Neutron Diffraction and Computational Study of Zeolite NaX: Influence of SIII′ Cations on Its Complex with Benzene

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The crystal structure of zeolite NaX (Si:Al = 1.2) and that of its complex with benzene have been determined at 5 K by Rietveld analysis of powder neutron diffraction data in space group *Fd*3. For NaX, $a = 25.0328$-(5) Å, $R_{wp} = 4.25\%$, and $R_p = 3.27\%$. For NaX + benzene, $a = 25.0496(7)$ Å, $R_{wp} = 4.60\%$, and $R_p = 3.52\%$. The sodium ions were located preferentially in sites SI′ and SII, both of which are fully occupied. The remaining cations were found at the SIII′ site in the 12-ring window. These cations are coordinated by two oxygen atoms, O(1) and O(4), in a corner of the 4-ring window where the aluminum is located. Our simulations on cation positioning in NaX (Si:Al = 1) predict the preferred occupancy of SIII′ sites that are facing AlO$_4$ tetrahedra and support our crystallographic results. Less than half the benzene molecules were found at the six-ring window in the supercage, where they interact with the SII cations. No benzene was found in the 12-ring window, presumably because of the presence of the SIII′ sodium cations, but there remains a possibility that undetected benzene is adsorbed near these cations.

Introduction

A substantial number of diffraction studies have examined the location of extraframework cations in faujasite type zeolites, including hydrated and dehydrated forms of zeolites X and Y.[1] However, in the case of monovalent cation forms of zeolite X, a significant proportion of the cations are often undetected in X-ray studies. In hydrated NaX,[2] KX,[3] and TlX,[4] for example, the proportion of undetected cations is almost 50%, leading Baur[5] to conclude that many of the water molecules and exchangeable cations in faujasite zeolites move freely through the aluminosilicate framework. The dehydrated forms of zeolites find utility in a number of commercial separation processes, including air[6−8] and hydrocarbon separations,[9] and a comprehensive determination of the cation positions in such materials is an important prerequisite for understanding their properties.[10,11] It is surprising to find, therefore, that in the prototypical system, NaX, where the numbers of cations in the SI, SI′, and SII sites (Figure 1) appear to be well-established, the precise location of the remaining cations remains uncertain. For example, a recent single-crystal X-ray study of NaX[12] describes three additional positions for these Na ions, a result that contrasts with an earlier single-crystal structure[13] in which only one extra site was detected. In view of the important role that these cations are believed to play in adsorption and separation processes, it is clear that a resolution of the current uncertainty is needed. In the present work, we describe a powder neutron diffraction study of zeolite NaX and its complex with benzene and try to elucidate the influence of cation positioning on benzene adsorption. We also perform computational simulations to corroborate our conclusions regarding the location of cations. The combination of the Monte Carlo packing and minimization procedures, used previously to study the Li−ABW,[14] 4A,[14] and ETS-10 [15] structures, is used for simulating nonframework cation positions in the NaX structure.

The most favored sites for the location of the remaining monovalent cations in zeolite X are those in the vicinity of the four-membered rings of oxygen atoms in the supercage (Figure 1). Unlike the SI, SI′, and SII sites, which are on special
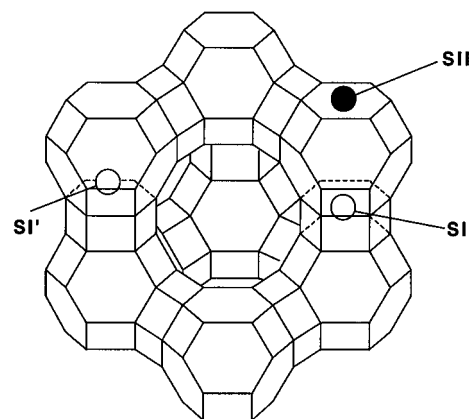

Figure 1. Representation of the extraframework cation positions SI, SI′, and SII in zeolites X and Y.

positions, these are low-symmetry sites with low occupancy factors and are therefore more difficult to pinpoint by diffraction methods, a problem that is aggravated when compared with zeolite Y by the lowering of symmetry from *Fd*3*m* to *Fd*3 due to Si,Al ordering. It is important to note that Na,[12,13,16] Li,[17] and K and Cs ions[18] have been reported to occupy sites in the vicinity of the SIII site above the 4-ring window but that some monovalent, as well as divalent, cations have been found on the edges of the 4-ring window, i.e., in the 12-ring window, the so-called SIII′ site. Those cations reported in these positions include Rb,[18] K,[18] Mg,[19] Cu,[20] and Na.[12,21]

Not only has the location of extraframework cations in faujasite type zeolites attracted a great deal of attention but so too has the location of guest molecules within the supercage cavity.[22−29] Benzene has been found to be adsorbed in two different positions: at the SII cation site and in the plane of the 12-ring window. In a neutron diffraction study of benzene in NaY,[22] the sorbate (at a loading of eight molecules per unit cell) was found to be preferentially adsorbed at the SII site cation (∼6.65 molecules) with only one molecule per cell in the 12-ring window. The precise nature of the SII cation−benzene interaction is unclear, but charge-quadrupolar terms are believed to be important.[28] Neutron diffraction studies of benzene adsorbed in H-SAPO-37[23] and in D-Y[24] (at low coverage) show

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that benzene is again adsorbed at the SII site and in the plane of the 12-ring window. However, a higher proportion of benzene molecules was found in the latter position. The precise location of the cations in NaX is therefore of particular interest, since the presence of cations in the SIII′ sites may prevent benzene from occupying a position in the plane of the 12-ring window.

Experimental Section

The sample of NaX was the same as that used in our recent NMR study.[29] Approximately 5 g of NaX was activated in a furnace under dynamic vacuum to 723 K and held there for 12 h. The thermal ramp to 723 K was controlled at a rate of 1 K/min with a 120 min hold at 393 and 573 K. After activation, all further manipulations were carried out in an inert atmosphere glovebox. The Si:Al ratio was determined to be 1.2 by ^{29}Si MAS NMR, and the composition of the anhydrous unit cell of the dehydrated NaX is therefore $\sim Na_{87}Si_{105}Al_{87}O_{384}$.

The samples for neutron diffraction were packed into thin-walled vanadium cans and screw-sealed using indium wire. A known amount (1 molecule/supercage) of deuterated benzene was added gravimetrically to one of the cans before sealing it. The NaX + benzene sample was allowed to equilibrate in the sealed can at 333 K in an oven for 2 days.

Neutron diffraction data were collected at 5 K using the powder diffractometer, DUALSPEC, at Chalk River Laboratories, Canada. The data were collected with a neutron wavelength of $\lambda = 1.5043$ Å, between 6° and 120° 2θ. The diffraction data were analyzed by the Rietveld method[30] using the GSAS[31] package. Trial structures were visualized using the MSI Catalysis and Sorption package.[32]

Rietveld analysis of the NaX and NaX + benzene diffractograms produced models with sodium ions in the SI′, SII, and SIII′ cation positions, as described below. An NaX starting model in space group $Fd3$, based on the framework structure of Ca−LSX reported in ref 10, was used. Difference Fourier maps were calculated to localize the extraframework cations and the benzene molecules. There was no density at the SI position, which is often occupied by sodium ions in NaY, but the maps clearly showed cations at the SI′ and SII cation positions. The occupancy factors for sodium ions at these sites refined to slightly greater than 1, so their occupancy factors were constrained to unity. The 12-ring region was then investigated to localize the remaining sodium ions. Fourier maps initially showed density near the SIII position, but the sodium ions were finally located in the general SIII′ position in the 12-ring window.

For the NaX + benzene refinement, difference Fourier maps showed benzene molecules adsorbed at the SII site, the primary adsorption site found for benzene adsorbed in NaY.[22] Because of the low symmetry of the space group $Fd3$, it was necessary to specify two carbon atom and two deuterium atom positions for the benzene in this site. The benzene molecules adsorbed in the SII site were constrained to their ideal geometry, using soft constraints for the C−C bond (1.396 Å) and C−D bond (1.08 Å). It did not prove possible to locate benzene molecules at other positions (see below).

Separate isotropic temperature factors were refined for the framework and extraframework atoms, as well as for the benzene molecules. The lattice parameters, zero points, scale factors, U, V, W, X, Y, Z parameters, and asymmetry corrections were refined, in addition to the positional, thermal, and occupancy parameters. The refinements yielded the models presented below. For both refinements, the low-angle (111) peak was excluded from the refinement because it exhibited

TABLE 1: Diffractogram Information[a]

data type	neutron NaX	neutron NaX + benzene
data collection temperature (K)	5 K	5 K
space group	$Fd3$	$Fd3$
a (Å)	25.0328(5)	25.0496(7)
profile factor R_p	0.0327	0.0352
weighted profile factor R_{wp}	0.0425	0.0460
structure R factor (R_F)	0.112	0.121
χ^2	2.075	2.062
wavelength (Å)	1.5043	1.5043
zero correction (deg)	2.90	2.91
scale factor	1560.2	901.08
number of reflections	1028	1028
profile function	pseudo-Voigt	pseudo-Voigt
asymmetry correction	6.9536	5.8122
U, V, W	104.9, −416.5, 39.9	235.8, −413.7, 63.8
X, Y, Z	0.300, 7.081, 9.45	4.660, 0.00, 7.866
background function	24 coefficient cosine Fourier series	24 coefficient cosine Fourier series

[a] Rietveld refinement was used to minimize $\sum w_i(I_{o,i} - I_{c,i})^2$ where $I_{o,i}$ and $I_{c,i}$ are the observed and calculated powder diffraction intensities for the ith point, respectively. Weights w_i are $1/I_{o,i}$. Weighted and unweighted profile R factors are defined as $R_{wp} = \{[\sum w_i(I_{o,i} - I_{c,i})^2]/[\sum w_i(I_{o,i})^2]\}^{1/2}$ and $R_p = \sum|I_{o,i} - I_{c,i}|/\sum I_{o,i}$. The structure R factor is defined as $R_F = \sum(F_o - F_c)^2]/[\sum(F_o)^2]$. The expected R factor (the statistically best possible value for R_{wp}) is defined as $R_e = [(N - P)/(\sum w_i I_{o,i}^2)]^{1/2}$ where N is the number of observed powder diffraction data points and P is the number of refined parameters. χ^2 was calculated from $(R_{wp}/R_e)^2$.

significant asymmetric broadening that could not be properly treated by the software.

Computational Methodology

Although the location of Na ions in SI′ and SII is clearly established, the location of the remaining Na ions in the so-called SIII or SIII′ sites is known to be difficult to pinpoint when using diffraction methods because of their general positions and low occupancies. In addition, the statistical disorder associated with their partial occupancies is a real barrier to a precise knowledge of the distribution of these cations. Furthermore, the influence of even small amounts of residual water molecules may have to be taken in account to explain the variety of crystallographic positions reported in diffraction studies. Our purpose in this computational section was to simulate the positioning of these cations in the dehydrated NaX structure. The use of Monte Carlo techniques for generating nonframework positions in the zeolite is therefore of special interest, since it circumvents the preassignement of SIII or SIII′ sites occupancies and permits energy minimizations to be performed without any structural hypothesis concerning the cations positions. Our simulations were carried on a NaX structure having the composition $Na_{96}Si_{96}Al_{96}O_{384}$ with strict alternation of SiO_4 and AlO_4 tetrahedra. The starting host structure consisted of a unit cell made of the framework, 32 Na ions in sites SI′, and 32 Na ions in sites SII, using the coordinates from the NaX of the present work. In the first step of the simulation, the 32 missing Na cations were inserted into the host structure using the Monte Carlo packing procedure of the Catalysis package (MSI).[32] The packing involved the random selection of positions in the unit cell followed by a calculation of the trial interaction energy for the cation−host system. If this energy was below a definite threshold, the packed configuration was accepted. This energetic criterion prevents selection of nonrelevant starting configurations. Dummy atoms assigned with high repulsive Lennard-Jones parameters were placed at the center of the sodalite cages so that insertions of cations

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TABLE 2: Atomic Parameters for NaX

atom	site multiplicity	x	y	z	U_{iso} (Å^2)	fractional occupancy
Si	96	−0.0521(4)	0.0344(6)	0.1242(5)	0.006(3)	1
Al	96	−0.0565(4)	0.1244(5)	0.0371(5)	0.014(4)	1
O(1)	96	−0.1064(5)	0.0026(7)	0.1090(6)	0.023(3)	1
O(2)	96	−0.0012(3)	−0.0021(3)	0.1420(4)	0.033(3)	1
O(3)	96	−0.0345(3)	0.0722(4)	0.0753(5)	0.023(2)	1
O(4)	96	−0.0700(4)	0.0691(5)	0.1763(5)	0.019(2)	1
Na(I′)	32	0.0459(5)	0.0459(5)	0.0459(4)	0.034(7)	1
Na(II)	32	0.2324(4)	0.2324(4)	0.2324(4)	0.019(3)	1
Na(III′)	96	0.432(2)	0.280(2)	0.172(2)	0.037(1)	0.25(2)

TABLE 3: Atomic Parameters for NaX + Benzene

atom	site multiplicity	x	y	z	U_{iso} (Å^2)	fractional occupancy
Si	96	−0.0523(5)	0.0335(6)	0.1251(6)	0.004(4)	1
Al	96	−0.0563(6)	0.1269(6)	0.0369(7)	0.006(6)	1
O(1)	96	−0.1055(5)	−0.0002(8)	0.1104(5)	0.016(3)	1
O(2)	96	−0.0010(5)	−0.0021(4)	0.1445(3)	0.015(2)	1
O(3)	96	−0.0337(3)	0.0741(5)	0.0765(5)	0.019(2)	1
O(4)	96	−0.0695(4)	0.0665(5)	0.1773(5)	0.017(3)	1
Na(I′)	32	0.0505(6)	0.0505(6)	0.0505(6)	0.040(7)	1
Na(II)	32	0.2344(5)	0.2344(5)	0.2344(5)	0.005(4)	1
Na(III′)	96	0.457(3)	0.281(3)	0.167(3)	0.054(3)	0.26(2)
C(A1)	96	0.2926(7)	0.3320(2)	0.2532(2)	0.083(4)	0.080(3)
C(A2)	96	0.3320(2)	0.2926(6)	0.2532(2)	0.083(4)	0.080(3)
D(A1)	96	0.2926(4)	0.3625(2)	0.2227(2)	0.097(5)	0.080(3)
D(A2)	96	0.3625(3)	0.2926(6)	0.2227(2)	0.097(5)	0.080(3)

happened exclusively in the supercages. This whole procedure was reiterated to generate a set of 15 initial structures. They were then subjected to partial structure optimization with the Discover 3.2 program and the cvff_aug force field,[32] keeping the framework and the Na ions in sites SI′ and SII fixed and allowing the 32 inserted Na ions to relax. The zeolite was presumed to be semi-ionic with atoms carrying the following partial charges: Si(+2.4), Al(+1.4), O(−1.2), Na(+1). The total nonbonded energy included a Coulombic term calculated using an Ewald summation, and a repulsive−dispersive term described with a Lennard-Jones potential and calculated with a short-range cutoff of 12.5 Å. The energy optimization calculations were performed in the triclinic $P1$ space group.

Results and Discussion

Details of the refinements are given in Table 1. Atomic parameters for NaX and NaX + benzene are shown in Tables 2 and 3, respectively, and framework interatomic distances and angles in Table 4. The final observed, calculated, and difference plots for the neutron diffraction datasets of NaX and NaX + benzene are shown in Figures 2 and 3, respectively.

The introduction of benzene molecules into the zeolite produces a small increase in the lattice parameter (Table 1), though there are no striking differences between the bond lengths or angles in the two structures. The correctness of our choice of the noncentrosymmetric symmetry space group, $Fd3$ is confirmed by the bimodal distribution of Si−O and Al−O distances (Table 4); no geometrical constraints were used for these distances. Furthermore, unlike the case for Ca−LSX,[10] we can detect no significant influence by the cations on the spread of T−O distances. Although the SI site offers a favorable octahedral coordination environment and is significantly occupied in NaY, it is unoccupied in NaX. This probably arises because any sodium ion that occupies an SI position would exclude two sodium ions in the SI′ site (which has a higher multiplicity), thus forcing additional cations to occupy the energetically less favorable SIII′ sites. A similar observation was found in previous work on NaX.

Parts a and c of Figure 4 and Figure 5 show the location of the sodium ions near the SIII′ site for NaX and NaX + benzene. The sodium ions do not occupy sites above the center of the 4-ring window (the so-called SIII site reported by Hseu[13] and others) but are found approximately in the plane of the 12-ring window at an SIII′ type site. In this respect our findings are qualitatively similar, at least in part, to the recent single-crystal results of Olson,[12] but our cations are found only at the side of the ring where the aluminum atom is located, a finding that seems reasonable in relation to charge compensation (see below). Our SIII′ cations are bonded to two oxygen atoms: O(1) and O(4). Of the three different positions reported recently by Olson for the sodium ions in the 12-ring window, one is identical with that found in this work. The second is also in a SIII′ position but is closer to the silicon atom in the 4-ring window rather than to Al. The third is between our SIII′ position and the Hseu SIII position and is equivalent to that reported in ref 21 for the gallosilicate analogue of NaX refined in $Fd3m$. Our Fourier maps did not show other positions for sodium ions near the 4-ring window, but we tried adding the additional positions reported in ref 12 to our refinements. There was no improvement of the fit, and the occupancies of the extra sodium atoms were very low. The discrepancies between our findings and those in Olson's single-crystal study may represent genuine differences among samples differing in their Al distributions with the same nominal composition. We believe that such variations in Al distributions could explain the diversity of Na locations reported in the available diffraction studies for NaX zeolites.

The minimized structures were analyzed by considering the local framework environment of each of the 32 packed Na ions. The striking feature is that the most stable structures have all 32 Na ions located at the edges of the 4-rings in SIII′ type sites. The cations are coordinated by two oxygens, O(1) and O(4), at average distances of 2.36 and 2.42 Å, respectively. A further analysis of these low-energy structures showed that the Na ions are preferentially located in SIII′ sites facing AlO$_4$ tetrahedra (Figure 4b). The most stable structure we obtained has 82%
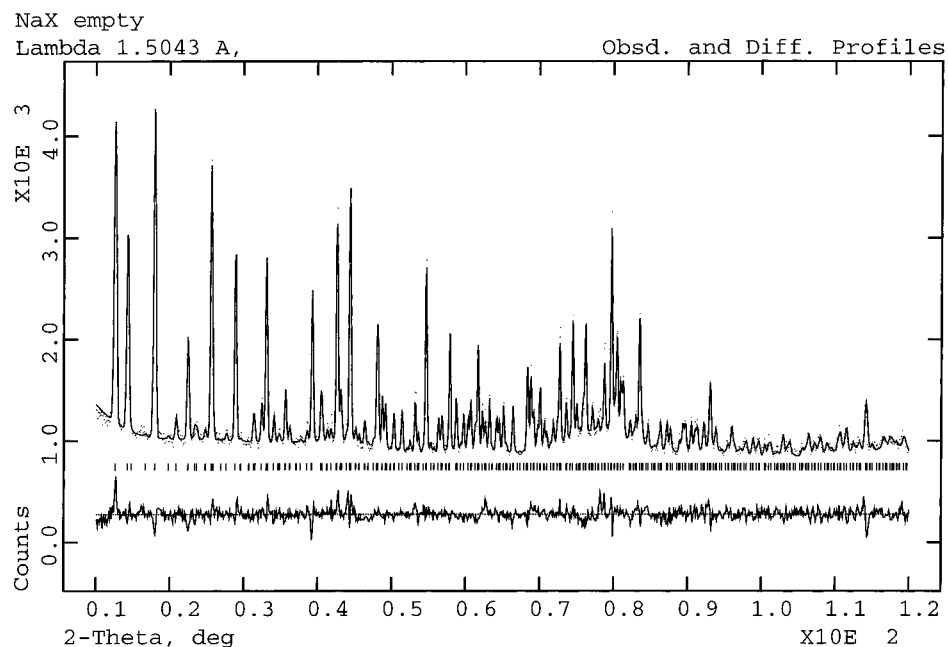
Figure 2. Plot showing the observed neutron diffraction pattern of NaX zeolite (dots) overlaid with a pattern calculated from the crystal structure (solid line). Directly below are vertical lines to indicate reflection positions and the deviations between the observed and calculated results, which are shown on the same scale as the observed pattern.

TABLE 4: Framework Interatomic Distances (Å) and Angles (Degrees)

	NaX		NaX + benzene	
	Si−tetrahedra	Al−tetrahedra	Si−tetrahedra	Al−tetrahedra
T−O(1)	1.619(2)	1.709(6)	1.620(10)	1.722(11)
T−O(2)	1.630(2)	1.721(10)	1.637(11)	1.714(19)
T−O(3)	1.611(2)	1.710(2)	1.652(10)	1.748(10)
T−O(4)	1.630(2)	1.719(2)	1.606(10)	1.710(10)
average T−O	1.623	1.715	1.629	1.724
O(1)−T−O(2)	116.4(11)	110.6(9)	115.3(12)	114.1(10)
O(1)−T−O(3)	109.8(9)	111.8(9)	112.7(10)	108.8(10)
O(1)−T−O(4)	102.6(8)	112.1(9)	103.4(11)	112.7(11)
O(2)−T−O(3)	108.8(9)	104.6(9)	109.5(10)	104.6(11)
O(2)−T−O(4)	107.2(9)	104.0(7)	104.5(10)	103.4(9)
O(3)−T−O(4)	111.8(9)	113.2(8)	111.0(10)	113.0(10)
average O−T−O	109.43	109.38	109.40	109.43
Si−O(1)−Al		133.5(6)		135.5(7)
Si−O(2)−Al		144.0(5)		142.2(7)
Si−O(3)−Al		141.9(6)		142.4(8)
Si−O(4)−Al		144.2(6)		143.4(8)
average Si−O−Al		140.90		140.88
Na(I′)−O(2)		2.935(9)		2.990(9)
Na(I′)−O(3)		2.241(8)		2.286(10)
Na(II)−O(2)		2.364(9)		2.333(11)
Na(II)−O(4)		2.906(10)		2.867(10)
Na(III′)−O(1)		2.58(5)		3.01(8)
Na(III′)−O(4)		2.77(5)		2.72(6)
Na(III′)−Al		3.23(5)		3.42(7)
Na(II)−C(A1)				2.887(19)
Na(II)−C(A2)				2.887(19)
Na(III′)−C(A1)				3.04(7)
Na(III′)−C(A2)				3.13(7)
Si−O(4)−Na(III′)		124.4(12)		116.4(21)
Al−O(4)−Na(III′)		88.6(11)		98.6(21)
Na(III′)−Na(III′)		5.39(7)		4.93(10)
Na(II)−center of benzene				2.52

of Na ions facing AlO$_4$ units, the remaining cations facing SiO$_4$ units with a similar framework environment. It is noteworthy that a higher number of Na ions are found in SIII′ sites facing SiO$_4$ tetrahedra when higher energy configurations are considered. Both a higher number of Na ions in SIII′ sites facing SiO$_4$ tetrahedra (up to 45%) and Na ions located in SIII type sites (up to 10%) are found in the less stable structures. Regarding the most stable structures, the predominant occupancy of sites facing AlO$_4$ tetrahedra is in agreement with our

diffraction results and is understandable on the basis of the local compensation of the anionic charge of the framework. The distribution of the 32 Na ions over the 96 allowed SIII′[AlO$_4$] sites is then driven by a minimization of long-range electrostatic repulsions between the cations themselves. The small number of cations facing SiO$_4$ tetrahedra is probably a result of site exclusions, since the location of Na ions in the neighboring available AlO$_4$ units could lead to short Na−Na distances and strong electrostatic repulsions. As a consequence, the location

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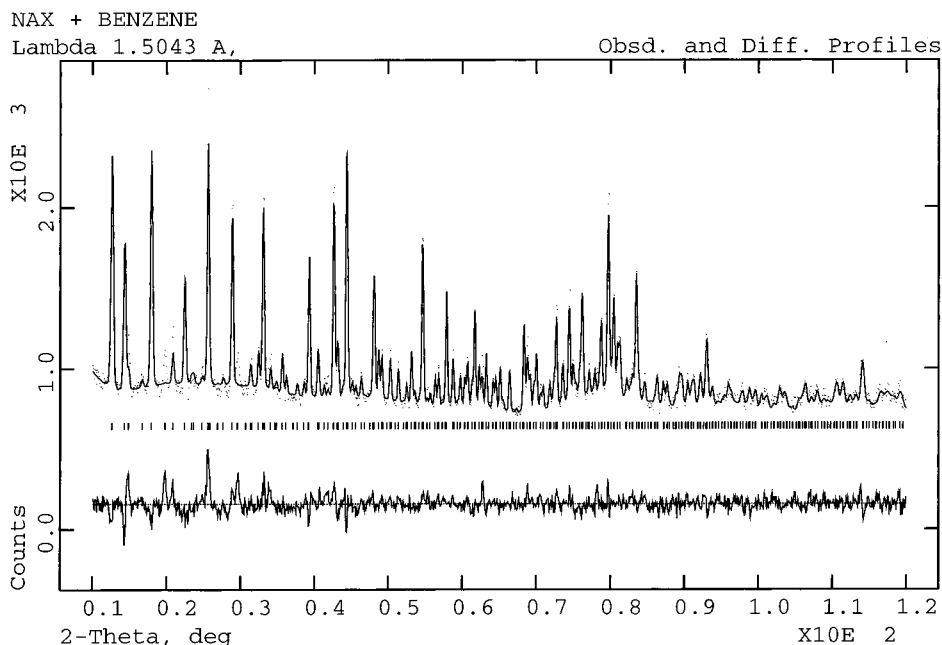
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Figure 3. Plot showing the observed neutron diffraction pattern of NaX + benzene (dots) overlaid with a pattern calculated from the crystal structure (solid line). Directly below are vertical lines to indicate reflection positions and the deviations between the observed and calculated results, which are shown on the same scale as the observed pattern.
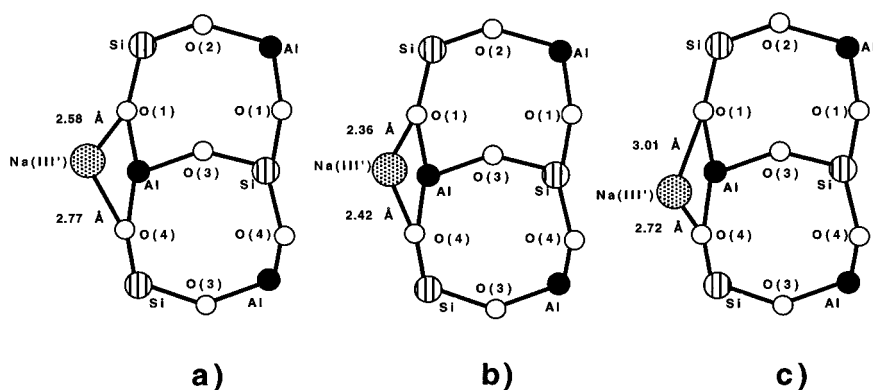

Figure 4. Na ions located at the edge of the four-ring on the side of the aluminum framework atom: (a) NaX without benzene (Rietveld refinement); (b) NaX without benzene (simulation); (c) NaX with benzene (Rietveld refinement).
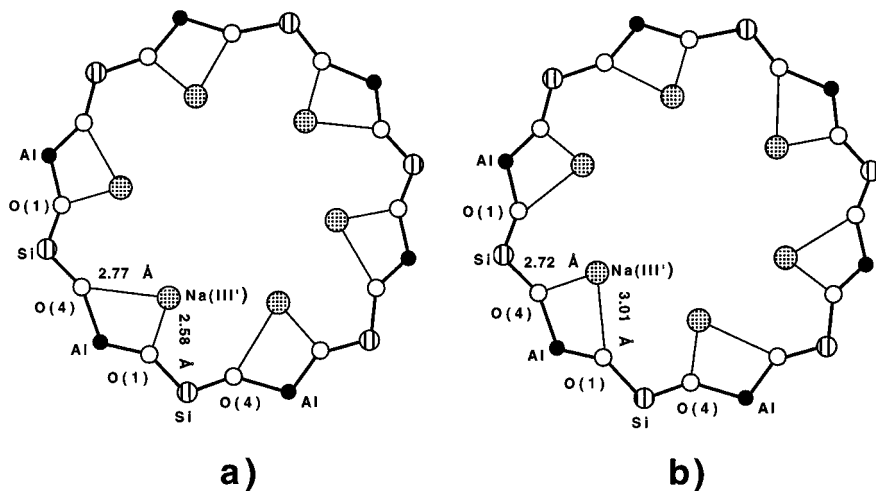

Figure 5. Another view of the Na ions located at the edge of the four-ring window as located in the Rietveld refinements: (a) NaX without benzene; (b) NaX with benzene.

of Na cations in SIII′ sites is a result of a cooperative and disordered placement of Na ions with respect to one another. When extrapolating our computational results to the NaX (Si: Al = 1.2) structure having a lower number of cations, as in our

diffraction study, we anticipate that the number of Na ions facing SiO$_4$ units would be even lower.

In relation to our study of the NaX + benzene system, we can detect benzene coordinated to the SII cation but, unlike for

NaY, not in the plane of the 12-ring window. It seems likely that the presence of the SIII′ cations, with an average occupancy in excess of 1 sodium/window (∼1.5), prevents benzene from occupying this position. However, we are accounting for less than half the benzene that was introduced into the sample, and the difference plot (Figure 3) suggests that our model may be imperfect. The possibility remains, therefore, that additional benzene molecules remain undetected in disordered, low-symmetry positions, perhaps coordinated to the SIII′ cations. Previous IR studies on NaX + benzene support this possibility, since they have suggested that different adsorption sites could be occupied at loadings less than 1 molecule/supercage.[33] We observe that the distance Na(III′)−O(1) is shorter than the distance Na(III′)−O(4) in NaX itself, but the introduction of benzene molecules increases the Na(III′)−O(1) distance. Aside from this minor change, the presence of benzene appears to have no significant influence on the cation positions. The distance from Na(II) to the center of the benzene molecule is 2.52 Å, which is slightly shorter than the values of 2.70 and 2.64 Å for benzene adsorbed in NaY at low and high coverages, respectively.[22] The temperature factors obtained at 5 K for the benzene molecules are rather high, indicating that there may be static disorder due to local variations in the environment of the sorbate.

References and Notes

(1) Mortier, W. J. *Compilation of Extra-Framework Sites in Zeolites*; Butterworth Scientific Ltd.: Guildford, U.K., 1982.

(2) Olson, D. H. *J. Phys. Chem.* **1970**, *74*, 2758.

(3) Mortier, W. J; Bosmans, H. J. *J. Phys. Chem.* **1971**, *75*, 3327.

(4) de Boer, J. J.; Maxwell, I. E. *J. Phys. Chem.* **1974**, *78*, 2395.

(5) Baur, W. H. *Am. Mineral.* **1964**, *49*, 697.

(6) Sircar, S. *Sep. Sci. Technol.* **1988**, *23*, 2379.

(7) Coe, C. G. *Gas Separation Technology*; Elsevier: Amsterdam, 1989.

(8) Baksh, M. S.; Kikkinides, E. S.; Yang, R. T. *Sep. Sci. Technol.* **1992**, *27*, 277.

(9) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; Wiley: New York, 1984.

(10) Vitale, G.; Bull, L. M.; Morris, R. E.; Cheetham, A. K.; Toby, B. H.; Coe, C. G.; MacDougall, J. E. *J. Phys. Chem.* **1995**, *99*, 16087.

(11) Mellot, C.; Lignieres, J. *Mol. Simul.* **1997**, *18*, 349.

(12) Olson, D. H. *Zeolites* **1995**, *15*, 439.

(13) Hseu, T. Ph.D. Thesis, University of Washington, Seattle, 1972.

(14) Newsam, J.; Freeman, C.; Gorman, A.; Vessal, B. *Chem. Commun.* **1996**, *16*, 1945.

(15) Grillo, M. E.; Carrazza, J. *J. Phys. Chem.* **1996**, *100*, 12261.

(16) Shepelev, Y. F.; Anderson, A. A.; Smolin, Y. I. *Zeolites* **1990**, *10*, 61.

(17) Forano, C.; Slade, R. C.; Andersen, E. K.; Andersen, I. G.; Prince, E. *J. Solid. State Chem.* **1989,** *82*, 95.

(18) Shepelev, Y. F.; Butikova, I. K.; Smolin, Y. I. *Zeolites* **1991**, *11*, 287.

(19) Anderson, A. A.; Shepelev, Y. F.; Smolin, Y. I. *Zeolites* **1990**, *10*, 32.

(20) Maxwell, I. E.; de Boer, J. J. *J. Chem. Soc., Chem. Commun.* **1974**, 814.

(21) Newsam, J. M.; Jacobson, A. J.; Vaughan, D. E. *J. Phys. Chem.* **1986**, *90*, 6858.

(22) Fitch, A. N.; Jobic, H.; Renouprez, A. *J. Phys. Chem.* **1986***, 90*, 1311.

(23) Bull, L. M.; Cheetham, A. K.; Powell, B. M.; Ripmeester, J. A.; Ratcliffe, C. I. *J. Am. Chem. Soc.* **1995**, *117*, 4328.

(24) Vitale, G.; Bull, L. M.; Powell, B. M.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1995**, *22*, 2253.

(25) Goyal, R.; Fitch, A. N.; Jobic, H. J. *J. Chem. Soc., Chem. Commun.* **1990**, *17*, 1152.

(26) Czjzek, M.; Fuess, H.; Vogt, T. *J. Phys. Chem.* **1991**, *95*, 5255.

(27) Mellot, C.; Espinat, D.; Rebours, B.; Baerlocher, Ch.; Fischer, P. *Catal. Lett.* **1994**, *27*, 159.

(28) Henson, N. J.; Cheetham, A. K.; Redondo, A.; Levine, S. M.; Newsam, J. M. In *Proceedings of the 10th International Zeolite Conference*; Weitkamp, J., et al., Eds.; Elsevier: Amsterdam, 1994; p 2059.

(29) Auerbach, S. M.; Bull, L. M.; Henson, N. J.; Metiu, H. I.; Cheetham, A. K. *J. Phys. Chem.* **1996**, *100*, 5923.

(30) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

(31) Larson, A. C.; Von Dreele, R. B. GSAS *Generalised Crystal Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1987.

(32) *Calalysis 4.0 Software Suite and Discover*, Version 3.2; MSI: San Diego, CA.

(33) de Mallmann, A. Thèse de 3ème Cycle, Université Pierre et Marie Curie, Paris, 1986.