

Host–Guest Interactions in Pure-Silica and Aluminosilicate Sodalites Containing Ethylene Glycol as a Guest Molecule

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Abstract: Four sodalite materials with Si/Al ratios of ∞ , 23.0, 11.0, and 5.7 are synthesized from essentially nonaqueous media in which ethylene glycol is acting both as a solvent and as a structure-directing agent. Elemental and thermal analyses, X-ray powder diffraction, multinuclear MAS NMR, and vibrational spectroscopies are employed to extensively investigate the host–guest interactions in as-synthesized materials. It is found that the hydrogen-bonding feature of the ethylene glycol molecules encapsulated within the β -cages of sodalites is strongly affected by the Al content in the framework. The overall results of this study lead us to conclude that the molecular conformation of ethylene glycol in the pure-silica β -cage may be tGg' stabilized only by one intramolecular hydrogen bond, while that of the guest molecule in the β -cage with a Si/Al ratio of 5 is gGg' stabilized by one strong hydrogen bond to the framework in addition to one intramolecular hydrogen bond.

Introduction

Since the first synthesis of a pure-silica form of sodalite in ethylene glycol by Bibby and Dale,¹ the use of organic solvents in the synthesis of zeolites has received much attention over the last decade. It has been shown that several other structure types of zeolites such as ZSM-5, ZSM-35, and ZSM-48 also can be prepared from essentially nonaqueous media,^{2,3} although trace amounts of water are involved in their synthesis. The nonaqueous solvents which have been used in zeolite synthesis include propanol, hexanol, sulfolane, pyridine, and ethylenediamine, as well as ethylene glycol. Apparently, the presence of nonaqueous solvents during the crystallization process of zeolites can modify the distribution and structure of aluminosilicate or silicate species in a significantly different manner than those in aqueous media, due to distinct differences in the physicochemical properties of nonaqueous solvents and water. However, little attention has been devoted to the elucidation of the exact role of nonaqueous solvents during zeolite synthesis. In particular, even less attention has been directed toward the understanding of host–guest interactions in as-synthesized zeolites.

The conformation of ethylene glycol, HOCH₂CH₂OH, in the solid, liquid, and gas phases, as well as in aqueous and CCl₄ and other solutions, has been the subject of a wide variety of experimental^{4–9} and theoretical^{10,11} investigations. Because of

the presence of three internal rotors in the molecule, there are a number of possible conformations. If only the rotation with respect to the C–C bond is considered, the gauche and trans conformers would be the two most stable forms.¹¹ Intermolecular hydrogen bonding is an important feature of ethylene glycol, regardless of the type of conformations (except possibly in the gas phase or in dilute solutions where solvents have no proton-accepting properties). In addition, due to the presence of two OH groups in the molecule, the possibility of intramolecular hydrogen bonding in some gauche conformers must be considered. Previous investigations on conformational isomerism of ethylene glycol have revealed that it is difficult to obtain results that are quantitative as well as non-contradictory.^{10,11} However, there appears to be a general acceptance that the ethylene glycol molecule exists primarily as the gauche conformer in the solid and gas phases due to stabilization by intramolecular hydrogen bonding, while it has both gauche and trans conformations with respect to the C–C bond in the liquid state.^{7,8}

The purpose of our work is to investigate the host–guest interactions in pure-silica and aluminosilicate sodalites containing ethylene glycol as a guest molecule, with attention to both intramolecular hydrogen bonding and intermolecular hydrogen bonding to the framework oxygens. It has been shown that each β -cage in pure-silica sodalite contains one ethylene glycol molecule after the crystallization process is complete.^{1,12} Thus, a particular type of conformation of ethylene glycol can be dominant in this sodalite because intermolecular hydrogen bonds between the encapsulated ethylene glycol molecules are not possible. However, previous single-crystal X-ray and powder neutron diffraction investigations on pure-silica sodalite have left open the question of the preferred conformation of the ethylene glycol encapsulated inside the β -cage.¹² Here we present the results obtained from powder X-ray diffraction, elemental and thermal analyses, ¹H, ¹³C, ²⁷Al, and ²⁹Si MAS NMR, IR, and Raman spectroscopic measurements of four

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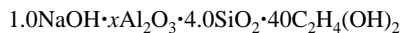
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sodalite materials with an Si/Al ratio ranging from ∞ to 5.7 in order to show that the conformation of the organic species present in zeolites can be altered according to the framework composition of zeolites, due to changes in the nature of host–guest interactions.

Experimental Section

Synthesis. The chemical reagents used in the synthesis of sodalites included NaOH (98%, EM), amorphous silica (Cab-O-Sil M-5), sodium aluminate ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, VWR), and ethylene glycol (Mallinckrodt). Four sodalite samples were synthesized from the reaction mixtures with Si/Al ratios of ∞ , 20, 10, and 5. Here we refer to these four samples as Si-SOD, Al-SOD-I, Al-SOD-II, and Al-SOD-III, respectively. The overall oxide composition of the reaction mixtures used in the synthesis of the first three samples was



where x is 0, 0.1, and 0.2. The reaction mixture was stirred at room temperature for 1 day and then allowed to proceed in a Tenfold-lined 23-mL Parr bomb at 175 °C for 3 weeks. After this period, the bomb was quenched to room temperature. The resulting white solid was filtered, washed repeatedly with water, and dried at room temperature overnight. Pure-silica sodalite was also prepared using deuterated ethylene glycol ($\text{DOCH}_2\text{CH}_2\text{OD}$, 98% atom % D, Aldrich) instead of normal ethylene glycol in the synthesis conditions stated above. When x was increased to 0.4 (Si/Al = 5), however, the reaction mixture remained amorphous even after heating at 175 °C for 3 weeks. Thus, we increased the NaOH content and added intentionally a small amount of water to get a reaction mixture with the following oxide composition:



The subsequent steps were the same as in the procedure given above.

Analytical Methods. Crystallinity and phase purity of the solids were determined by powder X-ray diffraction (XRD) using a Scintag XDS-2000 diffractometer (Cu $K\alpha$ radiation). The XRD patterns of all sodalite samples prepared in this study show that they are highly crystalline and no impurity phases are detected. The unit-cell parameters were determined by indexing the XRD patterns recorded with fluorophlogopite as an internal standard (experimental conditions: step mode, 0.02°; step size, 23 s; step time and 2θ range 7 to 50°). No deviations from the cubic symmetry were observed in the 2θ range studied and systematic absences were consistent with a body-centered lattice. The unit cell parameters were then refined using a least-squares procedure. The difference between the experimental 2θ values and the calculated values from the refined cubic parameter was below 0.01° in all cases.

Thermogravimetric analyses (TGA) were performed in air on a DuPont 951 thermogravimetric analyzer. Approximately 10 mg of sample were used at a heating rate of 10 °C·min⁻¹. Chemical analysis for Si, Al, and Na was performed by a Jarrell-Ash Polyscan 61E inductively coupled plasma (ICP) spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The C and H contents of the samples were analyzed by using a Carlo Erba 1106 elemental organic analyzer.

The ²⁷Al MAS NMR spectra were measured on a Varian VXR 400SWB spectrometer operating at a spinning rate of 5 kHz. The operating frequency of ²⁷Al was 104.21 MHz and the spectra were obtained with an acquisition of ca. 300 pulse transients, which was repeated with a $\Pi/20$ rad pulse length of 0.6 μs and a recycle delay of 1 s. The ²⁷Al chemical shifts are referenced to an $\text{Al}(\text{H}_2\text{O})_6^{3+}$ solution. The ²⁹Si MAS NMR spectra at a spinning rate of 5 kHz were recorded on the same spectrometer at a ²⁹Si frequency of 79.459 MHz with a $3\Pi/8$ rad pulse length of 3 μs . The recycle delay for sodalite samples with different Si/Al ratios was varied between 120 and 160 s. Typically, 350–500 scans were accumulated and the ²⁹Si chemical shifts are referenced to TMS. The ¹H MAS NMR spectra were recorded at room temperature on a Chemagnetics CMX-500 spectrometer operating at a proton Larmor frequency of 498.63 MHz and a spinning rate of 6 kHz. The spectra were obtained with an acquisition of 32 pulse transients,

Table 1. Chemical Compositions and Cubic Unit Cell Parameters of Sodalite Samples Prepared in This Study

sample	unit cell composition	Si/Al	a , Å	
			exptl ^a	calcd ^b
Si-SOD	$2.0\text{C}_2\text{H}_4(\text{OH})_2\cdot\text{Na}_{0.1}\text{Si}_{12}\text{O}_{24}$	∞	8.840	8.840
Al-SOD-I	$2.0\text{C}_2\text{H}_4(\text{OH})_2\cdot\text{Na}_{0.5}\text{Al}_{0.5}\text{Si}_{11.5}\text{O}_{24}$	23.0	8.832	8.872
Al-SOD-II	$1.9\text{C}_2\text{H}_4(\text{OH})_2\cdot\text{Na}_{1.0}\text{Al}_{1.0}\text{Si}_{11.0}\text{O}_{24}$	11.0	8.825	8.904
Al-SOD-III	$2.0\text{C}_2\text{H}_4(\text{OH})_2\cdot\text{Na}_{1.8}\text{Al}_{1.8}\text{Si}_{10.2}\text{O}_{24}$	5.7	8.829	8.954

^a From XRD data. ^b Calculated from eq 1, assuming no change in T–O–T angles.

which was repeated with 10-s recycle delay and 6.5- μs pulse length. The deconvolution of the ¹H MAS NMR spectra obtained was performed using the Origin curve-fitting software. The ¹³C NMR spectra were recorded on the same spectrometer at a ¹³C frequency of 125.38 MHz with a 90° pulse length of 5.8 μs . For CP and ¹H-decoupled spectra, recycle delays were 5 s and 10 to 20 s, respectively. Typically, 120 acquisitions were accumulated. For MAS ¹³C NMR experiments, the sample was spun at 3.5 kHz. Both ¹H and ¹³C chemical shifts are reported relative to TMS and zero line broadening was applied. The ¹³C NMR spectra were deconvoluted using the Felix Gaussian-fitting program.

The IR spectra in the region of 300–4000 cm⁻¹ were measured on a Nicolet 800 FT-IR and a Nicolet 710 FT-IR spectrometer using the KBr pellet technique. The Raman spectra between 200 and 3100 cm⁻¹ were recorded on a Bio-Rad FT Raman spectrometer. The excitation source was the 1064-nm line of a Nd:YAG laser at an intensity of about 120 mW at the sample. A capillary tube was used as the sample holder. Typically, 700 scans were accumulated for obtaining the Raman spectra and 500–1000 scans for the IR spectra. The Raman spectra between 3100 and 3800 cm⁻¹ were measured at 441.6 nm using a Liconix He–Cd laser (model 4240 NB) and a Spex 1403 0.85 m double spectrometer with photon counting electronics. The laser power at the sample was approximately 50 mW and the spectral slit widths were 5 cm⁻¹. The scan time was 1 s per wavenumber and 5 scans were accumulated in obtaining the Raman spectra in the OH region.

Results and Discussion

Chemical Compositions. Table 1 lists the chemical compositions of all sodalite samples prepared in this study. The Si/Al ratio of each product was found to be close to the value for its reaction mixture. Additionally, all the β -cages of these four sodalite samples contain one ethylene glycol molecule. An unexpected observation obtained from the unit cell composition data listed in Table 1 is the presence of a small amount of Na in Si-SOD where the framework is electrically neutral. A detailed discussion on the charge balance in the pure-silica sodalite will be given elsewhere.¹³

The syntheses reported here reveal that aluminosilicate sodalite materials with Si/Al ratios as low as about 5 can be prepared by using ethylene glycol, and fill in a gap in the compositional range of previously synthesized aluminosilicate sodalites.¹⁴ Therefore, it is now possible to synthesize sodalites in a full range of Al concentrations, from a pure-aluminate to a pure-silica form, via various synthetic routes: firing pellets of stoichiometric mixtures of the appropriate oxides at 1350 °C for aluminate and aluminosilicate materials with Si/Al ratios below 1;¹⁵ hydrothermal inorganic synthesis for aluminosilicate sodalite with Si/Al = 1;¹⁴ tetramethylammonium (TMA) ion-mediated hydrothermal synthesis for samples with Si/Al ratios up to 5;¹⁶ and nonaqueous phase synthesis using ethylene glycol for sodalites with Si/Al ratios from 5 to ∞ . For a high-silica composition range, it is also reported that sodalites having Si/

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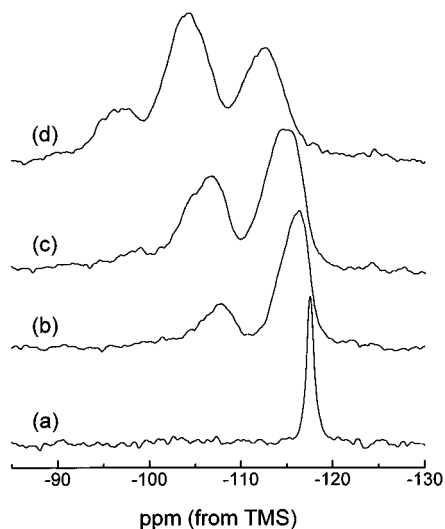


Figure 1. ^{29}Si MAS NMR spectra of pure-silica and aluminosilicate sodalites synthesized with ethylene glycol: (a) Si-SOD, (b) Al-SOD-I, (c) Al-SOD-II, and (d) Al-SOD-III.

Al ratios from 20 to ∞ can be hydrothermally synthesized with 1,3,5-trioxane as a structure-directing agent.¹⁷

Variation in Unit Cell Parameters. Table 1 also lists the unit cell parameters of the four sodalite materials determined by indexing their XRD patterns. It is clear that the unit cell parameter diminishes as the Al content per unit cell increases. This trend is completely different from that usually observed in zeolites because the distance (1.75 Å) of Al–O bonds is longer than that (1.62 Å) of Si–O bonds. The sample with the highest Al content (Al-SOD-III) slightly deviates from this trend, but it still shows a unit cell parameter smaller than that from Si-SOD or Al-SOD-I. If substitution of Si by Al would not affect the T–O–T angles, then the theoretical variation of the unit cell parameter for sodalite materials could be calculated from the following equation:

$$a_c^3 = V_{\text{Si}} + nV_{\text{Si}}[(d_{\text{Al-O}}/d_{\text{Si-O}})^3 - 1] \quad (1)$$

where a_c is the calculated cubic unit cell edge, V_{Si} is the unit cell volume of Si-SOD, and $d_{\text{Al-O}}$ and $d_{\text{Si-O}}$ are the Al–O and Si–O distances, respectively. n indicates the Al/(Al + Si) ratio in the aluminosilicate sodalite. As shown in Table 1, significant differences between the experimental unit cell parameter and the calculated value are observed for all the aluminosilicate sodalites synthesized in this work. For example, the unit cell parameter of Al-SOD-III was calculated to be 8.954 Å, which is much higher than the experimental value (8.829 Å) of the corresponding sample. This clearly shows that the T–O–T angle of the framework of sodalite materials prepared with ethylene glycol is dependent on the degree of the isomorphous substitution of Si by Al.

^{29}Si and ^{27}Al MAS NMR Spectroscopies. Figure 1 shows the ^{29}Si MAS NMR spectra of the four sodalite materials studied in this work. The spectrum of Si-SOD in Figure 1a gives only one narrow line at -117.5 ppm, which can be assigned to Si(0Al) tetrahedral units in the framework. This result is consistent with that reported in previous ^{29}Si MAS NMR studies.^{18,19} As seen in parts b–d of Figure 1, on the other hand, the ^{29}Si MAS NMR spectra of the three aluminosilicate

sodalite samples are characterized by Si(n Al) lines with $n = 0$ and 1 for Al-SOD-I, $n = 0, 1, 2$ for Al-SOD-II, and $n = 0, 1, 2, 3$ for Al-SOD-III, respectively. Attempts to deconvolute the ^{29}Si NMR spectra of these samples by assuming each Si(n Al) line as a single Si environment gave $(\text{Si}/\text{Al})_{\text{NMR}}$ values of 17.8, 9.7, and 4.7 for Al-SOD-I, Al-SOD-II, and Al-SOD-III, respectively. These values are in reasonable agreement with those obtained from chemical analysis (see Table 1).

Table 2 lists the ^{29}Si NMR chemical shift data for the four sodalite samples. These data reveal that as the Al content in the sample increases, the chemical shift of each Si(n Al) line is shifted to a lower field. Table 2 also lists the average T–O–T angles calculated from the observed chemical shift of the Si(0Al) line using the equations derived by Thomas et al.²⁰ The T–O–T angle calculated for Si-SOD (159.0°) using the equation of Thomas et al. agrees well with the previously reported value calculated from X-ray single-crystal analysis (159.7°) or that from neutron powder diffraction Rietveld refinement (159.6°).¹² For the rest of the samples, a distinct decrease in the T–O–T angle is found. Therefore, it is clear that the average T–O–T angles of the sodalite framework decrease with increasing Al content. On the other hand, the ^{27}Al MAS NMR spectra (not shown) of aluminosilicate sodalite samples show only a single resonance in the range 50–55 ppm. This indicates that all the Al atoms in these samples are isomorphously substituted into the T sites of the sodalite framework. That is, no extraframework Al species are present. The average Si–O–Al angle of the framework of each aluminosilicate sodalite was calculated from the chemical shift of the Al(4Si) line using the equation derived by Jacobsen et al.²¹ and is also listed in Table 2. Notice that as the Al content increases, the calculated Si–O–Al angle decreases. This trend is in good agreement with that found in aluminosilicate and aluminate sodalites containing alkaline halide.^{21,22} Therefore, the ^{27}Al NMR chemical shift data clearly support the conclusion drawn from ^{29}Si NMR experiments, although they have not been corrected for second-order quadrupolar effects.

It is well-known that small inorganic cations can exert an effect of contraction of the zeolite framework, due to their high polarization power. In aluminosilicate sodalite with a Si/Al ratio of 1, for example, a noticeable contraction in the unit cell is observed when the inorganic cation is Li^+ instead of Na^+ .²³ This is accompanied by a decrease in the mean T–O–T angles,²⁴ and such a decrease must be larger when the inorganic cations in the zeolite are dehydrated. TGA (not shown) and ^1H NMR experiments (*vide infra*) reveal that only Al-SOD-III contains a small amount of water, while the other samples are completely water free. This suggests that most, if not all, the Na^+ ions present in our sodalite samples except in Al-SOD-III are essentially in a dehydrated state. Therefore, the observed contraction of the framework upon increasing the Al content can be attributed to an increase in the amount of dehydrated Na^+ ions in the sodalite samples prepared here.²⁵ The small deviation of Al-SOD-III from the unit cell shrinkage shown in Table 1 can be due to water in the hydration sphere of a fraction of the Na^+ ions.

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Table 2. ^{27}Al and ^{29}Si MAS NMR Chemical Shift Data

sample	^{29}Si MAS NMR				$\angle\text{T-O-T}^a$	^{27}Al MAS NMR	
	δ , ppm					δ , ppm	$\angle\text{Al-O-Si}^b$
	Si(0Al)	Si(1Al)	Si(2Al)	Si(3Al)			
Si-SOD	-117.5				159.0		
Al-SOD-I	-115.9	-107.5			156.2	50.95	156.1
Al-SOD-II	-114.8	-106.1	-98.1		154.3	52.56	153.9
Al-SOD-III	-113.7	-105.0	-97.1	-90.8	152.4	54.85	150.7

^a T-O-T angle in degrees calculated from Si(0Al) chemical shifts using the equation of Thomas et al.²⁰ ^b Al-O-Si angle in degrees calculated from the uncorrected ^{27}Al chemical shift using the equation of Jacobsen et al.²¹

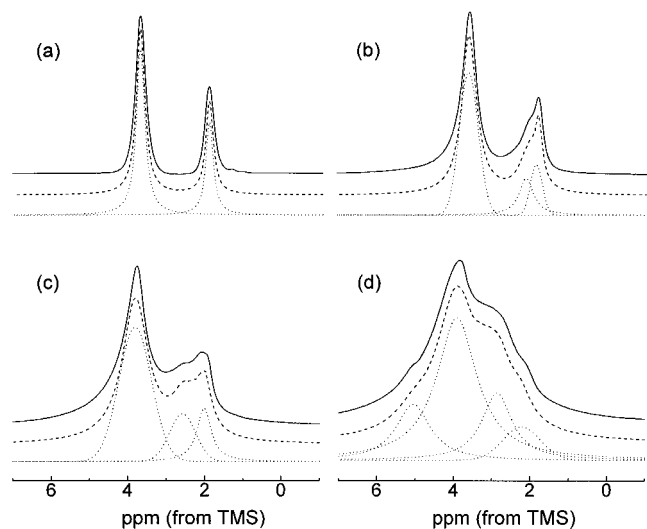


Figure 2. Curve deconvolution of the ^1H MAS NMR spectra of sodalite samples: (a) Si-SOD, (b) Al-SOD-I, (c) Al-SOD-II, and (d) Al-SOD-III. The solid lines represent the experimental spectra and the dashed lines are the simulated spectra. The deconvoluted components of each simulated spectrum are shown with dotted lines.

The sodalite structure affords a considerable degree of distortion by just merely rotating the TO_4 tetrahedra.²⁶ This flexibility can be deduced from the very broad range of T-O-T angles ($125\text{--}160^\circ$) found in sodalite materials with a wide variety of chemical compositions.²² In the so-called fully expanded framework, the T-O-T angle is 160° . If no distinctions between T atoms are made, rotation of the TO_4 tetrahedra about their $\bar{4}$ axes can move the oxygen atoms out of the β -cage and change the space group from $Im\bar{3}m$ to $I43m$, while maintaining the framework connectivity. This causes a unit cell contraction with a decrease in T-O-T angles, and it is referred to as a collapse of the framework.²⁶ Table 2 clearly shows that the contraction of the sodalite unit cell upon increasing the Al content is accompanied by a decrease in T-O-T angles from near 160° in the fully expanded Si-SOD to around 152° in Al-SOD-III. This collapse of the sodalite framework may have an influence on the preferred conformation of the encapsulated ethylene glycol, because it results in a significant decrease of the void volume inside the β -cage.

^1H MAS NMR Spectroscopy. Figure 2 shows the ^1H MAS NMR spectra of the four sodalite samples together with the simulated spectra and their deconvoluted components. Table 3 summarizes results obtained from the spectral deconvolution.

Neat ethylene glycol exhibits two ^1H NMR resonances at 3.75 and 5.41 ppm with an intensity ratio of 2:1 (see Table 3), which can be attributed to the CH_2 protons and the OH groups of the ethylene glycol molecule subject to extensive intermolecular hydrogen bonding, respectively. As seen in Figure 2a, in contrast, the ^1H MAS NMR spectrum of Si-SOD shows two

Table 3. Chemical Shifts, Line Widths, Relative Intensities, and Assignments of the ^1H MAS NMR Lines of Sodalite Samples^{a,b}

sample	chemical shift, ppm from TMS, for components I-V				
	I ^c	II ^d	III ^e	IV ^f	V ^g
neat ethylene glycol	5.41		3.75		
Si-SOD	[0.49]		3.72 (140)		1.90 (130)
			[1.00]		[0.49]
			3.74 (310)	2.27 (230)	2.00 (230)
Al-SOD-I			[1.00]	[0.27]	[0.23]
			3.80 (510)	2.58 (420)	2.04 (240)
Al-SOD-II			[1.00]	[0.31]	[0.20]
		5.05 (550)	3.91 (660)	2.86 (500)	2.21 (580)
Al-SOD-III		[0.28]	[1.00]	[0.35]	[0.14]

^a The values given in parentheses are full widths at half-maximum (fwhm's) of the deconvoluted components in Hz. ^b The relative intensities of deconvoluted components are referenced relative to the intensity of the CH_2 line of the ethylene glycol molecule and are given in square brackets. ^c The OH protons of the ethylene glycol molecule subject to extensive intermolecular hydrogen bonding. ^d Water associated with Na^+ ions. ^e The CH_2 protons of the ethylene glycol molecule. ^f The OH protons of ethylene glycol involved in intermolecular hydrogen bonding to the sodalite framework. ^g The OH protons of ethylene glycol not involved in hydrogen bonding to the framework.

narrow resonances at 1.90 and 3.72 ppm. Due to their integral intensity ratio of 1:2, these two lines have to be assigned to the OH and CH_2 protons of the ethylene glycol molecule entrapped within the β -cages of Si-SOD, respectively. The strong high-field shift of the OH line in comparison to neat ethylene glycol clearly shows that the encapsulation of the ethylene glycol molecule within the β -cage prevents the intermolecular hydrogen bonds between two ethylene glycol molecules. Typically, the ^1H NMR spectra of zeolites and related materials show broad lines or a wide distribution of spinning side bands even under MAS conditions,²⁷ mainly due to the strong dipolar interactions of the protons and the small ^1H chemical shift range. However, the ^1H - ^1H dipolar interactions are considerably reduced or even eliminated when the protons are sufficiently separated to remove the mutual interaction of the dipolar fields, or when they are involved in the dynamic site exchange which is faster than the NMR time scale and thus averages the dipolar interaction as in a liquid state. Then, dipolar broadening could be removed by MAS of the sample at high spinning speeds. This is the case for Si-SOD in which the isolated ethylene glycol molecule may undergo fast dynamic reorientation. The narrow feature of the ^1H NMR lines found in Figure 2a supports the speculation given above. Let us further consider the origin of the line appearing at 1.90 ppm in the ^1H NMR spectrum of Si-SOD. As stated earlier, intermolecular hydrogen bonds between two ethylene glycol molecules in this sample are not possible. However, we cannot rule out the possibility of intramolecular hydrogen bonding in the isolated guest molecule. Actually, the IR and Raman spectra of Si-SOD show that the guest molecule contains

almost equal amounts of free and intramolecularly hydrogen-bonded OH groups (*vide infra*). Therefore, the high-field line of Si-SOD in Figure 2a 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. This can be rationalized when the strength of intramolecular hydrogen bonding in ethylene glycol cannot be strong enough to cause differences in the ^1H chemical shift between the free OH proton and the intramolecularly hydrogen-bonded OH proton of the isolated ethylene glycol molecule. In fact, any conformation of ethylene glycol does not allow its geometry to linearly orient the OH proton toward the free electron pairs of the oxygen atom in the other OH group. On the other hand, the alternative way to rationalize the occurrence of the single OH ^1H NMR line in Figure 2a can be achieved by the consideration that the mutual exchange between the free and hydrogen-bonded OH groups of the guest molecule in Si-SOD is very fast with respect to the NMR time scale, although it is slow with respect to the IR or Raman time scale.

The most important observation obtained from Figure 2 is that unlike pure-silica sodalite, aluminosilicate sodalites show an additional signal whose chemical shift varies from 2.3 to 2.9 ppm. This line becomes stronger with a simultaneous decrease in intensity of the OH line at about 2.0 ppm as the Al content in these samples increases. In addition, the curve deconvolution data in Table 3 show that the total intensity of the two lines appearing at 2.0 and 2.3–2.9 ppm in the simulated spectra of aluminosilicate sodalites is just half the intensity of the low-field line at about 3.8 ppm in the corresponding spectra. Apparently, intermolecular hydrogen bonds between two ethylene glycol molecules are not possible because of their encapsulation within the β -cages. However, intramolecular hydrogen bonds and/or hydrogen bonds to the sodalite framework oxygens are still possible (*vide infra*). Such hydrogen bonds are expected to primarily depend not only on the conformation of the molecule inside the β -cage but also on the charge density of framework oxygen atoms. In addition, each single negative charge in aluminosilicate sodalites is created by isomorphous substitution of Si by Al in the framework and is distributed on the four oxygen atoms of the AlO_4^- tetrahedral units. Therefore, the formation of linear hydrogen bonds between the OH protons of the guest molecule and the negatively charged framework oxygen atoms of aluminosilicate sodalite samples may be possible, if no restrictions other than those imposed by this type of hydrogen bonding on the orientation of ethylene glycol inside the essentially spherical β -cage are considered. This is because the guest molecule can reorient itself in order to form a linear hydrogen bond to the negatively charged oxygen of the AlO_4^- framework units. If such is the case, hydrogen bonds between the OH protons of the guest molecule and the framework oxygens should be much stronger than intramolecular hydrogen bonds. This may lead to the occurrence of a new NMR line at a lower field than that from the free OH or the intramolecularly hydrogen-bonded OH groups in the guest molecule. Therefore, the NMR line at 2.3–2.9 ppm can be assigned to OH protons of the guest molecule forming intermolecular hydrogen bonds to the framework oxygen atoms.

Figure 3 shows plots of the relative intensities of the deconvoluted ^1H NMR components from the free OH proton and hydrogen-bonded OH proton to the framework versus the number of Al atoms per unit cell of sodalites containing ethylene glycol. Here we assign the high-field OH NMR line from Al-SOD-I, Al-SOD-II, and Al-SOD-III to the free or intramolecularly hydrogen-bonded OH group of the guest molecule, like

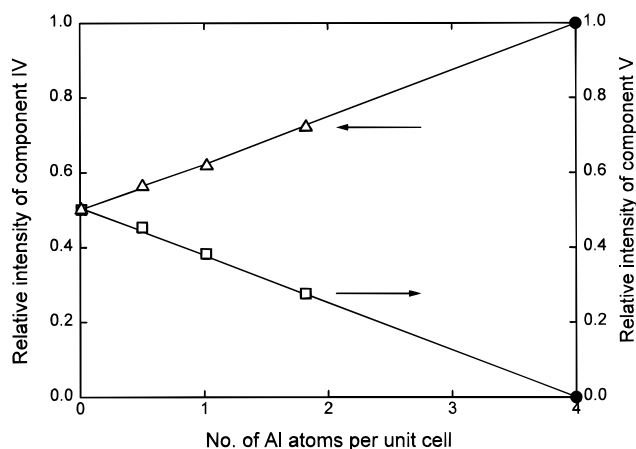


Figure 3. Plots of relative intensities of the deconvoluted ^1H MAS NMR components IV and V vs number of Al atoms per unit cell. The components IV and V represent the OH groups of the encapsulated ethylene glycol involved and not involved, respectively, in hydrogen bonding to the sodalite framework. Both the expected decrease and increase in intensities of these two components are plotted as solid lines. The extrapolated number of Al atoms per unit cell of sodalites where the OH groups of the guest molecule are not free but exclusively hydrogen bonded to the framework is indicated by a solid circle.

that from Si-SOD. As seen in Figure 3, a linear relationship between the line intensities and the number of Al atoms per unit cell is observed. Therefore, it is clear that the number of hydrogen bonds between the OH group of ethylene glycol and the framework oxygen atoms with a high negative charge density increases with increasing concentration of AlO_4^- units in the framework. Figure 3 also shows that both OH groups of the encapsulated ethylene glycol would not be free but exclusively hydrogen-bonded when there are 4 Al atoms per unit cell, i.e., 2 Al atoms per β -cage. This is not unexpected because in that case the number of Al atoms per β -cage is the same as that of OH groups in the encapsulated ethylene glycol molecule.

The curve deconvolution results in Figure 2 and Table 3 reveal that all the deconvoluted components are continuously broadened and shifted to lower field as the Al content in the sodalite framework increases. This suggests that with an increase in the framework Al content the extent of hydrogen bonds of ethylene glycol to the framework increases, while the mobility of the encapsulated ethylene glycol molecule decreases. The curve deconvolution also shows that Si-SOD, Al-SOD-I, and Al-SOD-II do not exhibit an NMR line between 4.5 and 5.5 ppm due to water molecules associated with Na^+ ions.²⁸ Therefore, it is clear that these sodalite samples are essentially water free, although they were not purposely dried prior to ^1H NMR measurements. However, the Al-SOD-III sample with the highest Al content exhibits a line at 5.1 ppm, indicating that Al-SOD-III contains a small amount of water molecules coordinated to the Na^+ ions. On the other hand, the ^1H MAS NMR spectra of high-silica zeolites such as ZSM-5 or ZSM-12 prepared with the organic quaternary ammonium cations are reported to exhibit a line at 10.0 ± 0.2 ppm, due to $\text{SiO}^- \cdots \text{HOSi}$ hydrogen bonds in the defect site produced to balance the charge of cationic structure-directing organics.²⁸ None of the sodalite samples studied here show a ^1H NMR line around 10 ppm, indicating the absence of $\text{SiO}^- \cdots \text{HOSi}$ hydrogen bonds. This can be attributed to the non-charged nature of the organic guest molecule (ethylene glycol) in our sodalites, which does not require the presence of $\text{Si}-\text{O}^-$ defects for charge balance. In addition, it should be noted that all sodalite samples prepared

(28) Koller, H.; Lobo, R. F.; Burkett, S. L.; Davis, M. E. *J. Phys. Chem.* 1995, 99, 12588.

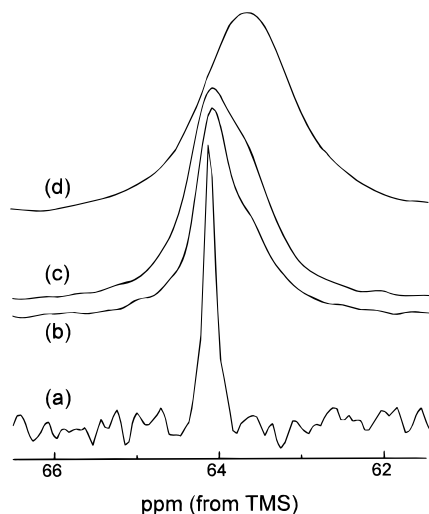


Figure 4. ^{13}C - ^1H CP/MAS NMR spectra of (a) Si-SOD, (b) Al-SOD-I, (c) Al-SOD-II, and (d) Al-SOD-III.

here give no ^1H NMR line around 6.5 ppm corresponding to silanol groups not involved in $\text{SiO}^-\cdots\text{HOSi}$ hydrogen bonding.²⁸

^{13}C MAS NMR Spectroscopy. Figure 4 shows the ^{13}C CP/MAS NMR spectra of a series of sodalite samples. The spectrum of Si-SOD in Figure 4a exhibits a very narrow line at 64.1 ppm, which is in good agreement with the result reported by Herreros et al.¹⁹ As seen in spectra b and c of Figure 4, however, Al-SOD-I and Al-SOD-II show a shoulder around 63.6 ppm as well as the broad resonance at 64.1 ppm. On the other hand, a broad but symmetric NMR line is observed at 63.6 ppm in the ^{13}C NMR spectrum of Al-SOD-III with the highest Al content (Figure 4d). The appearance of two lines in the ^{13}C MAS NMR spectra of Al-SOD-I and Al-SOD-II indicates that at least two different types of ethylene glycol carbon species can exist and that their relative concentrations depend on the Al content in the framework. Although these two carbon species cannot be completely identified by ^{13}C MAS NMR experiments, it appears that they may originate from differences in conformation of the guest molecule and/or in intramolecular hydrogen bond features forcing tetrahedral angles on the carbon atom. In addition, a symmetric nature of the ^{13}C NMR line obtained from Al-SOD-III indicates that the ethylene glycol molecules in this sample have only one type of carbon species.

Currently, it is not possible to make quantitative correlations between carbon species of the guest molecule and the framework Al concentration from the ^{13}C NMR data. However, Figure 4 clearly shows that the carbon species responsible for the signal at 63.6 ppm is not present in Si-SOD at all, but it is the only species observed in Al-SOD-III. If we assume a statistical distribution of Si and Al on the sodalite framework, Al-SOD-III with a Si/Al ratio of 5.7 contains approximately one Al atom per β -cage. Then, the end-members of a series of sodalites prepared here possess 0 and 1 net negative charge per cage, respectively. This implies that only one compositional type of β -cages is present in both Si-SOD and Al-SOD-III. In contrast, it is expected that Al-SOD-I and Al-SOD-II may contain two types of β -cages whose net negative charges are 0 and 1, respectively. This appears to be the reason why two ^{13}C NMR lines are observed for these two aluminosilicate sodalites. Table 4 summarizes the ^{13}C - ^1H -decoupled MAS NMR data of the four sodalite samples. For all the samples, ^{13}C CP/MAS NMR experiments gave resonances at the same chemical shifts as observed in the ^1H decoupled experiments.

The ^{13}C CP/MAS NMR spectra in Figure 4 also demonstrate that the spectrum of Si-SOD was much noisier than that obtained

Table 4. ^{13}C - ^1H -Decoupled NMR Chemical Shift Data

sample	δ , ppm from TMS	intensity ratio	
Si-SOD	64.08		
Al-SOD-I	64.08	63.60	4.3:1
Al-SOD-II	64.12	63.66	1.8:1
Al-SOD-III		63.56	

from any of the three aluminosilicate samples, even after an acquisition of a larger number of scans. This indicates that the carbon atoms of the guest molecule in Si-SOD did not cross-polarize as efficiently as those in aluminosilicate samples. As seen in Figure 4a, however, the ^{13}C CP/MAS NMR signal of Si-SOD is extremely narrow. The full width at half-maximum (fwhm) of the line from this pure-silica sodalite was found to be 15 Hz. The static ^{13}C spectrum (not shown) of this sample gives only one NMR line with a fwhm of 240 Hz, which is approximately one order of magnitude broader than that in the corresponding MAS spectrum. However, the observed line is still narrow for solid-state NMR, indicating that line-broadening interactions are small. Moreover, the line in the static spectrum is not shifted relative to the position of line in the MAS spectrum. Thus, we conclude that the ethylene glycol molecules are undergoing rapid motions within the β -cages of Si-SOD. On the other hand, Al-SOD-I and Al-SOD-II showed broader ^{13}C NMR signals. For example, the fwhm of the resonance at 64.1 ppm from Al-SOD-I is 58 Hz which is approximately four times larger than that of the line obtained from Si-SOD. Also, a higher cross-polarization efficiency, especially for the high-field ^{13}C NMR signal, is observed from Al-SOD-I and Al-SOD-II samples. This indicates that the guest molecules in these aluminosilicate sodalites are not as mobile as those in pure-silica sodalite. The restricted mobility appears to originate from the framework negative charges, more specifically from hydrogen bonds of ethylene glycol to the framework, because the high-field signal in Figure 4 is due to the carbon species from the ethylene glycol molecule in the β -cage with one net framework negative charge. The single negative framework charge caused by each framework Al in aluminosilicate samples cannot be exclusively localized at a specific framework oxygen atom surrounding the guest molecule. Therefore, we speculate that the guest molecule can jump from one hydrogen-bonding position to another one involving a different framework oxygen atom. This suggests that restrictions in mobility of ethylene glycol inside the β -cages with one negative charge may be due to several possible hydrogen-bonding positions where the residence time of the organic molecule is different.

IR Spectroscopy. Figure 5 shows the IR spectra of the structural region for all sodalite samples used in this study. The IR spectrum of pure ethylene glycol in this region is also compared in Figure 5. Although most of the structural vibration bands found in the 300–1500- cm^{-1} region overlap partially with the bands originated from the guest molecule, it is clear that the positions of some structural bands are dependent on the Al content in the sodalite framework, as found in the IR studies of many other zeolites.²⁹ For example, the asymmetric T–O stretching band appearing at 1114 cm^{-1} in the IR spectrum of Si-SOD (Figure 5a) is linearly shifted to a lower wavenumber region as the Al content in the sodalite framework increases.²⁵ This trend is also apparent for the T–O–T bending and the symmetric T–O–T stretching vibrations which appear in the regions of 453–459 and 762–777 cm^{-1} , respectively. Thus, isomorphous substitution of Si by Al in the sodalite framework again can be ascertained by IR spectroscopy.

(29) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

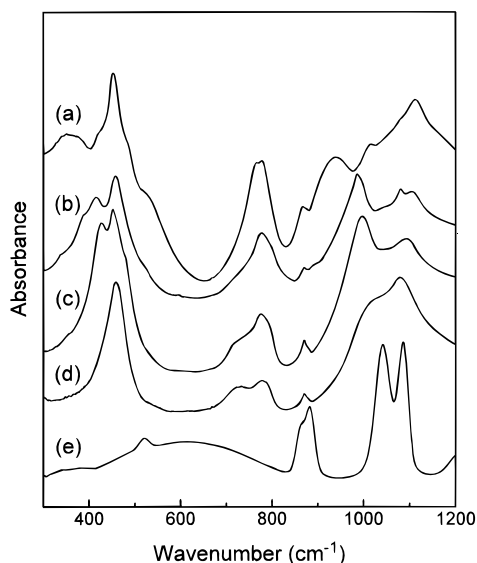


Figure 5. IR spectra of sodalite samples and neat ethylene glycol in the 300–1200-cm⁻¹ region: (a) Si-SOD, (b) Al-SOD-I, (c) Al-SOD-II, (d) Al-SOD-III, and (e) neat ethylene glycol.

Several unexpected results are obtained from the IR spectra given in Figure 5. First, a broad band at 358 cm⁻¹ in the spectrum of Si-SOD shifts to a higher wavenumber region and becomes narrower for the samples with higher Al contents: 415 and 427 cm⁻¹ in Al-SOD-I and Al-SOD-II, respectively. Liquid ethylene glycol exhibits no detectable bands in this region. Thus, the band that varies in position between 350 and 430 cm⁻¹ appears to be from the sodalite framework rather than from the guest molecule. On the contrary, no band is observed at 350–430 cm⁻¹ in the spectrum of Al-SOD-III. Most likely, this may be due to overlap with the more intense T–O–T bending band around 450 cm⁻¹. Second, a new framework band is observed near the T–O–T symmetric stretching band of the samples with higher Al contents: a shoulder at 718 cm⁻¹ for Al-SOD-II and a well-resolved band at 728 cm⁻¹ for Al-SOD-III. This can be attributed to the splitting of the T–O–T symmetric stretching band. Third, a small but rather sharp band appears at 866–870 cm⁻¹ in the IR spectra of sodalite samples. Neat ethylene glycol exhibits two strong bands at 864 and 883 cm⁻¹, which correspond to the C–C and C–O stretching modes, respectively. Thus, the band at 866–870 cm⁻¹ is probably from the encapsulated ethylene glycol molecule. However, it is not clear why the encapsulated molecule gives only one band in this region. Fourth, a band at 939 cm⁻¹ in Si-SOD shifts to higher wavenumbers as the Al content increases: 985, 996, and 1020 cm⁻¹ (shoulder) in Al-SOD-I, Al-SOD-II, and Al-SOD-III, respectively. Si-SOD and Al-SOD-I also show a band at 1016 and 1080 cm⁻¹, respectively, which is not visible in the samples with higher Al contents. These bands are probably due to the splitting of the asymmetric T–O stretching band. Therefore, it appears that the aluminosilicate samples may have lower than cubic symmetry, despite the XRD results. Actually, van Santen and Vogel³⁰ concluded from the IR spectrum of a pure-silica sodalite containing trioxane that the structure is not strictly cubic, because all the framework bands show some degree of fine structure. They found that deconvolution of the spectrum gave more IR bands than those expected from ideal cubic symmetry.

Figure 6 shows the IR spectra of neat ethylene glycol and the four sodalite samples in the 2600–3800-cm⁻¹ region. The OH stretching region of Figure 6a reveals that pure ethylene

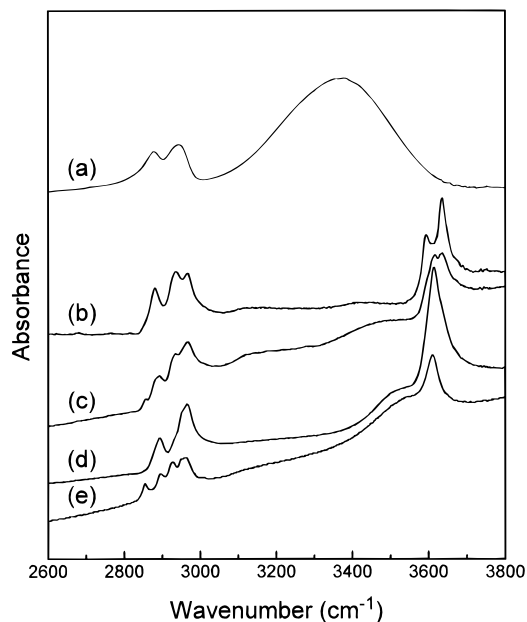


Figure 6. IR spectra of neat ethylene glycol and sodalites with different Si/Al ratios in the C–H and O–H stretching regions: (a) neat ethylene glycol, (b) Si-SOD, (c) Al-SOD-I, (d) Al-SOD-II, and (e) Al-SOD-III.

glycol gives a very broad and strong band around 3360 cm⁻¹ due to extensive intermolecular hydrogen bonding. Since we could not make self-supported pellets of sodalites used in this study, their IR spectra were obtained using the KBr technique. Prior to IR measurements, however, the KBr pellets containing sodalites were heated in air at 180 °C for about 4 days to completely remove water from KBr. The IR spectra (not shown) of the dried pellets in the 1500–2000-cm⁻¹ region did not show any band around 1640 cm⁻¹ due to bending vibration of water. Therefore, it is clear that the bands appearing in the OH region of spectra b–e in Figure 6 are not from water in KBr but from the guest molecules in sodalites.

The IR spectrum of Si-SOD in Figure 6b gives no noticeable band in the 3200–3500-cm⁻¹ region, unlike that of pure ethylene glycol. This is not unexpected because intermolecular hydrogen bonding between the guest molecules in Si-SOD is prevented by their encapsulation in the β -cages. However, all aluminosilicate sodalites exhibit a broad OH band between 3400 and 3600 cm⁻¹. As seen in spectra c–e of Figure 6, this broad band is observed at about 3460, 3510, and 3540 cm⁻¹, respectively. Because no water is now present in all aluminosilicate sodalites, this band cannot be attributed to water in the samples. Rather, we believe that it must be attributed to hydrogen bonds to the framework oxygens in AlO_4^- tetrahedra. Notice that the OH band at 3400–3550 cm⁻¹ in the IR spectra of aluminosilicate samples becomes stronger with its simultaneous shift to a higher wavenumber region as the Al content in the framework increases. This clearly shows that the extent of hydrogen bonding of ethylene glycol to the framework is dependent on the amount of the framework Al content, as evidenced by ¹H NMR experiments.

Next, we consider the OH stretching vibration bands appearing at the position higher than 3550 cm⁻¹ in the four sodalite samples. As seen in Figure 6b, Si-SOD gives two sharp bands of about equal intensities at 3634 and 3592 cm⁻¹ due to the encapsulated ethylene glycol molecules. This can be further supported by the fact that the IR spectrum (not shown) of pure-silica sodalite containing deuterated ethylene glycol shows two OD stretching bands at 2654 and 2683 cm⁻¹, which are shifted by the expected isotopic factor of about 1.35 to lower wavenumber regions. Kuhn⁴ reported that very dilute solutions of

(30) van Santen, R. A.; Vogel, D. L. *Adv. Solid State Chem.* **1989**, *1*, 151.

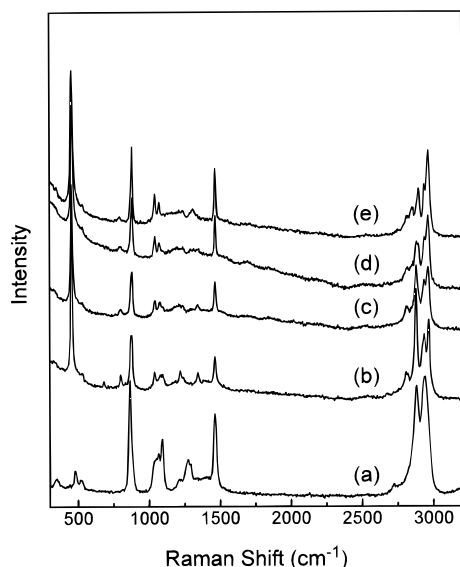
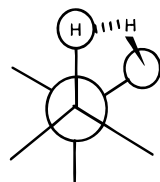


Figure 7. Raman spectra in the 200–3200-cm⁻¹ region of (a) neat ethylene glycol, (b) Si-SOD, (c) Al-SOD-I, (d) Al-SOD-II, and (e) Al-SOD-III.

ethylene glycol in CCl₄ ($<5 \times 10^{-3}$ M) present two bands at 3644 and 3612 cm⁻¹ with roughly equal intensities. He assigned these two bands to the free OH and the OH group forming an intramolecular hydrogen bond in gauche conformers. Therefore, two bands at 3634 and 3592 cm⁻¹ in Figure 6b can be attributed to the free OH group of the isolated ethylene glycol and the OH group in which the proton is involved in a weak intramolecular hydrogen bond. Also, the vapor phase ethylene glycol in the temperature range 50–125 °C has been reported to exhibit free and intramolecularly hydrogen-bonded OH bands is 3677 and 3644 cm⁻¹, respectively.³¹ Since both CCl₄ molecules and the pure-silica framework should have relatively low affinity for the OH groups of ethylene glycol, the interaction of ethylene glycol with CCl₄ or with the Si-SOD framework is expected to be weak. However, the observed differences in the OH band position of ethylene glycol in CCl₄ solution and that in Si-SOD reveal that the matrix effect on the OH band position of the guest molecule is not negligible. From the IR spectrum in Figure 6b, it can be concluded that the ethylene glycol conformer inside the β -cages of pure-silica sodalite is the gauche conformer with only one intramolecular hydrogen bond, labeled tGg', as depicted below in the Newman projection:



On the other hand, the substitution of Al for Si in the sodalite framework causes a disappearance of two OH bands at 3634 and 3592 cm⁻¹ with a simultaneous occurrence of a new band between them. As seen in Figure 6c, Al-SOD-I gives a band at 3615 cm⁻¹. The band at 3634 cm⁻¹ from this sample is still clear, but that at 3592 cm⁻¹ is hardly observed. From the spectrum of Al-SOD-II in Figure 6d, a broad but strong band at 3611 cm⁻¹ with a shoulder at 3634 cm⁻¹ is found. Finally, Al-SOD-III (Figure 6e) exhibits only one band at 3607 cm⁻¹. These observations suggest that the conformation of ethylene glycol in sodalites is dependent on the framework Al content.

(31) Buckley, P.; Giguere, P. A. *Can. J. Chem.* **1967**, *45*, 397.

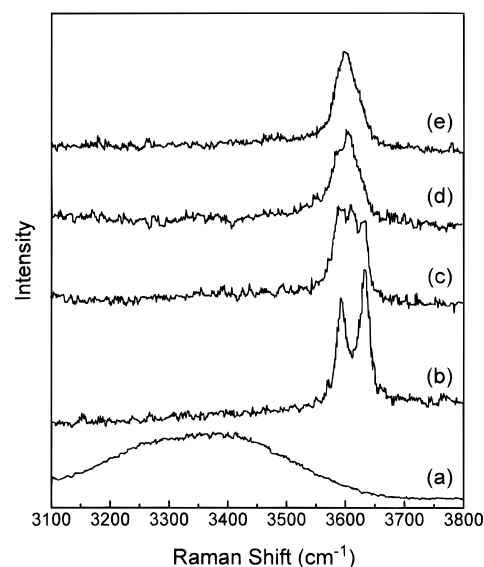


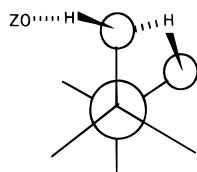
Figure 8. Raman spectra in the OH region of (a) neat ethylene glycol, (b) Si-SOD, (c) Al-SOD-I, (d) Al-SOD-II, and (e) Al-SOD-III.

If this speculation is correct, a logical next step would be to consider the possible conformations of ethylene glycol in aluminosilicate sodalites. First of all, let us discuss the possibility that the conformation of the isolated ethylene glycol molecule changes gradually from the gauche to the trans conformer, labeled tTt, as the framework Al content increases. Since the formation of intramolecular hydrogen bonds in this trans isomer is not possible, the band at 3607 cm⁻¹ in the IR spectrum of Al-SOD-III with the highest Al content (Figure 6e) should be considered as the free OH groups of the guest molecule. However, notice that the band position is approximately 30 cm⁻¹ lower than the free OH band of ethylene glycol in Si-SOD. This indicates that the OH groups of the guest molecules in Al-SOD-III are partially disturbed by intramolecular hydrogen bonding. Therefore, the trans conformer is unlikely to exist in aluminosilicate sodalites. This can be further supported by the IR–Raman mutual exclusion rule. If the OH groups of the trans isomer are regarded as single atoms, the trans isomer would have ideal C_{2h} symmetry. Thus, no OH bands should be observed in the Raman spectra of aluminosilicate sodalites because of the presence of an inversion center. However, the Raman spectra given in Figure 8 show the same spectral changes in the OH region as those found in the IR spectra (*vide infra*).

A more plausible situation is the the conformation about the C–C bond of the guest molecule is not changed to the trans conformation, even though the framework Al content increases. Apparently, the framework contraction upon increasing the Al content (with long Al–O distance compared to Si–O) in the sodalite framework requires more acute T–O–T angles with the oxygens displaced toward the β -cage. Thus, we can assess that the free volume available for ethylene glycol in the cages diminishes as the Al content increases. This speculation may be more reliable when we consider the fact that the content of Na⁺ ions present inside the β -cage increases with an increase in the framework Al content. The ethylene glycol conformer with two intramolecular hydrogen bonds leading to a cyclic (OH)₂, labeled g'Gg', has been proposed to exist,³² although this conformer has the unfavorable orientation of the OH groups for double hydrogen bonding. Since both OH groups in g'Gg' are equivalent, its IR spectrum could show a single band in the OH stretching vibration region as found in spectra c and d of

(32) Krueger, P. J.; Mettee, H. D. *J. Mol. Spectrosc.* **1965**, *18*, 131.

Figure 6. However, $g'Gg'$ cannot be considered as a predominant species in the aluminosilicate sodalite sample with a high Al content because of the presence of a broad OH band at $3460\text{--}3540\text{ cm}^{-1}$ in the IR spectra. When hydrogen bonds to the framework exist in this sodalite, the relative importance of the intramolecular hydrogen bonds leading to the stabilization of the gauche conformer may lessen. However, it must be weak enough to give the OH band at 3607 cm^{-1} , as found in Figure 6. Therefore, we believe that the most probable conformation of ethylene glycol in Al-SOD-III with the highest Si/Al ratio is gGg' . In this conformer one OH group is hydrogen bonded to the framework oxygen, while the other OH group is still involved in a weak intramolecular hydrogen bond:



where Z denotes the framework Al atom. Because of its small size, gGg' would fit better in the β -cages of the samples with higher Al content. Therefore, it is most likely that the conformation of ethylene glycol in Si-SOD is tGg' , while that of the guest molecule in Al-SOD-III with the highest Si/Al ratio is gGg' . To the contrary, the Al-SOD-I and Al-SOD-II samples with intermediate Si/Al ratios may contain both tGg' and gGg' . The interpretation given above is based on our ^1H NMR results showing that the amount of free OH groups that become involved in strong hydrogen bonds to the framework increases continuously as the Al content increases. Therefore, the disappearance of two bands at 3634 and 3592 cm^{-1} with the simultaneous shift of the weak band from 3460 to 3540 cm^{-1} upon increasing Al content in the sodalite samples can be understood. Finally, it should be noted from the IR spectra in Figure 6 that the C–H stretching region between 2800 and 3000 cm^{-1} of the guest molecule is also influenced by the Al content in the sodalite sample, although detailed discussion on this region is out of the scope of this study.

Raman Spectroscopy. Figure 7 shows the Raman spectra in the $200\text{--}3200\text{-cm}^{-1}$ region of the four sodalite samples. The Raman spectrum of neat ethylene glycol is also compared in Figure 7. It is clear that all the structural Raman bands found in the $300\text{--}1000\text{-cm}^{-1}$ region do not overlap heavily with the bands from the guest molecule because of their narrow feature. Generally, the strongest structural Raman band of zeolites is found in the $300\text{--}600\text{-cm}^{-1}$ region and is assigned to the motion of the oxygen atom in the plane perpendicular to the T–O–T bond.³³ As seen in spectra b–e of Figure 7, all four sodalite samples exhibit the T–O–T bending vibration band at $451\text{--}453\text{ cm}^{-1}$. Also, a weak band appearing at 797 cm^{-1} in the Raman spectra can be due to the symmetric T–O stretching vibration.³³ On the other hand, two weak bands at $1035\text{--}1040$ and 1070 cm^{-1} are difficult to ascribe solely to the framework bands or to the encapsulated ethylene glycol molecule. This is because both the encapsulated ethylene glycol and the sodalite framework exhibit C–O stretching and CH_2 rocking vibrations,⁸ and asymmetric T–O stretching vibrations^{34,35} in the $1000\text{--}1200\text{-cm}^{-1}$ region. However, two important features can be obtained from the Raman spectra of the structural region for the four sodalite samples in Figure 7. First, the positions of all

structural bands are almost independent of the Al content in the sodalite framework. This is consistent with the trend found in the Raman studies of other zeolites.³⁶ Second, the strong band appearing at 862 cm^{-1} in Figure 7a, due to the combination of the C–C and C–O stretching vibrations of ethylene glycol, is observed at $876\text{--}878\text{ cm}^{-1}$ in the Raman spectra of the four sodalite samples (see parts b–e of Figure 7). This demonstrates the tight fit of ethylene glycol in the β -cage. The shift of a specific vibration band from the guest molecule to a higher wavenumber region is also observed in the Raman spectra of the TMA ions within the β -cages of sodalites with different framework compositions.³⁷ The C–H stretching vibration region between 2800 and 3000 cm^{-1} of the guest molecule in the four sodalite samples is generally similar to the same region of the IR spectra of the corresponding samples, although there are small differences in the spectral changes caused by Al substitution.

Figure 8 shows the Raman spectra of neat ethylene glycol and sodalite samples in the OH region, which are quite similar to the OH region of the IR spectra in Figure 6. Liquid ethylene glycol shows a broad band around 3340 cm^{-1} , as seen in Figure 8a. This band is assigned to intermolecular hydrogen-bonded OH groups. Two rather sharp bands are observed at 3634 and 3595 cm^{-1} in the spectrum of Si-SOD in Figure 8b, which can be attributed to the free OH and the intramolecularly hydrogen-bonding OH group of the isolated ethylene glycol (*vide ante*). Also, a new band at 3610 cm^{-1} appears as the Al content increases (see spectra c–e of Figure 8). This observation also confirms that the hydrogen-bonding feature of the sodalites studied in this work depends highly on the Al content in the framework. However, all the observed Raman bands in the OH region from the four sodalites are considerably weak as compared to those in the corresponding region of the IR spectra. Thus, the broad and weak bands due to strong hydrogen bonds to the framework are not detectable in these spectra. This may be due to the low sensitivity of Raman spectroscopy to the OH vibrational modes. On the other hand, the OH stretching bands are observed at 2681 and 2651 cm^{-1} in the Raman spectrum (not shown) of Si-SOD containing deuterated ethylene glycol, because of isotopic effects.

The previous Raman study reported that pure liquid ethylene glycol exhibits two bands at 480 and 1062 cm^{-1} , which could be assigned to the C–O bending and stretching vibrations of the trans conformer present as a minor species in liquid ethylene glycol.⁸ A similar result was observed from ethylene glycol in DMSO.³¹ However, there is no indication of the presence of these bands in the Raman spectra of all four sodalite samples (see Figure 7), suggesting the absence of the trans conformer. It has been repeatedly shown that the conformational analysis of ethylene glycol by means of vibrational spectroscopy is extremely difficult and controversial.^{4–11} Further study is necessary to completely understand changes in the IR and Raman spectra caused by isomorphous substitution of Si by Al in the sodalite framework.

Finally, one may speculate that the reason the conformation of the encapsulated ethylene glycol is altered by increasing the level of Al substitution in the sodalite framework is that the guest molecule does not form a hydrogen bond with the framework, but fills open coordination sites of the dehydrated Na^+ ions. However, this possibility can be ruled out by the result obtained from the IR spectra of aluminosilicate sodalites in the OH region. As shown in the IR spectra of Figure 6, the appearance of a broad band around 3500 cm^{-1} upon increasing

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the framework Al content clearly indicates the presence of strong hydrogen bonds between the guest molecule and the framework oxygens. Thus, if the oxygen atoms of ethylene glycol are coordinated to the dehydrated Na^+ ions, such a broad band should not be observed in the IR spectra of aluminosilicate sodalite samples in the OH region. Obviously, the Na^+ ions balance the negative framework charges created by Al substitution. However, each single negative framework charge in aluminosilicate sodalite samples may be partially distributed on the four oxygen atoms of the AlO_4^- tetrahedral units, without locating on one specific framework oxygen atom. Furthermore, each AlO_4^- unit in the sodalite structure faces four β -cages. This allows the interaction of the partially charged framework oxygen atoms with the ethylene glycol molecule encapsulated within a different β -cage. Therefore, it is most likely that hydrogen bonding between the guest molecule and the framework is still possible, although the dehydrated Na^+ ions balancing the AlO_4^- tetrahedral units in sodalites have some open coordination sites.¹⁸

Conclusion

Sodalite materials with different Si/Al ratios have been synthesized in the presence of ethylene glycol and characterized by XRD, elemental and thermal analyses, multinuclear MAS NMR, IR, and Raman measurements. The overall results of this study demonstrate that hydrogen bond features of ethylene

glycol in the β -cages of sodalite samples depend on the aluminum concentration. It is found that the ethylene glycol in a pure-silica β -cage is tGg' stabilized only by intramolecular hydrogen bonds, while the guest molecule in a β -cage with Si/Al = 5 is gGg' stabilized by one intramolecular hydrogen bond and one bond to the framework. Between these two different types of gauche conformers, a better stabilization would be achieved from gGg'. To the best of our knowledge, our study is the first example where the conformation of the guest molecule in as-synthesized zeolites is considerably influenced by the formation of hydrogen bonds to the framework, which is a consequence of the net negative charge introduced by Al substitution.

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