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SiO^- Defects in As-Synthesized Pure-Silica and Aluminosilicate Sodalites

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The existence and distribution of $Si-O^-$ defects in pure-silica and aluminosilicate sodalites prepared from nonaqueous media containing ethylene glycol are investigated by ^{23}Na MAS NMR and XPS techniques. The overall results of this study demonstrate that $Si-O^-$ defects are predominantly present in the surface/near surface of pure-silica sodalite crystals and thus are not uniformly distributed. By contrast, the isomorphous substitution of Si by Al in the sodalite framework is found to produce nearly defect-free aluminosilicate sodalites.

Introduction

Very recently, we have reported extensive investigations of the host−guest interactions in pure-silica and aluminosilicate sodalites prepared from nonaqueous media in which ethylene glycol is acting simultaneously as a solvent and as a guest molecule.[1,2] Our investigations demonstrate that the molecular conformation of the ethylene glycol encapsulated within the β-cages of sodalites is altered according to the Al content in the sodalite framework. This has been attributed to the formation of hydrogen bonds between the framework oxygens and the OH groups of the encapsulated ethylene glycol molecule, which is a consequence of the net negative charge introduced by Al substitution.

One intriguing result obtained from our recent study is the presence of a small amount of Na^+ ions (approximately 0.1 ion/unit cell) in pure-silica sodalite where the framework, as well as the encapsulated ethylene glycol molecule, is electrically neutral. A similar result has been repeatedly reported for several other pure-silica sodalites prepared via different synthetic routes, from both aqueous and nonaqueous media.[3−6] Here we report the ^{23}Na MAS NMR and XPS spectra of the four sodalite materials with Si/Al ratios from ∞ up to 5.7 in order to show that the Na^+ ions in pure-silica sodalite balance the charge of $Si-O^-$ defects generated during the crystallization process. In addition, the intracrystalline distribution of such defects in sodalites is discussed on the basis of the overall results obtained from these two spectroscopies. Numerous papers on defect sites in zeolites have been published and demonstrated that the ion-exchange and adsorption properties of zeolites can be dependent on the type and amount of defects in their framework.[7−9] To the best of our knowledge, however, no studies have thus far focused on the intrazeolitic distribution of framework defects.

Experimental Section

Four sodalite materials with Si/Al ratios of ∞, 23.0, 11.0, and 5.7 were synthesized and characterized by XRD, elemental, and thermal analyses, as described in our previous report.[1] Here we denote these four sodalite samples as Si-SOD, Al-SOD-I, Al-SOD-II, and Al-SOD-III, respectively.

The crystal morphology and size were determined by a Hitachi Model X-650 scanning electron microscope.

^{23}Na MAS NMR spectra were obtained on a Bruker AM 300 NMR spectrometer operating at a ^{23}Na frequency of 79.39 MHz and a spinning rate of 3 kHz. The spectra were obtained with an acquisition of 200−1000 pulse transients, which was repeated with a pulse length of 2.0 μs and a recycle delay of 1 s. The ^{23}Na chemical shifts are referenced with respect to solid NaCl.

The XPS spectra were recorded on an SSI 2803-S X-ray photoelectron spectrometer with an Al Kα X-ray source (1486.6 eV). The Al anode was operated at 21 kV and 10 mA. A sodalite sample and gold powder (2 wt % of zeolite sample) were grounded with a mortar and pestle for about 0.5 h to achieve a homogeneous mixture. The mixture was compressed into a pellet of 2-mm thickness and then mounted on a sample holder by utilizing double-sided adhesive tape. The sample holder was then placed into the preparation chamber without exposure to air and evacuated under vacuum ($<10^{-6}$ Torr) overnight. Finally, the sample holder was transferred to the analysis chamber for XPS study. The pressure inside the analysis chamber was usually maintained at better than 5×10^{-9} Torr. The spectrometer was calibrated using the Au($4f_{7/2}$) line at 83.8 eV for gold metal. Typically, 20 scans were accumulated and all the binding energies are referenced to the C(1s) line at 284.6 eV from carbon atoms of the ethylene glycol encapsulated within the β-cages of sample or from adventitious carbon. The binding energy values reported here

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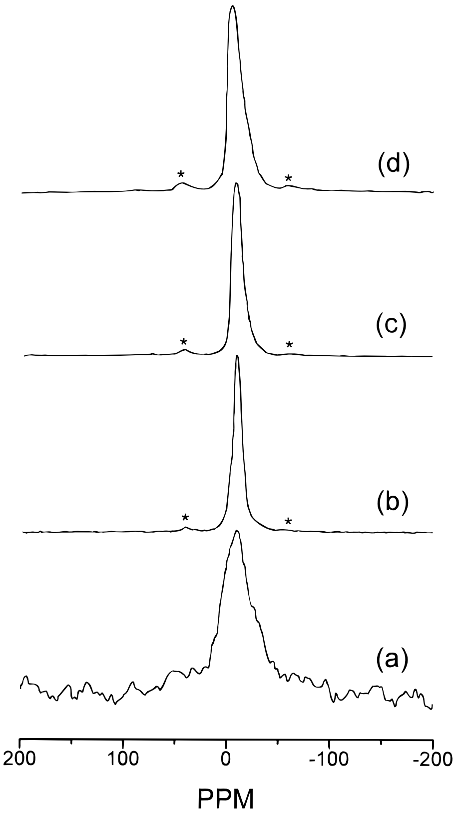

Figure 1. ^{23}Na MAS NMR spectra of pure-silica and aluminosilicate sodalites synthesized with ethylene glycol: (a) Si−SOD, (b) Al−SOD-I, (c) Al−SOD-II, and (d) Al−SOD-III. Spinning side bands are marked with an asterisk.

are within an accuracy of ±0.2 eV. The curve deconvolution was performed using the SSI S-PROBE Gaussian-fitting software.

Results and Discussion

The scanning electron microscopy reveals that Si-SOD is composed of single, cubic crystals of approximately 40 μm. By contrast, the morphology of the other three aluminosilicate sodalite samples studied here is based on a cubic morphology with dodecahedral modifications. Also, the crystal size of these aluminosilicate sodalites becomes smaller with increasing Al content in their framework. Thus, the average crystal size (3−4 μm) of the sample with the highest Al content (Al−SOD-III) is much smaller than that (ca. 20 μm) of Al−SOD-I. These observations are in good agreement with those reported by Bibby and Dale.[3]

Figure 1 shows the ^{23}Na MAS NMR spectra of the four sodalite materials used in this study. The spectrum of Si−SOD in Figure 1a is characterized by one broad and symmetric line at −6.0 ppm. The featureless line shape of this spectrum indicates the presence of a distribution of chemical shifts and/or field gradients of the ^{23}Na nuclei possibly modified by dynamic processes of the ethylene glycol molecules encapsulated within the β-cages of Si−SOD. A logical interpretation for the origin of the ^{23}Na NMR line appearing at −6.0 ppm in Figure 1a will be given later. As shown in parts b−d of Figure 1, on the contrary, the ^{23}Na MAS NMR spectra of all the three aluminosilicate sodalite samples exhibit a narrow but rather asymmetric line at −3.7 ± 0.1 ppm, which can be assigned to the Na$^+$ ions coordinated to framework oxygen atoms where the negative charges created by Al substitution are distributed. The chemical shift and line shape of the ^{23}Na NMR lines from these aluminosilicate sodalites are almost independent of Al content in the framework, but their line width becomes broader with increasing Al content. In addition, it should be mentioned that the ^{23}Na NMR spectra obtained from our aluminosilicate sodalites are noticeably different from those of aluminosilicate sodalites with the same framework Si/Al ratio (1.0) but different β-cage fillings,[10,11] although further ^{23}Na NMR studies at different magnetic fields are necessary to elucidate the influence of quadrupolar interaction on the asymmetric line shape. Engelhardt et al. have observed that the dehydrated hydroxysodalite $[Na_4OH]_2[SiAlO_4]_6$ exhibits a quadrupolar line with two sharp maxima at −6.4 and −17.0 ppm, while the hydrated hydroxysodalite $[Na_4(OH)\cdot H_2O]_2[SiAlO_4]_6$ gives only one broad and symmetric line at −2.5 ppm.[10] A narrow and symmetric ^{23}Na NMR line at −11.0 ppm has also been reported for the fully hydrated sodalite $[Na_3(H_2O)_4]_2[SiAlO_4]_6$. Therefore, it is most likely that the local environment of Na$^+$ ions in our aluminosilicate sodalites is different from that of the cations in any of the aluminosilicate sodalites studied by Engelhardt et al., which is mainly due to differences in the guest species together with Na$^+$ ions present in β-cages. The ^{23}Na MAS NMR spectra in Figure 1 also demonstrate that the spectrum of Si−SOD was much noisier than that obtained from any of the three aluminosilicate sodalite samples, even after an aquisition of a larger number of scans. This is not unexpected because the amount of Na$^+$ ions in Si−SOD is very small as compared to that of the cations in aluminosilicate sodalites (see Table 1).

The addition of NaOH in the nonaqueous synthesis mixture containing ethylene glycol is essential for the formation of pure-silica sodalite.[12] Therefore, one can speculate that the reason Si−SOD with a neutral framework shows a ^{23}Na NMR line at −6.0 ppm could be due to the presence of residual NaOH on the exterior surface of Si−SOD crystals or within the β-cages. However, washing of our Si-SOD sample with water did not affect its ^{23}Na MAS NMR spectrum. This clearly shows that the ^{23}Na NMR line appearing at −6.0 ppm in Figure 1 is not due to residual NaOH on the exterior surface of Si−SOD crystals. In addition, we can exclude the other possibility that this NMR line originates from the occluded NaOH in within the β-cages, because the ^{1}H MAS NMR spectrum of Si-SOD exhibits no NMR lines except those from the OH and CH_2 protons of the encapsulated ethylene glycol molecule.[1] On the other hand, the structures of high-silica zeolites are known to be rarely crystallographically perfect with framework defects that exist in form of SiO^- or SiOH groups.[8,9,13−15] In particular, it has been repeatedly shown that SiO^- defects can be present for charge compensation when an inorganic or organic cation is used as a structure-

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Table 1. XPS Binding Energies and Bandwidths of Pure-Silica and Aluminosilicate Sodalites

sample	Si/Al ratio	no. of Na^+ ions per unit cell	binding energy[a] (fwhm[b]), eV O(1s)		Si(2p)		ref
Si−SOD	∞	0.1	532.8 (2.3) 57%[c]	531.3 (1.7) 43%[c]	103.2 (1.7) 72%[c]	101.7 (1.7) 28%[c]	this work
Si−SOD	∞		532.45 (2.2)		103.2 (2.6)		4
Al−SOD−I	23.0	0.5	532.7 (2.3)		103.2 (2.2)		this work
Al−SOD−II	11.0	1.0	532.5 (2.1)		103.4 (2.0)		this work
Al−SOD−III	5.7	1.8	532.1 (2.4)		103.3 (2.0)		this work
Al−SOD	1.05		530.9 (2.2)		101.5 (2.2)		4

[a] Binding energies are referenced to C(1s) = 284.6 eV. [b] Full width at half-maximum of the XPS band. [c] Area percent of the deconvoluted components.

directing agent in the synthesis of high-silica zeolites.[14,15] Therefore, we speculate that the negative charge of Si-O^- defects, if present in pure-silica sodalite, must be compensated by the Na^+ ions, because the ethylene glycol molecules in the β-cages of pure-silica sodalite cannot balance the charge of Si-O^- defects due to their noncharged nature. This led us to believe that the ^{23}Na NMR line appearing at −6.0 ppm in Figure 1a must be attributed to the Na^+ ions balancing Si−O^- defects in Si−SOD. It is well-established that the presence of Si−O^- or Si−OH groups, i.e., Si atoms connected via oxygen bridges to only three or even two other tetrahedral atoms (Q^3 and Q^2 units, respectively), can be confirmed by ^{29}Si MAS NMR.[8] As demonstrated in our previous work,[1] however, the ^{29}Si MAS NMR spectrum of Si−SOD exhibited only one narrow ^{29}Si NMR line at −117.5 ppm due to Si(0Al) tetrahedral units in the framework. This suggests that the amount of Si−O^- defects in pure-silica sodalite studied here is very small and thus is not sufficient to give any detectable ^{29}Si NMR lines responsible for Q^3 and/or Q^2 units.

Further evidence for the presence of Si−O^- defects in Si−SOD can be obtained from XPS measurements, because repetitive shifting patterns in the core-level and valence-band XPS spectra of zeolites provide valuable information on cation−framework interactions.[16−19] Figure 2 illustrates the O(1s) XPS spectra of pure-silica and aluminosilicate sodalite samples. A symmetric nature of the O(1s) bands observed in all the spectra except that from Si−SOD indicates the presence of a singular oxygen species in the framework of aluminosilicate sodalite samples. As seen in Figure 2a, however, the O(1s) XPS band of Si−SOD is broad and asymmetric. The same result was also obtained from Si−SOD synthesized with deuterated ethylene glycol. Curve deconvolution of the O(1s) band observed from Si−SOD reveals that the binding energy of the more abundant oxygen species is 532.8 eV and that of the less abundant species is 531.3 eV. The pure-silica sodalite used here is highly crystalline and contains no amorphous silica, as evidenced by XRD and ^{29}Si NMR experiments. Also, leaving Si-SOD in the monochromatized Al Kα X-rays (1486.6 eV) for several hours caused no changes in the shape and the position of the XPS band. These results clearly demonstrate that two different types of framework oxygen species exist in Si−SOD.

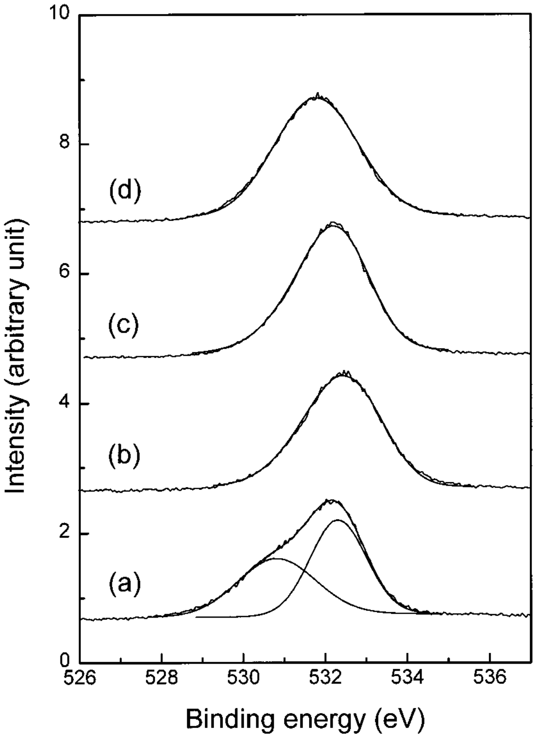

Figure 2. O(1s) XPS spectra of (a) Si−SOD, (b) Al−SOD-I, (c) Al−SOD-II, and (d) Al−SOD-III. The binding energy scale has been adjusted to C(1s) line at 284.6 eV.

Table 1 summarizes the XPS binding energies and bandwidths of the four sodalite samples. The XPS binding energies of zeolite framework elements are known to shift in the same direction with a change in the Si/Al ratio.[18] The same trend was observed from the O(1s) XPS binding energies (532.1−532.8 eV) of sodalite samples studied here, as listed in Table 1. On the basis of the binding energies, therefore, it is clear that the more intense O(1s) XPS band at 532.8 eV in Figure 2a can be attributed to the oxygen atoms in Si−O−Si unit of Si−SOD. On the other hand, a clue for assigning the less intense O(1s) band of Si−SOD can be obtained from the fact that Si−SOD contains 0.1 Na^+ ion/unit cell, despite the neutrality of the framework. This result suggests that the less intense O(1s) band at 531.3 eV can be attributed to Si−$O^-\cdots Na^+$ units in Si−SOD. In general, the more electropositive the countercation is, the lower the framework element binding energies are.[19] Again, the possibility that the less intense O(1s) band originates from the presence of NaOH has been ruled out, because of the absence of any noticeable lines other than those from the encapsulated ethylene glycol in the ^{1}H MAS NMR spectrum of Si−SOD.[1] In addition, the band at 531.3 eV in Figure 1a cannot be due to the oxygen atoms of the encapculated

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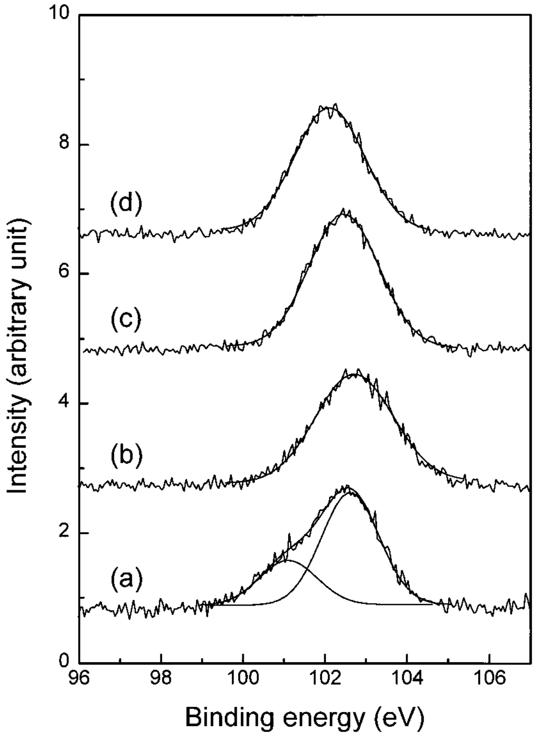

Figure 3. Si(2p) XPS spectra of (a) Si−SOD, (b) Al−SOD-I, (c) Al−SOD-II, and (d) Al−SOD-III. The binding energy scale has been adjusted to C(1s) line at 284.6 eV.

ethylene glycol molecules. This is because any of the XPS spectra obtained from aluminosilicate sodalite samples containing the same guest molecules exhibits no detectable O(1s) bands in the 531-eV region (see spectra b−d of Figure 2).

Figure 3 shows the Si(2p) XPS spectra of the four sodalite samples. Interestingly, the Si(2p) band obtained from Si−SOD is also broad and asymmetric, like the O(1s) band of the same sample. It splits into two distinct components at 101.7 and 103.2 eV, as seen in Figure 3a. On the contrary, the other three aluminosilicate sodalite samples give a symmetric Si(2p) band in the 103.2−103.4 eV region. Therefore, it is most likely that the deconvoluted component at 103.2 eV in Figure 3a is due to Si−O−Si units in the Si−SOD sample, while that at 101.7 eV is from Si−O$^-$···Na$^+$ units. Very recently, we have investigated the core-level binding energies of tetrasodium ionic clusters generated within the β-cages of zeolite NaY and found the splitting of the XPS bands from all framework elements into two distinct components.[20] This has been attributed to the short-range interaction between the single-electron ionic cluster Na_4^{3+} and the zeolite framework, i.e., the partial distribution of the negative charge in Na_4^{3+} on the framework Al, Si, and oxygen atoms. Like the case of Na_4^{3+} within zeolite Y, thus, we speculate that each single negative charge in Si−O$^-$···Na$^+$ units may be partially distributed on both Si and oxygen atoms, without locating only on the oxygen atom, resulting in the occurrence of the band at 101.7 eV in the Si(2p) XPS spectrum of Si−SOD. In addition, it appears that the extent of the distribution of the single negative charge on the Si atom in Si−O$^-$···Na$^+$ units is lower than that on the oxygen atom, because the relative intensity ratio (1.3) of the more intense to the less intense O(1s) XPS band is half that (2.6) of the more intense to the less intense Si(2p) XPS band (see Table 1).

The curve deconvolution of the O(1s) and Si(2p) XPS spectra obtained from Si−SOD can provide some insight into the intracrystalline distribution of Si−O$^-$···Na$^+$ units. The outer surface of the zeolite crystals is normally terminated by Si−OH groups, to finish the structure. However, the termination by Si−O$^-$···M$^+$ units, where M$^+$ is inorganic or organic cation used as the structure-directing agent, is also possible. If all Na$^+$ ions present in Si−SOD are assumed to balance Si−O$^-$ defects, the percentage of Si−O$^-$···Na$^+$ units to Si−O−Si units in the framework of this material could not exceed 1% (see Table 1). This suggests that the observed O(1s) and Si(2p) XPS bands would be nearly symmetric, if Si−O$^-$ defects are homogeneously distributed throughout the Si−SOD crystals. As seen in Table 1, however, the less intense O(1s) band at 531.3 eV of Si−SOD represents 43% of the total oxygen. In addition, the less intense Si(2p) band at 101.7 eV of Si−SOD represents 28% of the total Si atoms. All sodalite samples prepared here have been repeatedly washed with water after the crystallization process is complete. Thus, if all Si−O$^-$···Na$^+$ units in pure-silica sodalite crystals are exclusively present on their outer surface, they should be easily changed to Si−OH groups upon washing with water. If such is the case, the shape of O(1s) and Si(2p) XPS bands from pure-silica sodalite should be as symmetric as those from aluminosilicate sodalite samples. As shown in Figures 2a and 3a, however, both O(1s) and Si(2p) XPS spectra of Si−SOD are deconvoluted by two distinct components with relative intensity ratios of 1.3:1 and 2.6:1, respectively. Therefore, the less intense O(1s) and Si(2p) XPS bands must be attributed to Si−O$^-$···Na$^+$ units somehow buried in the near-surface of Si−SOD crystals, where Na$^+$ ions are not exchanged with protons during washing with water. This led us to conclude that Si−O$^-$···Na$^+$ units are predominantly distributed in the near-surface as well as in the outer surface of Si−SOD crystals (e.g., “egg-shell” type distribution). However, the precise reason for the concentrated distribution of Si−O$^-$ defects near the surface of pure-silica sodalite crystals still remains unknown. Are they in part responsible for terminating crystal growth because they are concentrated near the surface of the Si−SOD crystals? If not, are they formed to control crystal growth with a final leveling off? Further study is necessary to elucidate the factors influencing Si−O$^-$ defect formation in pure-silica sodalite. On the other hand, our previous study has shown that the number of Na$^+$ ions per unit cell of each aluminosilicate sodalite studied here is exactly the same as that of Al atoms,[1] which means the absence of Na$^+$ ions balancing Si−O$^-$ defects. This suggests that a symmetric nature of the O(1s) and Si(2p) XPS bands obtained from the three aluminosilicate sodalites is mainly due to the absence of Si−O$^-$ defects rather than to their homogeneous distribution throughout the crystals. For high-silica ZSM-5 zeolites with Si/Al ratios higher than 30, it is reported that the number of structural defects decreases significantly with increasing Al content in the zeolite.[21]

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Finally, XPS experiments showing that both O(1s) and Si(2p) bands of pure-silica sodalite are symmetric have been reported by Herreros et al.[4] The discrepancy with our results appears to be due to differences in the procedure by which the respective samples have been synthesized. It is most likely that a distinct difference between the crystallization time (3 weeks) in our synthesis and that (3 days) in the synthesis by Herreros et al. may be the main reason for the observed differences in the XPS spectrum, because the reaction mixtures used in these two syntheses have exactly the same molar ratio ($1.0NaOH \cdot 4.0SiO_2 \cdot 40C_2H_4(OH)_2$).

In summary, results from the ^{23}Na MAS NMR and XPS measurements demonstrate that pure-silica sodalite crystals synthesized using ethylene glycol contain $Si-O^-$ defects predominantly on their surface or near surface. Thus, the distribution of $Si-O^-$ defects in pure-silica sodalite is found to be inhomogeneous. It is also observed that the amount of such $Si-O^-$ defects in sodalites is significantly reduced when the Al atom is isomorphously substituted into the framework.

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