp singlets observed, three broad resonances are also present. The assignments of these are as follows. The resonance denoted as **3** is due to the Q¹ species in the linear trimer, substituted cyclic trimer, and substituted cyclic tetramer. The broad resonance denoted as **7** is assigned to the Q² resonances of the substituted cyclic tetramer and linear trimer, Q² groups of the tricyclic hexamer, and Q³ resonances of the substituted cyclic trimer and three of the four Q³ groups in the tricyclic hexamer. The resonance denoted as **10**, which appears to be a quartet, is assigned to the remaining Q³ resonances of the tricyclic hexamer²⁶ and the substituted cyclic tetramer. The assignments of **7** and **10** are not as straightforward as the other resonances observed but are consistent with the existing literature and are consistent with the absence of Q⁴ species and the 2D NMR spectrum described below. Table 1 summarizes the assignment of the spectrum in Figure 1.

Perhaps most noteworthy in the context of zeolite nucleation is the complete absence of any resonances assignable to fully connected silicon centers, that is, Q⁴. Previous works by Harris⁴³ as well as Kinrade and co-workers⁴¹ have shown that Q⁴ species in solution have resonances between −105 and −108 ppm. The complete absence of any resonance in that range in Figure 1 rules out the presence of Q⁴ species. One source of concern would be that any Q⁴ signals become saturated and hence are not observed (*T*₁ effects). Spectra were acquired with a range of recycle delays between 10 and 60 s (Figure 1 shows the spectrum with a recycle delay of 60 s). All of these spectra were essentially identical, leading us to believe that there are no artifacts due to *T*₁ effects in the spectra obtained. This is also consistent with the previous works where Q⁴ species were observed^{41,43} as in those works the recycle delay was 60 s or less. The assignments of the broad resonances for **7** and **10** were done on the basis of the absence of Q⁴ species. For instance, if Q⁴ species had been observed, the broad resonances could reasonably be interpreted as Q³ and Q² species associated with the fully connected Si centers.⁴¹ Our results, however, show this is not the case.

To study this further, 2D COSY measurements were performed (Figure 2). The spectrum contains two sets of cross-peaks, which are fairly weak in intensity. The 2D measurements show some of the limitations in the current work on the basis of the field strength and inherent line broadening because of the high silica concentration leading to relatively high solution viscosities. None of the singlets observed in the 1D spectrum should contribute off-diagonal peaks in the COSY as they are comprised of chemically equivalent Si centers, and this is in fact the case. The COSY cross-peak at −95 ppm in F1 is

TABLE 1: Summary of the Resonance Assignment of Figure 1^a

Resonance	Species	Chemical Shift (ppm) $\delta_{\text{TMS}} = 0$	Structure
1	Monomer	-71	
2	Ethoxy substituted monomer	-72.2	$(\text{HO})_3\text{Si}(\text{OC}_2\text{H}_5)$
3	Multiplet Linear Trimer, Substituted Cyclic Trimer and Tetramer (Q ¹)	-79.3	
4	Dimer	-79.8	
5	Substituted Cyclic Trimer (Q ²)	-80.9	
6	Cyclic Trimer	-81.2	
7	Multiplet Substituted Cyclic Trimer (Q ³), Substituted Cyclic Tetramer (Q ³), Tricyclic Hexamer (Q ² /Q ³)	~-89.5	
8	Cyclic Tetramer	-87.7	
9	Prismatic Hexamer	-88.0	
10	Multiplet: Tricyclic Hexamer, Substituted Cyclic Tetramer (Q ³)	~-97	
11	Tetrahedral Tetramer	-97.7	
12	Cubic Octamer	-98.3	

^a Solid circles are used to denote the Si centers responsible for the resonance.^{25,26,28,33,34,42}

consistent with the presence of the tricyclic hexamer; the absence of an off-diagonal peak at -95 ppm in F1 with the Q¹ species is inconsistent with the presence of the substituted cyclic trimer and tetramer. The cross-peak at -90 with the Q¹ is consistent with the presence of linear trimer and the substituted cyclic trimer and tetramer. This has been observed previously³⁴ and is consistent with the assignment of the 1D spectrum. The weak off-diagonal peaks highlighted have also been observed previously for TAAOH/silica solutions.⁴⁴ In summary, the COSY spectrum is consistent with the assignment of the 1D spectrum and is consistent with the majority of the species in the mixture possessing chemically equivalent sites.

The results in Figures 1 and 2 provide clear information about chemical speciation in this mixture after room-temperature aging. To the best of our knowledge, this is the first report to investigate this system (i.e., TPA/SiO₂ < 1) using NMR of isotopically enriched materials. The implications for these results will be discussed below. One concern, however, is that by using silica as compared to TEOS the speciation might be dramatically different. Several things would seem to indicate that is not the case. First, small-angle X-ray scattering measurements of the solutions studied clearly show the presence of small particles approximately 2 nm in diameter (Supporting Information), consistent with previous results. The mixtures also have a very

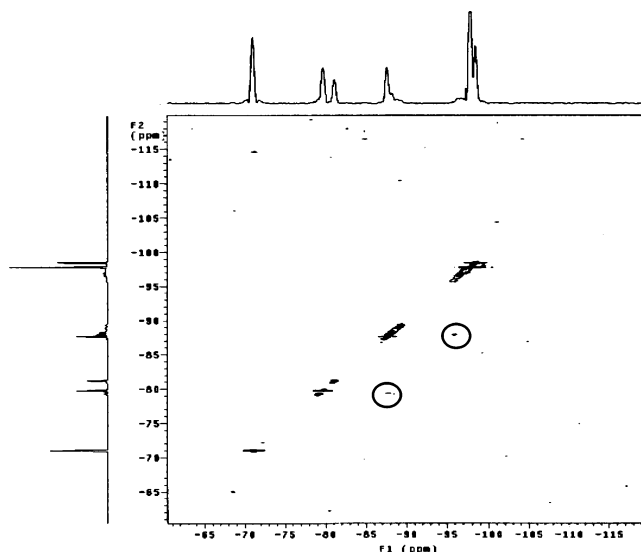


Figure 2. 2D COSY spectrum of the 1 SiO₂:4 C₂H₅OH:0.36 TPAOH:20 H₂O solution.

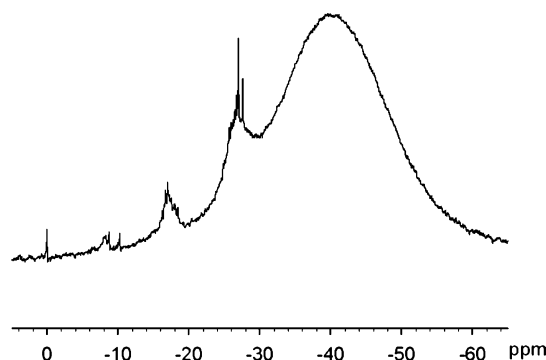


Figure 3. NMR spectrum of silicalite-1 precursor solution with composition of 1 TEOS:0.36 TPAOH:20 H₂O aged at room temperature for 24 h. Chemical shifts referenced to monomer as $\delta = 0$ ppm. The broad feature at -40 ppm is the probe background. Samples enriched in silica were measured in a 5-mm probe; samples at natural abundance were measured in a 10-mm probe.

small fraction of nanoparticles 20 nm in diameter. These particles do not contribute to the NMR because no Q⁴ species are observed. On the basis of the particle size and the viscosity of the mixture (7 cP), the correlation time τ for these particles is approximately 8 μ s, comparable to the NMR experiment time scale.⁶¹ This would be one explanation for the absence of the Q⁴ line in the spectra. Further, analysis of the SAXS data indicates that the concentration of the larger particles is at least 50 times less than the 2-nm particles. The low number density of the 20-nm particles as compared to the 2-nm particles would also explain why the 20-nm particles are not observed by NMR. Finally, the probe background leads to a broad resonance centered around -105 ppm, and it cannot be ruled out that the 20-nm particle Q⁴ resonance is obscured by this given its low concentration. These results suggest that the 20-nm particles do not contribute to the NMR spectra and that the larger particles have a much smaller number density than the 2-nm particles.

Other points also lead us to believe that the spectra reported in Figures 1 and 2 are not "artifacts" of the silica source. First, samples aged for various durations at room temperature (1–10 days) appear identical by NMR. Second, samples were measured that were the same nominal composition (1 SiO₂:4 C₂H₅OH:0.36 TPAOH:20 H₂O) using TEOS as the silica source (i.e., natural abundance), as shown in Figure 3. Close inspection of these spectra show two primary differences: (1) the probe

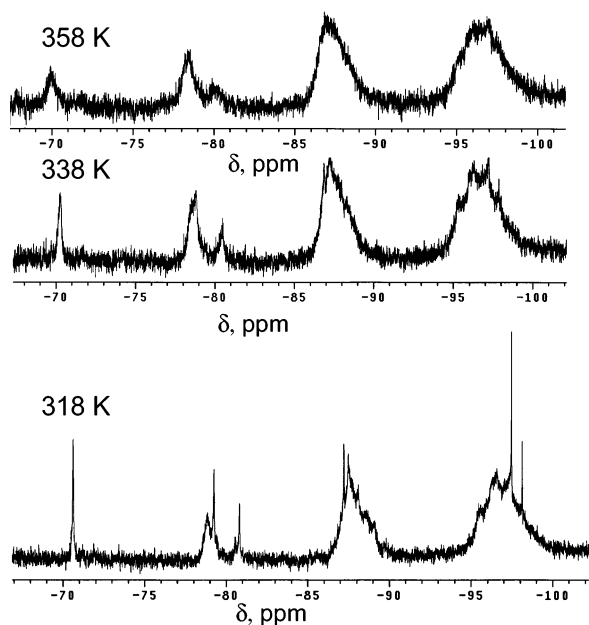


Figure 4. Variable temperature of ^{29}Si spectra of the $1 \text{ SiO}_2:4 \text{ C}_2\text{H}_5\text{OH}:0.36 \text{ TPAOH}:20 \text{ H}_2\text{O}$ solution.

background is very pronounced in the mixtures at natural abundance and (2) the resonance at ~ -97 ppm has no fine structural features, consistent with the absence of scalar J -coupling at natural abundance. These points indicate that the results reported in Figures 1 and 2 are not an artifact of the silica source.

Given that previous work has clearly shown that the spectra of these mixtures are sensitive to temperature, preliminary variable temperature measurements were performed. Figure 4 shows the variable temperature NMR of the TPA solution over the temperature range of 318–358 K. As can be seen, the spectrum at 318 K is comparable to the room temperature spectrum in Figure 1. However, by 338 K the sharp resonances have all broadened out, and by 358 K only five broad lines remain. This result is consistent with previous work by Kinrade's lab.²⁸ Given the clear and pronounced differences in the spectra between 318 and 338 K, ongoing work is exploring the temperature dependency of the signal intensities of the octamer and so forth in this range. The monomer resonance, while broadened at elevated temperatures, is always observable.

Cooling this mixture back to room temperature and remeasuring the sample gives a spectrum identical to Figure 1.

It has long been known in the zeolite science community that the TPA-silicalite-1 synthesis is exceptionally robust. With that in mind, studies have also been performed on silica–ethanol–water mixtures containing 4,4'-trimethylene-bis(1,1'-dimethylpiperidinium) dihydroxide (TMBDMP[OH]₂). Previous work from our lab has shown that mixtures containing this organocation, but otherwise identical to the TPA-silicalite-1 mixtures, are incapable of forming any zeolite phase over the period of months at 368 K.⁵⁶ Figure 5 shows the 1D spectrum of this mixture after aging at room temperature. Qualitatively, the spectrum is very comparable to the results shown in Figure 1 for the TPA–silicalite-1 mixture. The most notable difference for this spectrum is that the broad resonances denoted as **7** and **10** in Figure 1 are much less pronounced, though they are present (Supporting Information). This result suggests that the organocation does exert some influence on the relative populations of the species present, but the species present in the two mixtures are similar. Also, the resonances assigned to **11** and **12** are shifted upfield slightly as compared to the TPA solution (-98.2 , -98.6 ppm versus -97.7 , -98.3 ppm). Another possibility which cannot be completely ruled out is that the resonances assigned as **11** and **12** in Figure 5 are the deprotonated and singly protonated cubic octamers, respectively.

Variable temperature measurements were also performed on the TMBDMP solutions to draw additional comparisons with the TPA solutions. Figure 6 shows the variable temperature spectra of the TMBDMP solutions. The most interesting result is that the exchange properties of this mixture appear different from the TPA solutions. This can be deduced simply by the fact that the resonances for the cubic octamer, tetrahedral tetramer, and so forth can still be observed at 338 K. By contrast, all resonances due to high-symmetry species observed in the TPA solution (except for monomer and possibly the dimer) are undetectable by 338 K. This would suggest that while the organocation has at best a minor influence over speciation, the level of stabilization of the different species depends on the organocation geometry. While it is tempting to correlate this difference in exchange properties to the differences observed in zeolite nucleation and growth, given the complexity of silicate exchange in these mixtures, it is not warranted on the basis of just these results. In this mixture, similar to the TPA mixture, the resonances for the cubic octamer, tetrahedral tetramer, and

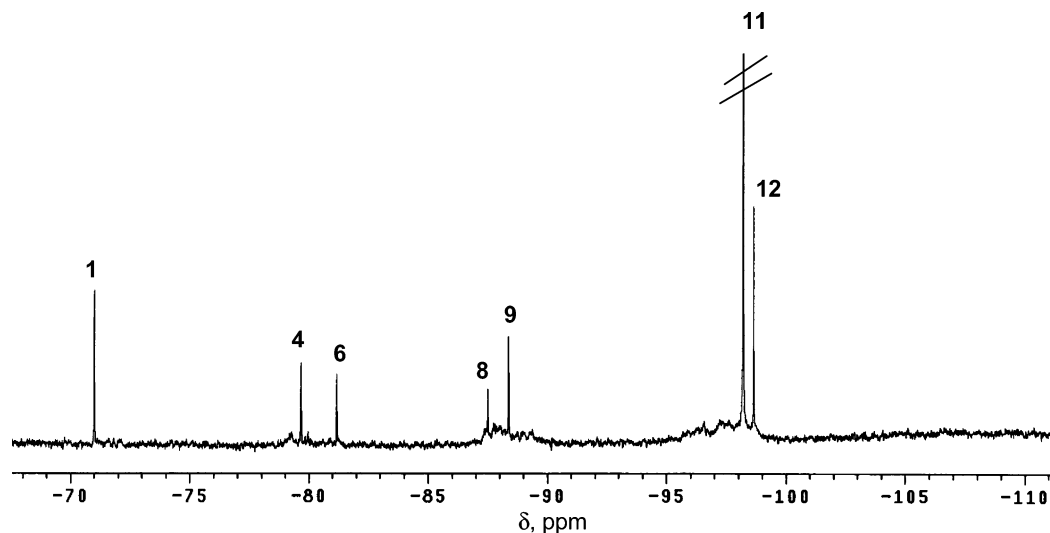


Figure 5. ^{29}Si NMR spectrum of $1 \text{ SiO}_2:4 \text{ C}_2\text{H}_5\text{OH}:0.18 \text{ TMBDMP}[\text{OH}]_2:20 \text{ H}_2\text{O}$ after aging at room temperature. Resonances are numbered using the same assignment notation as in Figure/Table 1.

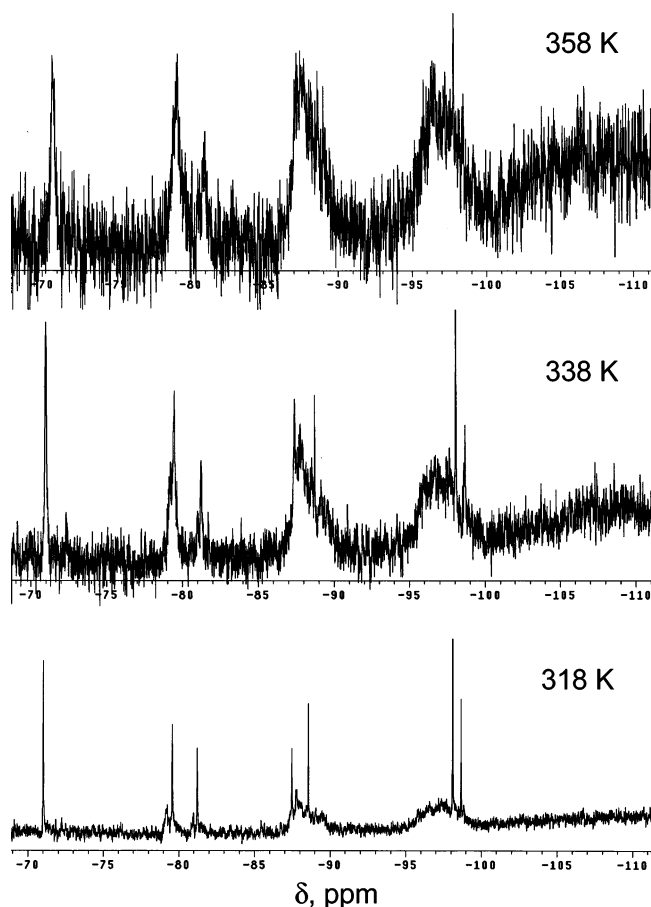


Figure 6. Variable temperature of ^{29}Si spectra of the $1 \text{ SiO}_2:4 \text{ C}_2\text{H}_5\text{OH}:0.18 \text{ TMBDMP}[\text{OH}]_2:20 \text{ H}_2\text{O}$ solution.

so forth are not observable at 358 K, 10 degrees below the synthesis conditions. This would lend further caution to extrapolating the exchange results into mechanistic implications. However, it is clear that the organocation influences the exchange of the species; ongoing work is exploring this in more detail and will be reported elsewhere.

Discussion

Three major conclusions can be drawn from the results above. First, in the TPA mixtures, there is no evidence for fully connected silicon centers or for any silicate species beyond those observed previously by the silicate chemistry community. Second, the TMBDMP mixture has essentially the same species present but in different populations. Third, the exchange dynamics of the high-symmetry silicate species do appear to be dependent on the organocation identity. These points and their implications for zeolite nucleation are described below.

The first point, in the context of the current debate over the nanoslab model, is the most significant. The spectra shown in Figures 1–4 are inconsistent with a model wherein there are (1) species containing fully connected silicon centers and (2) a predominance of low-symmetry species. Point 1 effectively rules out the presence of the 33-mer (Figure 9 ref 48). While one could debate the assignment of resonances of **7** and **10** in the current work, there are simply no Q^4 species observable in the mixtures studied here, both enriched and those at natural abundance. The second point is also inconsistent with the nanoslab model since, again referring to Figure 9 in ref 48, the only high-symmetry species attributed to the spectra⁴⁸ are the cyclic trimer and prismatic hexamer. The presence of the double-

five-ring species in silicate solutions remains a topic of controversy⁵¹ though the position listed for this resonance (-98.75 ppm)⁴⁸ is in the range one would anticipate observing the monoprotonated cubic octamer. It is also notable that the monomer peak is never observed; this is in contrast to the results reported here.

It should also be pointed out that comparison of the various spectra in the literature is not trivial. For instance, with the exception of a few works,^{41,43} researchers in the silicate chemistry community have generally focused on TAAOH solutions with $\text{TAAOH}:\text{SiO}_2$ of at least one at high pH. The work reported by Kirschhock and co-workers have employed several different temperatures and different compositions (water content), and many samples were extracted prior to NMR analysis. Comparison with the latter mixtures (i.e., after extraction) is likely not insightful given that it seems such a process will, at a minimum, alter the mixture composition. This, compounded with the short hydrolysis times employed ($<1 \text{ h}$), makes it very unclear as to the actual silica content of these mixtures. Not all the TEOS is expected to be hydrolyzed in this time frame, but the TEOS is reported to be extractable in the solvents used (octane). Further, the authors claimed that there is no TEOS/monomeric species in the mixtures. While some of the issues above can be further speculated upon, the clear absence of Q^4 species is inconsistent with the nanoslab or nanoblock model. Also, the mixtures reported here contain a small population of larger (20 nm) particles that are not observed in mixtures wherein TEOS is the silica source. However, the spectra for samples made using TEOS (Figure 3) and enriched silicon dioxide (Figures 1, 2, 4) appear very similar with the exception of the fine structure in the broad resonances, and this is consistent with the idea that the enriched silica does not introduce artifacts into the system. That the 20-nm nanoparticles are not observed by NMR is consistent with the correlation time of motion being comparable to the NMR time scale. The 2-nm particles in these mixtures, which are responsible for the observed spectra, yield spectra comparable to previous work found in the silicate chemistry literature.

The second point is consistent with the first in that the silicate chemistry community has long argued that the organocation has at best a secondary effect on speciation as compared to pH. Also, the geometry of these organocations is substantially different. TPA is an essentially spherically symmetric molecule whose charge is in the center of the molecule. By contrast, TMBDMP can be thought of as tubular in shape with charges on each end. It would seem logical that substantially changing the geometry and spatial charge distribution of the organocation would lead to some perturbations of the silicate speciation, which is consistent with the results above.

The third point may potentially have implications for a mechanistic description of zeolite nucleation. It is clear that some of the high-symmetry species, particularly the tetrahedral tetramer, have different exchange rates in the presence of TMBDMP as compared to TPA. One potentially simple explanation for this is that the TMBDMP cations can interact with the tetramer more strongly via electrostatic forces than TPA because of its geometry and that the charges are located on the end of the molecule as compared to the center. To understand this in more fundamental terms, ongoing work is attempting to quantify this by studying mixtures containing tripropylalkylammonium cations which we have shown lead to silicalite-1 formation at 368 K albeit with reduced growth rates.⁵⁷

Conclusions

The ^{29}Si NMR results reported here are, to the best of knowledge, the first on TPA solutions of comparable composition to the silicalite-1 "clear solution synthesis" that have employed isotopically enriched silica. Solutions containing TPA exhibit spectra that can be understood on the basis of well-established silicate chemistry and are inconsistent with the nanoslab or nanoblock model. Solutions containing TMBDMP contain the same species as the TPA solution but in different populations. The exchange dynamics of the high-symmetry silicate species, most specifically the tetrahedral tetramer, appears to be dependent on the organocation identity. The work reported here indicates that the organocation identity is not central to determining silicate speciation in mixtures aged at room temperature and refutes the presence of secondary building units or "specialized" silicate species in zeolite synthesis mixtures before hydrothermal treatment.

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Supporting Information Available: SAXS scattering curve of sample analyzed by NMR (Figures 1, 2, and 4). Calculation of relative amounts of 20- and 2-nm nanoparticles present in the mixtures. ^{29}Si NMR spectra of solutions of TMBDMP made with TEOS. Spectra shown in Figure 5 with the y-axis expanded. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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