The Structure of a Dehydrated Partially Magnesium Exchanged Zeolite A (~Mg$_2$Na$_8$–A) by Neutron Profile Refinement

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The structure of a dehydrated sample of partially magnesium-exchanged zeolite A [~Mg$_2$Na$_8$–A] has been determined by Rietveld profile refinement methods. The space group employed was $Fm\bar{3}c$ and a refined to 24.4244(14) Å. The final R_{pw} was 10.9%. Exchangeable cations were located in two sites, the first being on the threefold axis on the α-cage side of the 6-ring, while the second lies in the plane of the 8-ring. The magnesium ions and most of the sodium ions lie on the first site while the remaining sodium ions lie on the second. A small amount of water (~$\frac{3}{4}$ H$_2$O per α-cage) remained in the sample despite the vigorous dehydration conditions employed; this water lies on the threefold axis, further into the α-cage than the exchangeable cations in 6-ring sites, and is coordinated to some of the magnesium cations. Probably as a result of damage to the sample during the Mg^{2+} ion exchange, the peaks were broader than those found in some of the previous studies of ion-exchanged zeolite A samples. Attempts at refinement using Lorentzian, rather than Gaussian, peak-shape functions produced better fits to the experimental diffraction profile (R_{pw} = 7.9%) but did not improve the esd's in the atomic parameters. © 1986 Academic Press, Inc.

Introduction

Recently, the structure of zeolite A (Fig. 1) has been studied in great detail by magic angle spinning nuclear magnetic resonance spectroscopy (MASNMR, *1*), X-ray (*2*), and neutron diffraction (*1, 3–7*). These studies have confirmed that the Si/Al ordering is completely regular, that Loewenstein's rule (*8*) is obeyed, and that the most appropriate space group is $Fm\bar{3}c$ (*2, 3–7, 9*).

Zeolite A, in its sodium-exchanged form, has recently been introduced in large ton-nages as a "builder," i.e., ion-exchanger, in detergents to replace triphosphates. Na–A has been shown to be very selective to exchange with Ca^{2+} ions and quite selective for Mg^{2+} at low loadings (*10*). It has been postulated that the highly hydrated Mg^{2+} ions lose many molecules of water of hydration to enter the confined α-cages of zeolite A. In order to maintain the largest possible number of water ligands, the preferred site for Mg^{2+} in hydrated zeolite A would be the 8-ring site II, whereas Ca^{2+} would prefer to be in the 6-ring site I, as has been found experimentally (*10*). Such sitings
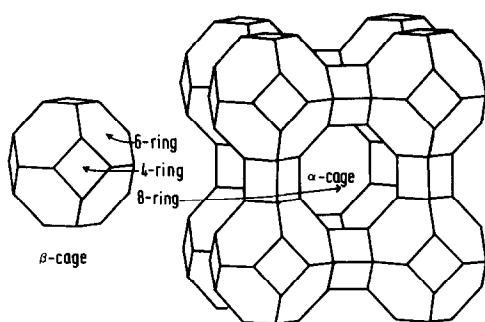
FIG. 1. Framework structure of zeolite A. Tetrahedral atoms (Al, Si) occur at the intersections of the lines; oxygen atoms are not shown, but are located approximately halfway between the tetrahedral atom sites. The 8-ring is at the entranceway to the α-cage.

would explain the ease with which Na–A accepts up to 2 Mg^{2+} ions from Ca^{2+}/Mg^{2+} mixtures. At higher Ca^{2+} loadings, the Mg^{2+} ions are then replaced by Ca^{2+}. Moreover, sorption studies have shown significant differences in the behavior of Ca^{2+}- and Mg^{2+}-exchanged zeolite A when the two divalent ions have been exchanged to the same degree (11). It was considered that these differences could be due to differences in location of Mg^{2+} or Ca^{2+} in the structure.

In order to increase our understanding of the exchange selectivities and sorption behavior, structural studies were undertaken on samples of Na–A which had been partially exchanged with Mg^{2+} ions. This work was considered to be complementary to that carried out previously on (Ca, Na)–A (5).

Experimental

A sample of Na–zeolite A was ion-exchanged in one step with magnesium perchlorate solution. Analysis of the fully hydrated sample gave 8.18% Na, 1.77% Mg, and 14.2% Al. ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MASNMR) were obtained from ~0.2-g sample in a JEOL FX-200 high-resolution

solid state NMR spectrometer operating at the NMR frequencies of 51.9 and 43.6 MHz, respectively. For ^{27}Al NMR, 100 scans at a rate of 0.1 sec were made before Fourier transformation. For ^{29}Si, 2500 scans at a rate of 5 sec were made. The MASNMR showed that the Si/Al ratio was very close to unity (between 1.0 and 1.06) and that there was no sign of any signal from octahedral aluminum (Fig. 2). From this information we deduce a formula near $Na_8Mg_2Al_{12}Si_{12}O_{48} \cdot nH_2O$. If the analytical values for Mg and Na (1.7 and 8.1) were taken at face value, $0.5H^+$ would also have to be present to maintain electroneutrality, yet the exchanging solution was alkaline.

The neutron powder diffraction data were collected on the high-resolution diffractometer D1A at the Institut Laue–Langevin, Grenoble (12). Five grams of the zeolite powder were loaded into a 16-mm-diameter vanadium sample can and dehydrated in situ on D1A. The sample was heated to 100°C under vacuum ($<10^{-3}$ Torr) for 6 hr, after which the temperature was raised slowly to 250°C. At this point the pressure built up to 2×10^{-2} Torr; the temperature was kept constant till the pressure fell again and was then increased to 330°C and maintained at this value for 10 hr. The sample was cooled to 25°C over the next 3 hr and the experimental run was then started. The vacuum was maintained dynamically throughout the data collection. A neutron wavelength of 1.909 Å was used and the data were collected in 0.05° steps from 6–158° (2θ). The background was estimated by linear interpolation from regions where no Bragg scattering occurred. The data were truncated at 143° (2θ), as the statistical scatter was found to be greater than any of the peak intensities. Peaks which occurred below 20° (2θ) were found to suffer from some degree of asymmetry and this part of the diffraction record was omitted from the refinement. In addition, five peaks due to boron nitride (in the furnace) oc-
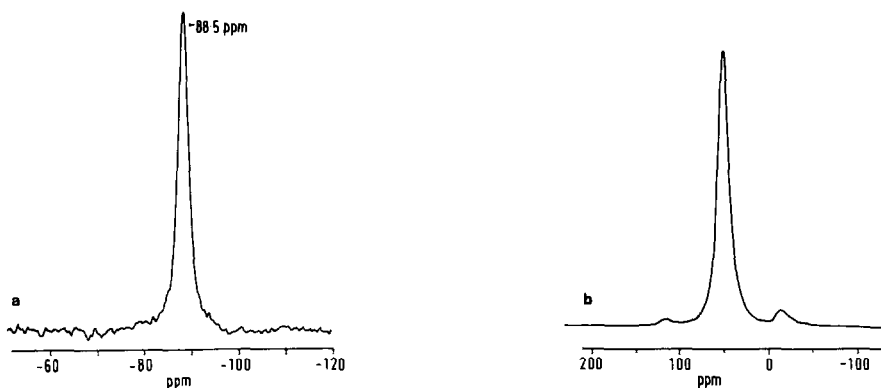
FIG. 2. (a) ^{29}Si MASNMR of the sample before dehydration. The peak position corresponds to Si(OAl)$_4$. (b) ^{27}Al MASNMR of the sample, again before dehydration. The main peak (and two spinning side bands) is from tetrahedral Al; there is no evidence for octahedral Al species.

curred in the diffraction trace and the small 2θ regions where these occurred were omitted from the calculations.

Structure refinement was carried out using the Rietveld technique (13) with (initially) the programs of Hewat (14) and then that of Wiles (15). The scattering lengths used were taken from the "International Tables for X-ray Crystallography" (16).

Structure Refinement

An initial structure refinement was carried out with the framework atoms only, using space group $Fm\bar{3}c$; the atom positions were based on those derived from a previous zeolite A structure determination (4). A difference Fourier map showed three extra framework peaks. The first, and largest, was in a 6-ring site just inside the α-cage. The second largest peak was in an 8-ring site, and in both cases the interpretation was that these sites contained exchangeable cations. Finally there was a third, smaller, peak about 2 Å along the $\bar{3}$ axis from the 6-ring cation site, further into the α-cage. This peak was considered on chemical grounds to be likely to be due to a little water which had not been removed from the sample despite the rigorous dehydration

conditions, or, possibly to a hydroxyl group (see Discussion).

There are three distinct possibilities for location of the $2Mg^{2+}$ and $8Na^+$ cations per α-cage:

A. 6-ring site (8 per α-cage), $2Mg^{2+}$ and up to $6Na^+$; 8-ring site (3 per α-cage), rest of the Na^+;

B. 6-ring site, up to $8Na^+$; 8-ring site, $2Mg^{2+}$ plus any Na^+ not in the 6-ring site;

C. Na^+ and Mg^{2+} randomly arranged in the two sites.

We "constructed" average exchangeable cations M, the scattering power of which was the average value of $2Mg + 8Na$, i.e., $b_M = 0.389$.

In the next stage of the refinement the positions and occupancies of the exchangeable cations and water molecules were allowed to vary. The site occupancies resulting were $7.6M$ in the 6-ring site, $2.4M$ in the 8-ring site and ~ 1 oxygen atom (of a water molecule or OH group). The interpretation of the exchangeable cation location is aided by consideration of the distance information in comparison with that for Na–A. At this stage in the refinement R_{pw} was 12.9% and the exchangeable cation to oxygen dis-

tances were

6-ring:
$M(1)-O(3)$, 2.25 Å
(2.32 Å in Na zeolite A, ref. *4*);
8-ring:
$M(2)-O(1)$, 2.61 } Av 2.56 Å
$M(2)-O(2)$, 2.51 }
(Av 2.59 Å in Na zeolite A);
Also:
$M(1)-O(4)$-water, 1.99 Å.

It was apparent, then, that the 6-ring $M(1)-O(3)$ distance is 0.07 Å shorter than that found in Na zeolite A which is consistent with a $Mg^{2+}:Na^{+}$ occupancy ratio of $\sim 1Mg^{2+}$ to $3Na^{+}$. In addition, the average $M(2)-O$ distance in the 8-ring is only 0.03 Å shorter than that in Na zeolite A, whereas it would be expected to be 0.3 Å (at least) shorter if all the cations in the 8-ring were Mg^{2+}. These facts suggest that it is likely that the Mg^{2+} cations are located in the 6-ring sites. Moreover, the distance from $M(1)$ to the water oxygen atom is much too short to be due to $Na^{+}-OH_2$, which is usually ~ 2.35 Å, but is much closer to the value found for hydrated magnesium ions (2.05 Å, *17*). Assuming that the Mg^{2+} ions

are located in the 6-ring sites gives $2.0Mg^{2+}$ and $5.4Na^{+}$ in the 6-ring sites and $2.6Na^{+}$ in the 8-ring sites.

Further refinement was carried out with average cations $(7.6M$ and $2.4M)$ in the 6- and 8-ring sites, but then the cations in the 6-ring sites were split into two components, one of $2Mg^{2+}$, the other of $5.4Na^{+}$. Initially, the centroid of the two types of cation was set equal to that found for the $7.6M$, with the added proviso that the $Na^{+}-O(3)$ distance should be equal to that found in Na–A (*4*). The positions of the ions were then allowed to refine freely along the $\bar{3}$ axis, as was the position of the water oxygen atom $O(4)$, although the thermal parameters for this atom were constrained to be equal to those of the Mg^{2+} ions to which it was bonded.

An attempt to locate the water hydrogen atoms from a Fourier difference synthesis proved unsuccessful for, although there was a negative "halo" around $O(4)$, it was not possible to locate definite minima in the scattering density. It was concluded that the hydrogen atoms must be disordered, either positionally or thermally, and consequently four partial hydrogen atoms were
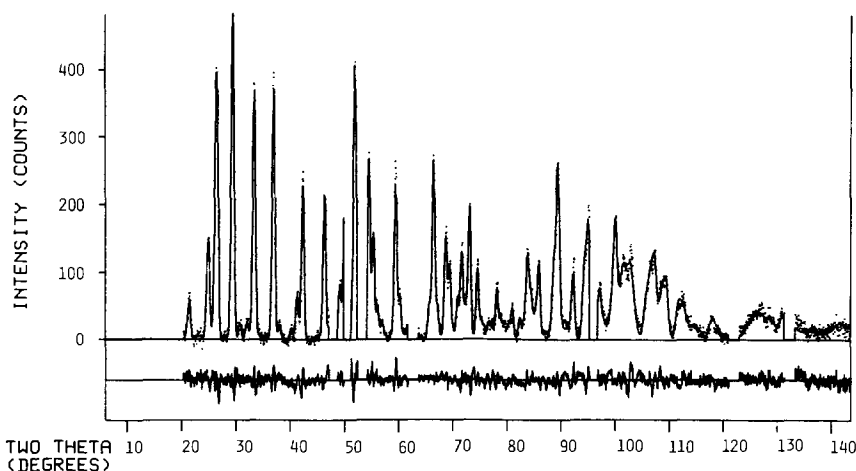

FIG. 3. Observed ($\cdots$) and calculated (—) diffraction patterns for the title compound at 300 K, together with a difference plot.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS

Site	Position	Population	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	96(i)	96	0	0.0946(4)	0.1837(4)	−3(1)	20(2)	18(2)	0	0	−5(1)
Al(1)	96(i)	96	0	0.1873(6)	0.0879(4)	33(4)	22(2)	−1(2)	0	0	1(1)
O(1)	96(i)	96	0	0.1085(2)	0.2470(3)	31(1)	29(1)	2(1)	0	0	5(2)
O(2)	96(i)	96	0	0.1467(2)	0.1481(3)	39(1)	11(2)	3(1)	0	0	9(1)
O(3)	192(j)	192	0.0538(2)	0.0577(1)	0.1676(1)	22(1)	8(1)	26(1)	5(1)	4(1)	−6(1)
Mg(1)	64(g)	14.4(11)	0.0952(12)	0.0952(12)	0.0952(12)	25	25	25	8	8	8
Na(1)	64(g)	45.2(11)	0.0996(6)	0.0996(6)	0.0996(6)	25(2)	25(2)	25(2)	8(2)	8(2)	8(2)
Na(2)	96(i)	21.3	0	0.2144(6)	0.2255(15)	12(6)	−12(3)	67(17)	0	0	−17(4)
O(4)	64(g)	5.9(7)	0.1433(12)	0.1433(12)	0.1433(12)	25	25	25	8	8	8
H(1)	192(j)		0.1385	0.1385	0.1865	50					
H(2)	192(j)		0.1700	0.1700	0.1215	50					
H(3)	192(j)		0.1811	0.1232	0.1522	50					
H(4)	192(j)		0.1232	0.1811	0.1522	50					

Note. Anisotropic displacement factor given by $10^4 \exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hk\beta_{13} + 2kl\beta_{23})$. $R_p = 100\Sigma \,|y(\text{obs})$ $- c^{-1} y(\text{calc})|/ \Sigma \,|y(\text{obs})|$; $R_{pw} = 100[\Sigma w(y(\text{obs}) - c^{-1}y(\text{calc}))^2/ \Sigma \,(y(\text{obs}))^2]^{1/2}$; w is the weight at each 2θ data point and $y(\text{obs})$ and $y(\text{calc})$ are the observed and calculated intensities at that point; c is the scale factor.

disposed around a circle constructed to give O–H distances of ~1.07 Å and Mg(1)–O(4)–H angles of ~109°. Since these hydrogen atoms were just off the $\bar{3}$ axis, 12 equivalent hydrogen atoms were generated around the circle. This was considered to approximate to the desired situation suggested by the Fourier map. The hydrogen atoms were constrained to move with O(4) in the refinement. The final R_{pw} value was 10.9%. The diffraction pattern is given in Fig. 3.

Visual inspection of the diffraction trace showed that the peaks were somewhat wider than those obtained previously for zeolite A samples on D1A. It has been suggested (*18*) that in cases where there is significant peak broadening, it is sometimes useful to employ a Lorentzian rather than Gaussian peak shape and, moreover, to calculate the contribution to the diffraction pattern rather more than the usual one and a half half-widths from the center of each peak. Consequently, a new refinement was carried out using DBW 3.2, the Rietveld refinement program of Wiles (*15*). Lorentzian peak shapes were used and intensity contributions up to three half-widths from the center of each peak were made. R_{pw} fell sharply to 7.9%, but the esd's of the atom positions were slightly worse than those given by the previous refinement. The data given in Tables I and II and in the figures is that derived from the refinement using Gaussian peak shapes, as this data can be compared directly with previous related studies (*3–6*).

Discussion

The mean Si–O and Al–O bond lengths show clearly the bimodal distribution expected from strict alternation of Si and Al tetrahedra, i.e., 1.60 and 1.72 Å, respectively. There are, however, significant distortions on the tetrahedra, which are reminiscent of, and in the same sense as, those found for dehydrated zeolite 5A which has Ca^{2+} and Na^+ exchangeable cations (*5*). Here the distance from the center of the 6-ring (CEN) to O(3) is only 2.23 Å compared with 2.35 Å in 3A(4), 2.32 Å in 4A(3), and 2.28 Å in 5A(5), which suggests that the assignment of the Mg^{2+} ions to the 6-ring site is correct. If we compare the CEN–O(2) distances we find 2.89 Å in 3A(4), 2.92 Å in 4A(3) and 2.95 Å here, showing that the shorter metal–O(3) distances are accommodated by sympathetic rotation of the tetrahedra making up the 6-ring.

TABLE II

BOND DISTANCES (Å) AND ANGLES (°)

Si(1) –O(1)	1.583(12)	O(1) –Si(1) –O(2)	112.0(6)
Si(1) –O(2)	1.542(11)	O(1) –Si(1) –O(3)	110.6(4)
Si(1) –O(3), O(3i)	1.642(7)	O(2) –Si(1) –O(3)	108.6(4)
Al(1) –O(iii)	1.682(15)	O(3) –Si(1) –O(3i)	106.4(5)
Al(1) –O(2)	1.773(13)	O(iii)–Al(1) –O(2)	106.6(6)
Al(1) –O(3iii), O(3iv)	1.705(7)	O(iii)–Al(1) –O(3iii)	114.5(5)
Mg(1)–O(3), O(3iii), O(3v)	2.23(3)	O(2) –Al(1) –O(3iii)	104.3(5)
Na(1)–O(3), O(3iii), O(3v)	2.249(15)		
Mg(1)–O(4)	2.03(4)	O(3) –Mg(1)–O(3iii)	119.8(13)
		O(3) –Na(1)–O(3iii)	118.5(6)
Na(2)–O(1)	2.64(2)	O(3) –Mg(1)–O(4)	92.4(14)
Na(2)–O(2)	2.51(3)		
O(4) –H(1), H(2), H(3), H(4)	1.07		

Note. Symmetry code used in tables: (i) $-x, y, z$, (ii) $x, 1/2 - z, y$, (iii) y, z, x, (iv) $-y, z, x$, and (v) z, x, y.

Some structural studies of ion-exchanged zeolite A samples have found evidence of "AlO$_4$" tetrahedral species in the β-cages of the zeolite, and it has been postulated that these ions are introduced during the ion-exchange process. Pluth and Smith (2) have found these species in Ca$_6$–A and Sr$_6$–A as did Adams and Haselden in the carbon monoxide adduct of Co$_{5.25}$Na$_{1.5}$–A (6). However, in their refinement of Ca$_5$Na$_2$–A (5), Adams and Haselden did not find any tetrahedral species in the β-cages, suggesting that their presence or absence must depend upon a precise ion-exchange procedure. In the present study there was no evidence on the Fourier map of any scattering density inside the β-cages.

As regards the small amount of residual water found in this structure, it should be stressed that the hydrogen atoms were not located precisely. In fact, it is possible that there could have been some hydrolysis of the water molecule (19–22), possibly of the type found in a recent study of La zeolite Y (23),

$$Mg - OH_2 \rightarrow Mg - OH + H^+.$$

This would have meant that protons could have been liberated and become bound to one of the framework oxygen atoms in the structure. However, the proton would have had to be well ordered over many unit cells to be located, since it would have been present in very small amounts.

This study has shown that in (almost) dehydrated Mg$_2$Na$_8$–A the Mg^{2+} ions are most likely located in 6-ring rather than 8-ring sites as is also the case in partially calcium exchanged zeolite A (5). This does not appear to be consistent with differences noted previously in the ion-exchange and sorption properties of Mg^{2+} and Ca^{2+} exchanged A (11). However, ion exchange, at least, occurs in aqueous conditions and it could be that Mg^{2+} ions could be in 8-ring sites when hydrated, but move to 6-ring sites upon dehydration. Redistribution of exchangeable cations on dehydration is well known (24). Further structural studies are needed on dehydrated samples having higher magnesium contents and also on dehydrated samples in order to fully explain the differences in chemical activity between samples of Mg^{2+} and Ca^{2+}–A.

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