Two Crystal Structures of Fully Dehydrated Partially Magnesium Exchanged Zeolite A, Mg₁.₅Na₉-A and Mg₂.₅Na₇-A

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Two Crystal structures of fully dehydrated partially magnesium exchanged zeolite A, stoichiometries of Mg₂.₅Na₇-A (a = 12.251 (1) Å) and Mg₁.₅Na₉-A (a = 12.214(1) Å) per unit cell, have been determined from the 3-dimensional X-ray diffraction data gathered by counter methods. All structures were solved and refined in the cubic space group *Pm3m* at 21(1)°C. The structures of the dehydrated Mg₂.₅Na₇-A and Mg₁.₅Na₉-A were refined to yield the final error indices R_1 = 0.042 and R_2 = 0.049 with 318 reflections, and R_1 = 0.034 and R_2 = 0.032 with 252 reflections, respectively, for which $I > 3\sigma(I)$. Both structures indicate that Mg²⁺ ions are coordinated by three framework oxygens and the angle substended at Mg²⁺ ions, O(3)-Mg(1)-O(3) is *ca.* 120°, close to the idealized trigonal planar value. Mg²⁺ ions preferentially occupy 6-ring sites and Na⁺ ions occupy 8-ring sites when total number of cations per unit cell is more than 8.

Introduction

If completely Mg²⁺-exchanged zeolite A could be prepared, the resulting material would be interesting because the volume of exchangeable cations would be the smallest possible (ignoring Be²⁺) in zeolite A. Upon dehydration, the zeolite A would have a large void space to encompass the incoming guest molecules. Furthermore, Mg²⁺-exchanged zeolite A would be useful for the adsorption of some guest molecules because Mg²⁺ ion have quite large ionic potential and will exert a great effect in polarizing the incoming guest molecules.

It was initially hoped that by flow method, the number of Mg²⁺ ions exchanged into the zeolite could be maximized without incurring crystal damage. If fully Mg²⁺ exchanged zeolite A could not be obtained, the structural basis of limit would be seen and the site selectivities for two ions (Mg²⁺ and Na⁺ ion) of different charges would be learned.

Experimental

Crystals of zeolite A were prepared according to the method of Charnell.[1] Ion exchange with repeatedly refreshed 0.1 M MgCl₂ aqueous solution at 75°C for 4 weeks yielded colorless crystals. Exchange limit of Mg²⁺ ions into zeolite A was determined by the EDTA method.[2] It was found that the composition of these crystals were Mg₂.₅Na₇-A per unit cell. A crystal, 0.08 mm along an edge was placed in a finely drawn pyrex capillary, attached to a vacuum system, and cautiously dehydrated by raising the temperature an increments of 25°C/h to 360°C. The temperature was maintained for 2 days at a pressure of 1 × 10⁻⁶ Torr. After the system had returned to ambient temperature, the crystal in its capillary was sealed off by torch. Microscopic examination showed the crystal to have remained colorless.

Crystals of Mg₁.₅Na₉-A were prepared by dry-mixing with calculated amounts of zeolite 4A and Mg₂.₅Na₇-A[3]. Enough water to submerge all solid zeolite crystals was added so that at equilibrium zeolites of Mg₁.₅Na₉-A were obtained. A crystal, 0.08 mm along an edge was selected in a pyrex capillary, evacuated at 360°C and 2 × 10⁻⁶ Torr for 2 days and sealed off in its capillary by torch.

Subsequent diffraction experiments were performed at 21(1)°C. The cubic space group *Pm3m* (no systematic absences) was used for reasons discussed previously.[4-7] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four circle Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromater. Mo Kα radiation was used for all experiments (K$_{\alpha1}$, λ = 0.70935 Å, K$_{\alpha2}$, λ = 0.71359 Å and K$_{\bar{\alpha}}$, λ = 0.71073). The cubic unit cell constants, as determined by least-squares refinements of 25 intense reflections for which 18° < 2θ < 24° are 12.251(1) Å for Mg₂.₅Na₇-A (D_{cal} = 1.491 g cm⁻³ and F(000) = 809) and 12.254(1) Å for Mg₁.₅Na₉-A (D_{cal} = 1.525 g cm⁻³ and F(000) = 819), respectively.

Reflections from which two intensity-equivalent regions of reciprocal space (*hkl*, $h \leq k \leq l$ and *lkh*, $l \leq k \leq h$) were examined ω-2θ scan technique. The data were collected by variable scan speeds. The maximum final scan time was 300 seconds per one reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and instrumental stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

For the crystal of Mg₂.₅Na₇-A, all unique reciprocal lattice points for which 2θ < 70° were examined. For the crystal of Mg₁.₅Na₉-A, all unique reciprocal lattice points for which 2θ < 60° were examined.

The raw data from each region were corrected for Lorentz and polarization effect, including that due to incident beam monochromatization, the reduced intensities were merged and the resultant estimated standard deviation were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT.[8]

Of the 873 unique pairs of reflections for the dehydrated Mg₂.₅Na₇-A and 595 for the dehydrated Mg₁.₅Na₉-A, only 318 and 252 pairs, for which $I > 3\sigma(I)$, respectively, were used in structure determinations. An absorption correction (μ_{Mo} = 5.07 cm⁻¹ for Mg₂.₅Na₇-A and μ_{Mo} = 5.16 cm⁻¹ for Mg₁.₅Na₉-A) was not applied because the crystals used were very small cubes; this correction in the similar case[9] had little effect on the final structure.

Full-matrix least-squares refinement of structure was initiated using the atomic parameters of Ag₇.₆Na₄.₄-A[10] for the

Table 1. *ª*Positional, Thermal and Occupancy Parameters

Crystal 1. Dehydrated $Mg_{2.5}Na_7$-A

Atom	Wyc. pos.	x	y	z	β_{11}^b or β_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si,Al)	24(k)	0	1835(1)	3719(1)	32(1)	28(1)	19(1)	0	0	8(1)	1^c
O(1)	12(h)	0	2255(5)	5000	61(4)	77(5)	32(4)	0	0	0	1
O(2)	12(i)	0	2913(3)	2913(3)	83(5)	40(2)	40(2)	0	0	42(6)	1
O(3)	24(m)	1125(2)	1125(2)	3421(3)	47(2)	47(2)	52(3)	14(4)	2(3)	2(3)	1
Na(1)	8(g)	2015(3)	2015(3)	2015(3)	39(2)	39(2)	39(2)	33(3)	33(3)	33(3)	11/16
Na(2)	12(i)	0	4248(10)	4248(10)	1.4(3)						3/24
Mg(1)	8(g)	1919(10)	1919(10)	1919(10)	151(9)	151(9)	151(9)	80(20)	80(20)	80(20)	5/16

Crystal 2. Dehydrated $Mg_{1.5}Na_9$-A

Atom	Wyc. pos.	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si,Al)	24(k)	0	1834(1)	3712(1)	37(1)	33(1)	22(1)	0	0	10(2)	1^c
O(1)	12(h)	0	2228(4)	5000	74(4)	92(5)	37(3)	0	0	0	1
O(2)	12(i)	0	2926(3)	2926(3)	94(5)	47(2)	47(2)	0	0	57(6)	1
O(3)	24(m)	1126(2)	1126(2)	3395(3)	60(2)	60(2)	64(3)	22(5)	-1(4)	-1(4)	1
Na(1)	8(g)	2047(2)	2047(2)	2047(2)	61(2)	61(2)	61(2)	24(3)	24(3)	24(3)	13/16
Na(2)	12(i)	0	4263(8)	4263(8)	100(10)	105(9)	105(9)	0	0	-90(20)	5/24
Mg(1)	8(g)	1840(8)	1840(8)	1840(8)	54(5)	54(5)	54(5)	50(10)	50(10)	50(10)	3/16

*ª*Positional and thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in units of the least significant digit given for the corresponding parameter. *ᵇ*The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Rms displacements can be calculated from β_{ij} values by using the formula $\mu_i = 0.225\,a\,(\beta_{ij})^{1/2}$, where $a = 12.251(1)$ Å for $Mg_{2.5}Na_7$-A and $a = 12.214(1)$ Å for $Mg_{1.5}Na_9$-A. *ᶜ*Occupancy for (Si) = 0.5; occupancy for (Al) = 0.5.

atoms of the aluminosilicate framework ((Si, Al), O(1), O(2) and O(3)). From the initial different Fourier map Na(1) and Na(2) were located and refined (see Table 1). The anionic framework of zeolite A is $[Al_{12}Si_{12}O_{48}]^{-12}$. Therefore only 12 monovalent cations (or 6 bivalent cations) should be located in the unit cell of zeolite A. From a subsequent Fouries map, Mg^{2+} ions at Mg(1) were located and refined. Na^+ ions at Na(1) and Mg^{2+} ions at Mg(1) lie on the threefold axes of unit cell. The sum of these two ions can not exceed 8.0. Otherwise unacceptable close interionic distance would occur. Therefore the occupancies of Mg(1) and Na(1) were refined with the constrain that the sum of occupancies be 8.0 (see Table 1). The final R values for the dehydrated $Mg_{2.5}Na_7$-A and those for the dehydrated $Mg_{1.5}Na_9$-A are $R_1 = 0.042$ and $R_2 = 0.049$, and 0.034 and 0.032, respectively.

The quantity minimized in the least-squares treatment was $\Sigma w(Fo - |Fc|)^2$, where the weight(w) are the reciprocal squares of $\sigma(F)$, the standard deviation of each observation.

Atomic scattering factor[11,12] for Mg^{2+}, Na^+, O^- and (Si, Al)$^{1.75+}$ were used. The function describing (Si, Al)$^{1.75+}$ is the mean of Si^0, Si^{4+}, Al^{3+}, and Al^0. All scattering factors were modified to account for the real component $(\Delta f')$ of anomalous dispersion correction.[13,14] Final position, thermal and occupancy parameters are presented in Table 1. Bond angles and lengths are given in Table 2.

Discussion

In both structures, Mg^{2+} ions at Mg(1) are located on the threefold axes of the unit cell. Each of these Mg^{2+} ions is coordinated to three O(3) framework oxygens at *ca.* 2.28 Å.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) of Dehydrated $Mg_{12-2x}Na_x$-A($x = 1.5$, and 2.5)

	$Mg_{2.5}Na_7$-A	$Mg_{1.5}Na_9$-A
(Si,Al)-O(1)	1.651(3)	1.645(2)
(Si,Al)-O(2)	1.649(3)	1.643(3)
(Si,Al)-O(3)	1.670(2)	1.671(2)
Na(1)-O(3)	2.312(3)	2.290(3)
Na(2)-O(1)	2.610(7)	2.644(6)
Na(2)-O(2)	2.31(1)	2.309(7)
Mg(1)-O(3)	2.297(6)	2.269(3)
O(1)-(Si,Al)-O(2)	108.7(2)	108.7(2)
O(1)-(Si,Al)-O(3)	111.7(2)	112.0(1)
O(2)-(Si,Al)-O(3)	106.6(2)	106.58(9)
O(3)-(Si,Al)-O(3)	111.2(1)	110.8(2)
(Si,Al)-O(1)-(Si,Al)	143.7(4)	146.0(3)
(Si,Al)-O(2)-(Si,Al)	163.6(2)	161.5(2)
(Si,Al)-O(3)-(Si,Al)	144.2(2)	143.1(2)
O(3)-Mg(1)-O(3)	119.9(2)	119.61(6)
O(3)-Na(1)-O(3)	118.7(1)	117.73(6)
O(1)-Na(2)-O(2)	65.7(3)	64.9(3)

Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

The O(3)-Mg(1)-O(3) angle is *ca.* 120°–near the idealized trigonal-planar angle. Mg^{2+} ions lie almost on the plane of three O(3) atoms–almost the center of (111) plane of three O(3) atoms.

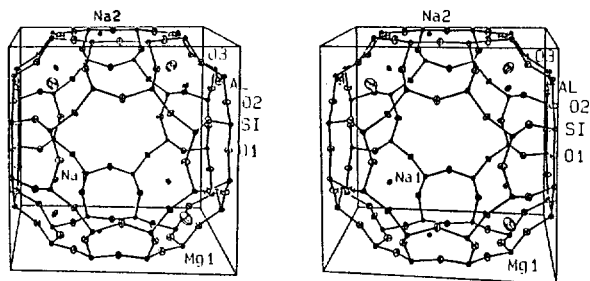The crystal structure of MgO has been determined. The

Figure 1. A stereoview of a large cavity of the dehydrated Mg$_{2.5}$ Na$_7$-A. 3 Mg^{2+} ions at Mg(1), 5 Na$^+$ ions at Na(1) and 1 Na$^+$ ions at Na(2) are shown. About 50% of unit cells have this stoichiometry. The remaining 50% of unit cells may have 2 Mg^{2+} ions at Mg(1), 6 Na$^+$ ions at Na(1) and 2 Na$^+$ ions at Na(2). Ellipsoids of 20% probability are shown.
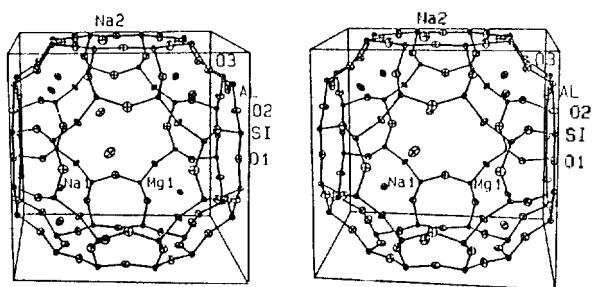

Figure 2. A stereoview of a large cavity of the dehydrated Mg$_{1.5}$ Na$_9$-A. 2 Mg^{2+} ions at Mg(1), 6 Na$^+$ ions at Na(1) and 2 Na$^+$ ions at Na(2) are shown. About 50% of unit cells have this stoichiometry. The remaining 50% of unit cells may have 1 Mg^{2+} ions at Mg(1), 7 Na$^+$ ions at Na(1) and 3 Na$^+$ ions at Na(2). Ellipsoids of 20% probability are shown.

Mg-O distance in MgO is 2.104 Å.[15] For comparison, the sum of the Mg^{2+} and O^{2-} radii is 1.98 Å.[16] Therefore, the relatively long bond distance of Mg^{2+}-O^{2-} in the present Mg$_x$Na$_{12-2x}$-A structures indicate that the bonds between Mg^{2+} ions and oxide ions of zeolite framework are relatively weak.

One would expect the conformation of a particular 6-ring to depend upon the identity and position of the cation associated with it. In this work, only the average conformation over eight such rings has been determined, and small errors in Mg-O distances due to this disorder are expected.

The fractional occupancy observed at Mg^{2+} ions at Mg(1) of the structure of Mg$_{2.5}$Na$_7$-A indicates that about 50% of unit cell may have 3 Mg^{2+} ions and 6 Na$^+$ ions, and the remaining 50% of unit cell may have 2 Mg^{2+} ions and 8 Na$^+$ ions per unit cell.

A plausible arrangement of the large cavity of the dehydrated Mg$_{2.5}$Na$_7$-A is presented in Figure 1. Figure 2 is shown a stereoview of large cavity of the dehydrated Mg$_{1.5}$Na$_9$-A. The Mg^{2+} ions have been placed within their partially occupied equipoints so as to maximize the distribution of positive charge (to balance most evenly the anionic charge of the framework) and to minimize their electrostatic repulsions (by maximize the shorter of their intercationic approaches). To minimize electrostatic repulsions, the Mg^{2+} ions at Mg(1) are placed triangular fashions and Na$^+$ ions at Na(1) are filled the remained threefold equipoints of the

Table 3. Deviation of atom (Å) from the (111) Plane at O(3)

Atom	Mg$_{2.5}$Na$_7$-A	Mg$_{1.5}$Na$_9$-A
O(2)	−0.109	−0.145
Na(1)	−0.226	−0.348
Mg(1)	−0.063	0.143

A positive deviation indicates that the atom lies on the same side of the plane as the origin.

6-rings (see Figure 1).

Na$^+$ ions at Na(1) are associated with 6-ring oxygens and are at the some position as was found in dehydrated Na$_{12}$-A. These ions are also distributed over the threefold axes of the unit cell and displaced into the large cavity from the O(3) planes of the oxygen 6-rings by *ca.* 0.3 Å. Each Na$^+$ ion is trigonally coordinated at *ca.* 2.30 Å to three O(3) framework oxygens (Figure 1 and 2).

The Na$^+$ ions at Na(2) lie in the plane of the eight-rings, but off their centers. Each of these is *ca.* 2.31 Å from the nearest framework oxide ion at O(2) and *ca.* 2.63 Å from two oxide ions at O(1). This coordination environment is unsatisfactory for the ion at Na(2), partly because its three ligand atoms are all to one side, not arranged around it. Also, these distances are somewhat greater than the sum of ionic radii, 2.30 Å. These sites do not appear to be as energetically favorable as the Na(1) and Mg(1) positions because of their longer and less symmetrical approaches to the framework oxygens.

The ionic radius of Na$^+$, 0.97 Å is much larger than that of Mg^{2+}, 0.66 Å.[16] Smaller Mg^{2+} ions prefer 6-ring sites and larger Na$^+$ ions prefer 8-ring sites when number of ions per unit cell is more than 8.

During this work, many other Mg^{2+}-exchanged zeolite A crystals were prepared by the dynamic flow method. These crystals whether they were hydrated or vacuum dehydrated did not give any single crystal diffraction patterns. This may be due to the hydrolysis and destruction of zeolite framework observed in the previous works of Fe^{2+}, Ba^{2+},[17] Ni^{2+},[18] and Cu^{2+} [19] exchanged zeolite A.

Also of interest in this work are the different results depending on the method of exchange. Single crystals ion exchanged with MgCl$_2$ by flow method at 23 °C produced no diffraction pattern. On the other hand, crystals ion exchanged by batch methods using identical solutions and temperature yielded a stable Mg^{2+}-exchanged zeolite A. Apparently, the static method allows the zeolite to equilibrate with solution; in the process the pH of the solution is increased, providing less harmful conditions to zeolite. The dynamic nature of the flow method, however, do not allow the pH to adjust, and encourage H$_3$O$^+$ exchange and attack. Also by flow method, Mg^{2+} ions may be exchanged into zeolite A more than 2.5 ions per unit cell. However, bivalent Mg^{2+} ions hydrolyze H$_2$O and the resulted H$_3$O$^+$ concentration is accumulating and destroying zeolite framework. Therefore it appears that the exchange limit for Mg^{2+} ions into zeolite A is 2.5 ions per unit cell. This result is consistent with the previous observation that Mg^{2+} ion is the lowest selective bivalent cations in zeolite A.[20]

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The Crystal and Molecular Structure of Maltitol

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The crystal structure of maltitol, 4-O-α-D-glucopyranosyl-D-glucitol, has been determined by X-ray diffraction method. The crystal is orthorhombic with cell parameters of $a = 8.170(1)$, $b = 12.731(1)$, $c = 13.679(3)$ Å, space group $P2_12_12_1$ and $z = 4$. The structure was solved by direct methods and refined to R = 0.030 for 1181 observed reflections measured on a diffractometer. The α-glucose ring has chair conformation. The carbon atom chain of the glucitol residue has the bent, *ap, Psc, Psc* conformation. The angle at the ring oxygen atom is 112.6° and the one at the glucosidic oxygen is 117.1°. The molecules are linked by very complicated hydrogen bonds, and there is an intramolecular hydrogen bond between O(1') and O(2').

Introduction

X-ray diffraction technique can be widely used in the determination of the conformations and the configurations of carbohydrates. The importance of the molecular conformations of carbohydrates has long been recognized, and therefore a number of structure investigations of monosaccharides, disaccharides, polysaccharides and their derivatives have been carried out using X-ray and neutron diffraction methods[1-3].

In this study, the crystal and molecular structure of maltitol (4-O-α-D-glucopyranosyl-D-glucitol) is determined from X-ray diffraction method to compare this conformation with those of maltose related compounds and derivatives[4-8] to be determined already.

Maltitol is derived from the disaccharide maltose and can be formed by reductive ring opening of its reducing pyranose ring. In this class of hexosylhexitols, composed of an aldopyranose linked to a hexitol by a C-O-C glycosidic bridge, the acyclic carbon chain of the molecule is much more flexible than the rigid pyranose ring.

In the work of Jeffrey and Kim[9] on the conformations of alditols, $HOCH_2(CHOH)_nCH_2OH$, acyclic carbon chains have the extended, planar, zigzag arrangement, unless this would give rise to a steric interaction between substituents on alternate carbon atoms. If such an interaction is possible, the carbon chain adopts, by a 120° rotation about a C-C bond, a non-linear, or bent chain conformation so that these interactions are avoided. The aim of the present study is also to examine the acyclic carbon chain conformation in this structure and to compare with that observed in D-glucitol compounds.