

Molecular Conformation of Hydrogen-Bonded Ethylene Glycol in Sodalite: A ^1H CRAMPS NMR, IR, and ^2H NMR Study

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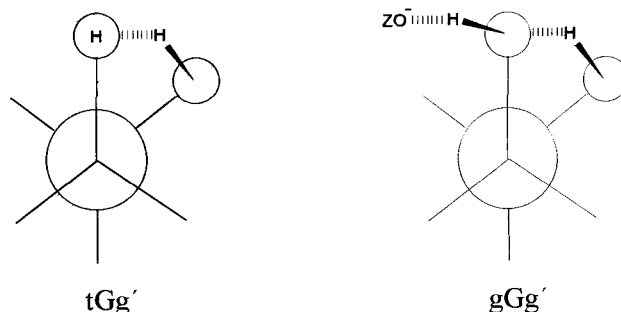
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Analysis of the variable-temperature ^1H CRAMPS NMR, IR, and ^2H NMR spectra obtained from the ethylene glycol molecules in two sodalite materials with Si/Al ratios of ∞ and ca. 5 reveals that the intermolecular hydrogen bonds between the framework oxygens and the OH groups of the guest molecule, which appear only in the isomorphously Al-substituted zeolite, are preserved even at 200 $^\circ\text{C}$, which is higher than the crystallization temperature (175 $^\circ\text{C}$) of the zeolite host. As a consequence, the conformations of the encapsulated ethylene glycol molecules in these two materials were found to maintain in a manner distinctly different from each other over the temperature range (25–200 $^\circ\text{C}$) studied here.

Introduction

The initial use of nonaqueous solvents in the synthesis of zeolites and related materials dates back to 1985, when Bibby and Dale reported the synthesis of a pure-silica form of sodalite in ethylene glycol and propanol.¹ Since then, a large variety of silicate- and phosphate-based molecular sieves, some of which are analogous to known zeolite structures while others have entirely novel structures, have been synthesized from essentially nonaqueous media.² On the other hand, it has been repeatedly shown that each β -cage in pure-silica sodalite contains one ethylene glycol molecule,^{1–4} which does not allow for the formation of intermolecular hydrogen bonds between the encapsulated ethylene glycol molecules. Thus, a particular type of conformation of ethylene glycol can be dominant in this sodalite. Stemming from our interests in the host–guest interactions within sodalite materials with a wide range of Si/Al ratios (5.7 to ∞) synthesized from nonaqueous media in which ethylene is acting both as a solvent and as a structure-directing agent (SDA),^{5–7} we have found that the molecular conformation of ethylene glycol in pure-silica sodalite (0 Al atoms per β -cage) is tGg' stabilized only by one intramolecular hydrogen bond, while that of the guest molecule in a material with Si/Al = 5 (1 Al atom per β -cage) is gGg' stabilized by one hydrogen bond to the framework in addition to one intramolecular hydrogen bond, as given below in the Newman projection:



where Z denotes the framework Al atom. This demonstrates that the hydrogen-bonding feature of the encapsulated molecule within the β -cages of sodalites is strongly affected by the presence of Al atoms in the framework, because the net negative charge introduced by Al substitution results in the formation of hydrogen bonds to the negatively charged oxygen of framework AlO_4^- units. Here, we use variable-temperature ^1H combined rotation and multiple-pulse spectroscopy (CRAMPS) NMR, IR, and ^2H NMR spectroscopies to show that this type of intermolecular hydrogen bond is preserved even at 200 $^\circ\text{C}$, which is higher than the crystallization temperature (175 $^\circ\text{C}$) of the zeolite host.

Experimental Section

Two sodalite materials with Si/Al ratios of ∞ and ca. 5 (4.7 or 5.7) were synthesized using the ethylene glycol- d_2 ($\text{DOCH}_2\text{-CH}_2\text{OD}$, 98 atom % D) deuterated at both hydroxyl positions, as well as using the normal ethylene glycol, according to the procedures described elsewhere.^{5,6} Here, we refer to these two samples as Si-SOD and Al-SOD, respectively. All of the materials were phase pure and highly crystalline as seen by

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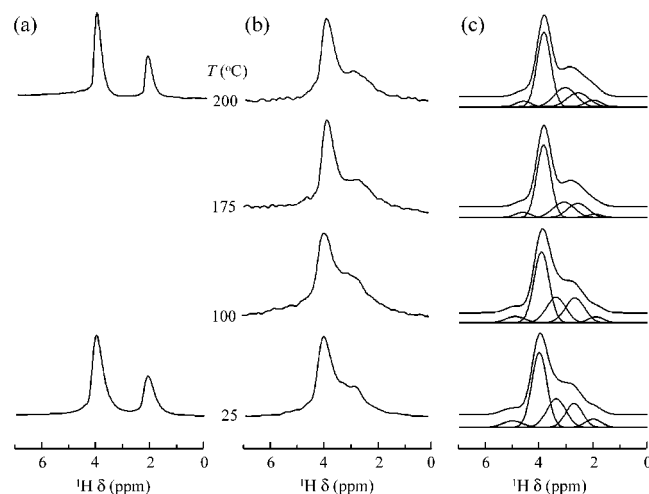


Figure 1. Variable-temperature ^1H CRAMPS NMR spectra of normal ethylene glycol (a) in Si-SOD (b) in Al-SOD. Panel c shows simulated spectra and their deconvoluted components of each experimental spectrum in panel b.

powder XRD experiments (Rigaku Miniflex, Cu K α radiation). Elemental analysis reveals, within experimental error, that each β -cage of the materials prepared here contains ca. one ethylene glycol molecule.

The ^1H CRAMPS NMR spectra at 25–200 °C were taken on a Varian Unity Inova 200 spectrometer at ^1H frequency of 200.256 MHz and a spinning rate of ca. 1.2 kHz, using the BR-24 multiple pulse sequence⁸ with a 90° pulse length of 1.2 μs , a recycle delay of 100–300 s, and an acquisition of 16 scans. The ^1H chemical shifts are reported relative to TMS. The ^1H CRAMPS NMR spectra obtained were deconvoluted using the Origin curve-fitting software. The static ^2H NMR spectra were recorded on the same spectrometer operating at a ^2H frequency of 30.741 MHz in the temperature range 25–200 °C, using the quadrupole echo pulse sequence with a 90° pulse length of 2 μs , an echo delay of 40–60 μs , and a recycle delay of 10–30 s. Typically, several hundred and several thousand scans were accumulated for obtaining the spectra of Si-SOD and Al-SOD, respectively. Simulation of the ^2H NMR spectra obtained was carried out using the Levenberg–Marquardt nonlinear least-squares algorithm. The IR spectra in the OD stretching vibration region were measured on a Nicolet Magna 550 FT-IR spectrometer using the KBr pellet technique. Prior to IR measurements, the pellets were placed inside a home-built IR cell with CaF_2 windows, which allowed in situ sample treatments and variable-temperature measurements.

Results and Discussion

Figure 1 shows the ^1H CRAMPS NMR spectra of normal ethylene glycol molecules in Si-SOD and Al-SOD (Si/Al = 5.7) materials recorded at 25–200 °C. The room-temperature spectrum in Figure 1a exhibits two lines at 3.8 and 1.9 ppm with an intensity ratio of 2:1 that must be due to the CH_2 and OH protons of the guest molecule, respectively.⁴ The strong high-field shift of the OH line in comparison to neat ethylene glycol clearly shows that both OH groups of the isolated molecule within the β -cages of Si-SOD are no longer involved in intermolecular hydrogen bonds with those of other ethylene glycol molecules. In addition, this line must be attributed to the combination of the free OH proton and the OH proton forming a weak, intramolecular hydrogen bond to the other OH group of the guest molecule, because the mutual exchange between the free and hydrogen-bonded OH groups of the

isolated ethylene glycol in Si-SOD is very fast with respect to the NMR time scale.⁵ Figure 1a also shows that the spectrum recorded at 200 °C is essentially the same as that at room temperature. It is thus clear that the encapsulated ethylene glycol remains intact in the temperature range studied here. As seen in Figure 1b, on the other hand, the room-temperature ^1H CRAMPS NMR spectrum of ethylene glycol in Al-SOD is characterized by the line shape consisting of five deconvoluted components at 5.0, 4.0, 3.4, 2.7, and 2.0 ppm. Although the general feature of this spectrum is similar to that of the ^1H MAS NMR spectrum previously reported by us,⁵ the component appearing at 3.4 ppm has not been resolved in the latter spectrum. Thus, the spectral resolution is better in the ^1H CRAMPS NMR spectrum shown here, permitting us a more accurate identification of distinct lines superimposed upon one another. Because much higher MAS rate (6.0 vs 1.2 kHz) and strength (12.2 vs 4.9 T) of the magnetic field were employed in ^1H MAS NMR experiments, the ^1H – ^1H dipolar interactions in Al-SOD appear to be so strong that they cannot be reduced or eliminated without either the use of extremely fast MAS or the combination of MAS with multiple-pulse line narrowing (CRAMPS).

Our previous work showed that the intermolecular hydrogen bonding between the isolated ethylene glycol molecule and the framework oxygens in Al-SOD is much stronger than the intramolecular hydrogen bonding within the guest molecule, because of the higher charge density of framework oxygen atoms in AlO_4^- units.⁵ Because the OH protons involved in hydrogen bonding normally exhibit a ^1H NMR line at lower field than that from free OH protons, the three ^1H lines appearing at 3.4, 2.7, and 2.0 ppm in the room-temperature spectrum of Al-SOD can be assigned to intermolecularly hydrogen-bonded OH protons, intramolecularly hydrogen-bonded OH protons, and free OH protons of the guest molecule, respectively. Also, the ^1H line around 5.0 ppm is mainly due to water molecules in Al-SOD.⁴ Assuming a random Al distribution in the framework of Al-SOD with Si/Al = 5.7, approximately 10% of the β -cages in this material are in the pure-silica form. This may be the reason that Al-SOD shows a small line at 2.2 ppm, assigned to the free OH protons of the encapsulated ethylene glycol molecule. On the other hand, the occurrence of a ^1H line around 2.7 ppm indicates that, unlike the case in Si-SOD, the intramolecular hydrogen bonding between the two OH groups of the guest molecule in Al-SOD is strong enough to shift its ^1H NMR line to a lower field compared to that observed for free OH protons. This can be rationalized by considering that the charge density of the OH oxygen atom of ethylene glycol involved in intramolecular hydrogen bonding may be higher in Al-SOD than in Si-SOD. As seen in the gGg' conformer depicted above, one of two OH oxygen atoms of the guest molecule in Al-SOD should have a higher charge density, because it is intermolecularly hydrogen-bonded to the negatively charged oxygen atom of the AlO_4^- framework units. This oxygen atom is the one to which the other OH group is intramolecularly hydrogen-bonded.

The most important observation obtained from Figure 1 is that no significant changes in the ^1H NMR line shape of ethylene glycol in Al-SOD are caused by increasing temperature to 200 °C, at which the barriers to molecular reorientation must be considerably lower than those at room temperature. As seen in parts b and c of Figure 1, even the spectrum recorded at 200 °C exhibits intermolecularly and intramolecularly hydrogen-bonded OH ^1H lines of the guest molecule at 3.2 and 2.7 ppm, respectively. This indicates that the molecular conformation (gGg') of ethylene glycol in Al-SOD remains essentially

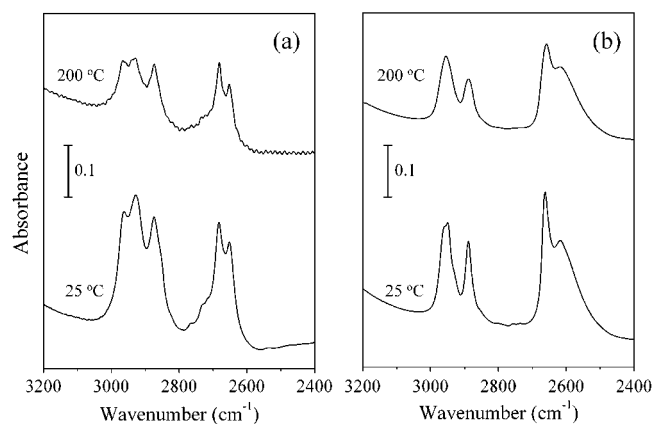


Figure 2. IR spectra in the 2000–3200 cm^{-1} region of ethylene glycol- d_2 molecules encapsulated within (a) Si-SOD and (b) Al-SOD materials.

unaltered even at the temperature that is higher than the crystallization temperature (175 $^{\circ}\text{C}$) of the zeolite host. When using the correlation between ^1H NMR chemical shifts and the $\text{O}\cdots\text{O}$ distances in $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds developed by Eckert et al.,⁹ the two ^1H NMR lines appearing around 3.2 and 2.7 ppm in the spectrum recorded at 200 $^{\circ}\text{C}$ were calculated to have almost the same $\text{O}\cdots\text{O}$ distance, ~ 3.0 Å. According to the classification of Jeffrey,¹⁰ this value falls into the $\text{X}-\text{H}\cdots\text{A}$ distance range (2.5–3.2 Å) for moderate hydrogen bonds, where X–H and A are proton donor and acceptor, respectively. In general, it is very difficult to directly measure the energies of hydrogen bonds in the solid state.¹¹ However, guiding values are available in the literature. In the case of moderate hydrogen bonds, for example, their dissociation energies are known to be 4–15 kcal mol^{-1} .¹⁰ Therefore, it appears that both intermolecular and intramolecular hydrogen bonds in Al-SOD are strong enough to overcome the thermal energy available to 200 $^{\circ}\text{C}$.

Figure 2 shows the IR spectra in the 2000–3200 cm^{-1} region of Si-SOD and Al-SOD (Si/Al = 4.7) materials synthesized with ethylene glycol- d_2 . We previously reported that the Si-SOD material containing normal ethylene glycol exhibits two sharp IR bands of about equal intensities at 3634 and 3592 cm^{-1} , assigned to the free OH group of the isolated molecule and the OH group in which the proton is involved in a weak intramolecular hydrogen bond, respectively.⁵ As seen in Figure 2a, the room-temperature spectrum of Si-SOD exhibits two sharp bands of about equal intensities at 2684 and 2654 cm^{-1} in the OD stretching region, both of which are shifted by a factor of about 1.35 to lower wavenumber regions, which is close to the expected isotopic factor of $2^{1/2}$. Unlike that of neat ethylene glycol- d_2 , however, no noticeable bands are observed in the 2400–2600 cm^{-1} region. This is not unexpected because intermolecular hydrogen bonds between the deuterated molecules are completely prevented upon their encapsulation in the β -cages of Si-SOD. On the other hand, the room-temperature IR spectrum of Al-SOD in the OD stretching region is characterized by a broad band around 2620 cm^{-1} , as well as a sharp band at 2670 cm^{-1} (Figure 2b). Notice that the position of this broad band is also lower in wavenumber by a factor of 1.35 than that (3540 cm^{-1}) of the OH band observed for the IR spectrum of Al-SOD containing normal ethylene glycol, assigned to hydrogen bonds between the guest molecule and the framework oxygen atoms.⁵ By contrast, the sharp band at 2670 cm^{-1} is considerably red-shifted compared to the free OD band observed for ethylene glycol- d_2 in Si-SOD, revealing that the OD groups of the guest molecule in Al-SOD are partially

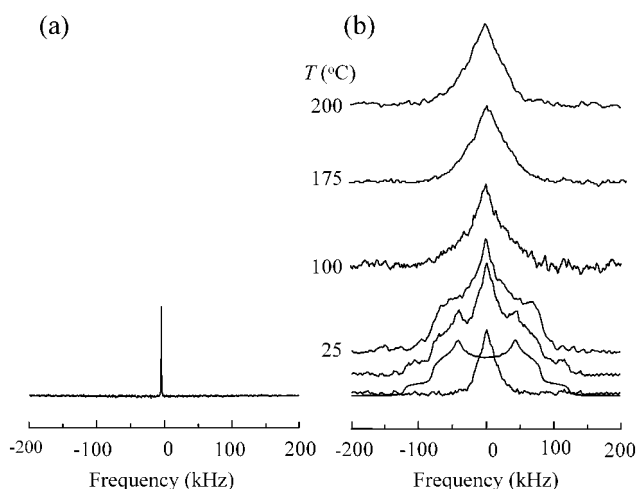


Figure 3. Variable-temperature ^2H NMR powder patterns of ethylene glycol- d_2 in (a) Si-SOD and (b) Al-SOD materials. The traces given below the room-temperature spectrum of the guest molecule in Al-SOD are the simulated spectrum and its deconvoluted components, respectively.

disturbed by intramolecular hydrogen bonding. Of particular interest is the observation that no noticeable changes in the number and band position of OD stretching vibrations are detected, although the IR spectra were taken at 200 $^{\circ}\text{C}$. From the IR data in Figure 2, therefore, it is clear that most, if not all, of the deuterated ethylene glycol molecules in Si-SOD and Al-SOD adopt essentially the same conformations as those (i.e., tGg' and gGg') of the normal ethylene glycol molecules in the corresponding materials, and their conformations maintain in a manner distinct from each other over the temperature range studied here. This can be further supported by the fact that the CH stretching vibrations between 2800 and 3000 cm^{-1} of the guest molecules in Si-SOD and Al-SOD are notably different in band position, but their general features remain almost unchanged even at 200 $^{\circ}\text{C}$. Prior to this work on the ethylene glycol in sodalite, the cobaltocenium ($\text{Co}(\text{C}_5\text{H}_5)_2^+$) ions occluded in the tectosilicate nonasil were the only known case in which the preservation of hydrogen bonds between the organic SDA molecules and the host framework at the crystallization temperature of the host has been established by IR spectroscopy.¹² Behrens et al. reported that the $\text{Co}(\text{C}_5\text{H}_5)_2^+$ ions in this clathrasil exhibit a splitting of the CH stretching vibration into two bands around 3130 and 3100 cm^{-1} because of the different strengths of the $\text{C}-\text{H}\cdots\text{O}-\text{Si}$ interactions and that this splitting still appears at 150–170 $^{\circ}\text{C}$ at which the nonasil host crystallizes.¹²

Figure 3 shows the solid-state ^2H NMR powder patterns of ethylene glycol- d_2 molecules encapsulated within Si-SOD and Al-SOD materials. When the spectrum of the organic species in Si-SOD was taken at room temperature, a sharp Lorentzian line with a full width at half-maximum (fwhm) of 0.6 kHz is observed. This reveals that the isolated ethylene glycol- d_2 undergoes rapid, isotropic molecular motion on the NMR time scale. On the contrary, the ^2H NMR powder pattern of the guest molecule in Al-SOD recorded at the same temperature shows signs of two components: a narrow feature superimposed on a broader line. This suggests severely restricted motion of the isolated organic species even at room temperature or inhomogeneous distribution of chemical shifts or both. Figure 3 shows that the broad component becomes weak at 100 $^{\circ}\text{C}$ or higher, while no significant changes in the central component are detected. It should be noted here that the powder pattern (not

shown) recorded at $-100\text{ }^{\circ}\text{C}$, which was found to be low enough to “freeze out” any motion of OD groups in the isolated molecule, exhibited a line shape essentially the same as that observed for the room-temperature spectrum. Because of both the temperature-insensitive nature of the central line and the lack of information on the character of motion associated with this line, therefore, we have used the spectrum obtained experimentally at $200\text{ }^{\circ}\text{C}$ as one of the deconvoluted components in fitting the room-temperature spectrum (this is why its simulated spectrum is somewhat noisy). The curve deconvolution results in Figure 3 reveal that the room-temperature powder pattern consists of two components, one Gaussian-shaped component with a fwhm of 55 kHz plus the other component with a quadrupole coupling constant (QCC) of 172(1) kHz and an asymmetric parameter (η) of 0.23(1). As stated earlier, the intermolecular hydrogen bonding between the isolated ethylene glycol molecule and the framework oxygens must be much stronger than the intramolecular hydrogen bonding within the guest molecule because of the higher charge density of framework oxygen atoms in AlO_4^- units. This led us to tentatively assign the central and quadrupolar components in the room-temperature powder pattern to internal reorientations of the OD groups involved in intermolecular and intramolecular hydrogen bonds, respectively. Although detailed information about the dynamics of each OD group cannot be obtained from the ^2H NMR spectra in Figure 3, it is again clear that the hydrogen bonding between the isolated ethylene glycol and the framework oxygens in Al-SOD is preserved even at $200\text{ }^{\circ}\text{C}$. This must be the main reason that the ethylene glycol molecule in Al-SOD adopts a conformation completely different than the one that it has in Si-SOD over the temperature region studied here. To the best of our knowledge, our work is the first example in which the organic SDA can exist as different conformers at the crystallization temperature or even higher in a particular structure type of zeolites.

Berglund and Vaughan have shown that there is a linear correlation between the ^2H QCC value and the $\text{O}\cdots\text{O}$ distance in $\text{O}-\text{D}\cdots\text{O}$ hydrogen bonds.¹³ When using their relationship, an $\text{O}\cdots\text{O}$ distance for the quadrupolar component with QCC = 172 kHz in the room-temperature ^2H NMR powder pattern of ethylene glycol- d_2 in Al-SOD was calculated to be 2.7 Å. This value is rather smaller than that (3.0 Å) derived from the ^1H CRAMPS NMR data using the relationship of Eckert et al.⁹ We believe that this discrepancy may result from the empirical nature of both relationships employed. While the ^2H NMR QCC value is a measure of the magnitude of the electric field gradients at the deuterium site, the η parameter gives information on the shape of the electric field gradient.¹⁴ Thus, η can be regarded as a useful indicator for estimating the $\text{O}-\text{D}\cdots\text{O}$ angles of bridging hydride systems. An attempt to calculate the $\text{O}-\text{D}\cdots\text{O}$ angle in the intramolecular hydrogen bond of the guest molecule in Al-SOD from its small but nonzero η value (0.23) using the correlation reported by Kim et al.¹⁵ gave a value of $130\text{--}140^{\circ}$. This appears to be reasonable because any conformation of ethylene glycol does not allow its geometry to orient the OH proton linearly or perpendicular to the free electron pairs of the oxygen atom in the other OH group.^{16,17} One may speculate that the reduced free space of the β -cages in Al-SOD is the major factor keeping the intra- and intermolecular hydrogen bonds at temperatures up to $200\text{ }^{\circ}\text{C}$, because isomorphous substitution of Si by Al in the framework of sodalites synthesized in ethylene glycol is accompanied not only by the introduction of Na^+ ions, together with a small amount of water, balancing the negative framework charges in the cages, but also

by the reduction in $\text{T}-\text{O}-\text{T}$ angles.⁵ As evidenced by the variable-temperature IR results in Figure 2, however, the intramolecular hydrogen bond in the ethylene glycol encapsulated within β -cages of Si-SOD much more spacious than those of Al-SOD is preserved even at $200\text{ }^{\circ}\text{C}$. Recall that the intramolecular hydrogen bonding between the two OH groups of the guest molecule is stronger in Al-SOD than in Si-SOD. This suggests that the increased spatial constraints in Al-SOD may not be the main driving force at least for the formation of the strong intermolecular hydrogen-bonding interactions, although the possibility that the small volume ($\sim 150\text{ }\text{\AA}^3$) of the β -cage itself may do well for keeping the intramolecular hydrogen bond in the guest molecule over the temperature range studied here cannot be ruled out.

There are many examples in which some organic SDAs can produce more than one zeolite structure, depending on the oxide composition of synthesis mixtures or the crystallization conditions employed or both.^{18–20} Because the organic SDAs used in zeolite synthesis usually end up trapped within the cavities of the crystallized products, they should be required to adopt distinct conformations closely related to the structural aspects of each zeolite host.^{21,22} This implies that the higher energy conformer could also serve as an SDA in its own right, especially when the energetic differences between some conformations of organic SDAs and the barriers to interconversions at synthesis conditions are not too large. It is interesting to note here that the free energy of the gGg' conformer for ethylene glycol in the gas phase has been repeatedly calculated to be higher only by 0.3 kcal mol^{-1} than that of the most stable tGg' conformer,^{16,17} although this result cannot be directly related to the ethylene glycol molecules occluded in sodalite materials due to matrix effects. The overall results of our study reveal that sodalite is so stable as to crystallize no matter what conformation ethylene glycol adopts. However, the structure-directing effect of ethylene glycol in the synthesis of sodalite is also well-known.^{3–5} The fact that the conformations of the encapsulated ethylene glycol molecules in our Si-SOD and Al-SOD materials maintain in a manner distinctly different from each other over the temperature range studied here strongly suggests that tGg' and gGg' may play a role during nucleation at the crystallization temperature ($175\text{ }^{\circ}\text{C}$) in the pure-silica and aluminosilicate synthesis mixtures, respectively. If such is the case, our work would have important implications in zeolite synthesis. We propose that if organic SDAs much longer and thus more flexible than ethylene glycol are used, the phase selectivity of the crystallization could be sensitive to the type of the conformation of organic molecules dominant at zeolite synthesis conditions, which should be greatly affected by the nature and extent of interactions between the organic and inorganic components in synthesis mixtures. This is because the number of conformations available to such organic SDAs and their geometric difference must be much higher than those for ethylene glycol. To prove whether the idea given above is an alternative strategy for the discovery of new structures, extensive zeolite syntheses through the control of conformations of flexible, hydrophilic organic SDAs as linear diquaternary alkylammonium ions with aliphatic or cyclic moieties or both by varying the concentrations of inorganic components in the aluminosilicate system are currently underway in our laboratory.^{22–24}

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