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The Structure of Dehydrated Zeolite 5A (Si/Al = 1.02) by Neutron Profile Refinement

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The structure of a commercially available, dehydrated sample of Linde Molecular Sieve 5A was refined using neutron powder profile analysis. Refinements were attempted in the accepted space group $Fm\bar{3}c$, in pseudo-cell $Pm\bar{3}m$, and also, using a lower-symmetry model, in space group $F432$. In $Fm\bar{3}c$, (a = 24.6497(8) Å) the final R_{pw} obtained was 13.6% while in $Pm\bar{3}m$ (a = 12.3254(4) Å) the final R_{pw} was 14.25%. The reasons for the relatively high values of R_{pw} compared with previous studies are discussed in terms of cation disorder and distortion of the framework. All the Ca^{2+} ions are located in a 6-ring site just inside the β cage while all the Na^+ ions are located in a 6-ring site just inside the α cage. No cations were found in the 8-ring site.

Introduction

Zeolite A is of considerable current commercial interest as an ion exchange in detergent formulations (*1*) and as a molecular sieve (*2*). It has been fully established that there is regular Si, Al alternation in the tetrahedra of the structure (*3–9*) in conformity with Loewenstein's rule (*10*). Moreover, X-ray and neutron diffraction studies of hydrated zeolite 4A (*3*), dehydrated zeolites 4A (*4, 5*), 3A (*6, 7*), thallium A (*8*), strontium A (*9*), and calcium A (*11*) have shown that the most appropriate space group for these materials is $Fm\bar{3}c$, although small deviations from this symmetry probably due to some disorder of exchangeable cations has been observed (*3, 5, 7*) and discussed (*5, 7, 12*). The space group $Pm\bar{3}m$ has also been used in many studies (e.g., *13–15*); in this case the unit cell dimensions are halved (12.3 Å compared with 24.6 Å in $Fm\bar{3}c$) and the model should be considered as "a first approximation of an ordered structure of lower symmetry" (*12*).

Here we have refined the structure of a commercially available sample of zeolite 5A, with an exchangeable cation composition of Ca_5Na_2. Three previous studies have been made of dehydrated zeolite A samples containing calcium—Ca_4Na_4–A (*13*) Ca_6–A (*14*), and $Ca_{5.2}Na_{0.4}$–A (*11*). However, both earlier refinements (*13, 14*) were only made in space group $Pm\bar{3}m$. Both of these structural investigations produced features which were somewhat unusual. In the Ca_4Na_4–A case Na^+ ions located near the six rings (Fig. 1) were inside the β cage (*13*), whereas similar ions in zeolite 4A have been found to be outside the β cages (*4, 5*) i.e. inside the large cavities of α cages. In the Ca_6–A structure (*14*) some Ca^{2+} ions were found in an 8-ring site and were considered to be "near zero coordinate." Recently Pluth and Smith (*11*) have determined the structure of $Ca_{5.2}N_{0.4}$–A in

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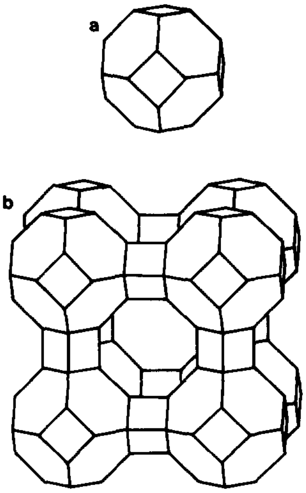

FIG. 1. A schematic representation of a zeolite A cuboctahedron (β cage) (a) showing the location of the 6 rings. In zeolite A these cuboctahedra are linked via the double 4 rings, thus generating the 8-rings and the larger α cages (b).

space group $Fm\bar{3}c$. They found only two Ca^{2+} sites located either side of the 6 ring. No separate Na^+ site was found because of the small amount of sodium present and its similar radius to Ca^{2+}. No zero-coordinate Ca^{2+} was found in the 8 ring and it was concluded that the electron density found in the 8 ring of Ca_6–A (*14*) was due to "scavenged K^+ ions."

It was considered fruitful to reinvestigate this structure using space group $Fm\bar{3}c$ with neutron data to confirm the absence of zero-coordinate exchangeable cations and to confirm the suitability of space group $Fm\bar{3}c$, for a sample containing both Na^+ and Ca^{2+} ions.

Experimental

The zeolite sample used in this structure determination was a commercially available Ca–5A manufactured by Union Carbide Corporation and supplied by BDH.

Chemical analyses were performed in these laboratories for calcium by EDTA titration using methyl thymol blue complexone indicator (*16*) and for sodium by flame photometry. Further analyses were carried out by English Clays Lovering Pochin and Company for calcium, sodium, silicon, and aluminium. The Si/Al ratio was 1.018 (±0.02); therefore the framework was stoichiometric within the analysis limit (*17*). The composition was determined as $Ca_{40}Na_{16}Si_{96}Al_{96}O_{384} \cdot 33H_2O$.

The powder diffraction data were collected on the high-resolution powder diffractometer D1A at the Institut Laue-Langevin, Grenoble (*18*). Approximately 5 g of the zeolite powder was loaded into a 16-mm-diameter vanadium sample can and dehydrated in a D1A vacuum furnace at 325°C and 2×10^{-6} Torr for 15 hr, after which the sample was allowed to cool to room temperature (300 K) before data collection commenced. During the cooling and data collection periods the sample was maintained under vacuum to prevent rehydration. Data ranging from 6.04 to 158.04°(2θ) were collected in 20 hr at a wavelength of 1.909 Å (3040 data points). The background was estimated by linear interpolation from regions where no Bragg peaks occurred. Structure refinement was carried out using the Rietveld technique of profile refinement (*19, 20*) with programmes of Hewat (*21, 22*). The scattering lengths used were obtained from the *International Tables for X-ray Crystallography* (*23*). Fourier maps (e.g., ΔF maps) were obtained using XRAY 72 (*24*). In the Rietveld technique, overlapping reflections are divided up according to the ratio of the calculated structure factors. For this reason all but the final Fourier syntheses were carried out using low angle data (i.e., the first 60°(2θ)) where no peak overlap occurs. The structure factors are then true F_o's.

Structure Refinement

Full structure refinements were carried out in the two space groups $Pm\bar{3}m$ and

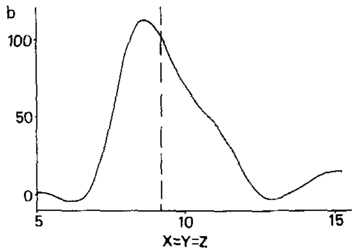

FIG. 2. A one-dimensional F_o trace along [111]. The abscissa is in hundredths of a unit cell edge.

$Fm\bar{3}c$. An attempt was also made to refine the structure in the lower symmetry space group $F432$, which had been suggested by Thöni (*25*) as a suitable space group for hydrated zeolite 5A, to model the loss of symmetry he found.

The initial refinement was made in $Pm\bar{3}m$ using the starting parameters for the framework atoms and exchangeable cations given by Seff and Shoemaker (*13*) with the population parameters of Ca(1) and Na(1) adjusted for the stoichiometry of our sample. Isotropic refinement of this model converged at $R_{pw}^{1} = 17.4\%$. However, it was found that the temperature factor for Na(1), which was located at the 6-ring site with $x = y = z = 0.17$ (i.e., just inside the β cage) became negative, whilst the temperature factor for Ca(1), which was also in a 6-ring site, but just inside the α cage (at $x = y = z = 0.20$) was very high. This suggested that too much scattering power had been placed in the site just inside the α cage and too little in the site just inside the β cage. An F_o Fourier map calculated at this stage showed that the maximum in the scattering density along [111] (Fig. 2) occurs on the β-cage side of the 6-ring plane. Since the cation composition of the sample is Ca_5Na_2–A, and since the scattering length for Ca is greater than that for Na, it was concluded that the designation of the two sites should be reversed i.e., five Ca ions were placed at Ca(1) just inside the β cage and two Na ions were placed at Na(1) just inside the α cage. Full anisotropic refinement using this model converged at $R_{pw} = 14.25\%$ with cell constant $a = 12.3252(4)$ Å.

The starting coordinates for the $Fm\bar{3}c$ refinement were taken from those of Adams *et al.* (*4*) for the framework coordinates, while the cation parameters were derived from the $Pm\bar{3}m$ refinement. Full isotropic refinement in this model converged at $R_{pw} = 16.54\%$. However, it was found that the coordinate shifts for O(2) were oscillatory; the symmetry of this site was constrained to 0 y y, after which the coordinate shifts became stable. This symmetry constraint was lifted prior to the final cycles of refinement and final convergence with anisotropic temperature factors occurred at $R_{pw} = 13.6\%$ ($a = 24.6497(8)$ Å); ($R_p^1 = 15.9\%$ compared with 6.7% expected on the basis of statistics).

A Fourier map obtained at this stage showed a small peak at ~0.19, 0.22, 0.0 in the plane of the 8 ring. Comparison of the height of this peak to that of Si(1) indicated that it was equivalent to approximately 12 Ca^{2+} ions per unit cell, i.e., 0.5 Ca^{2+} ions per 8 ring. However, attempts to refine the structure with Ca^{2+} ions in this site (Ca(2)) led to a final R_{pw} of 15.1%, i.e., 1.5% higher than previously with three more parameters being refined. It was therefore concluded that the Fourier peak was spurious.

At this stage because of the relatively high values of R_{pw} (compared with 10.3 and 7.9% for similar refinements of 3A (*6*) and 4A (*4*), respectively) an attempt was made to refine the structure in the lower symmetry space group $F432$. This space group had previously been suggested by Thöni (*25*) to model the lower symmetry he found in hydrated Ca–5A arising from the high degree of ordering of the Ca^{2+} positions. The coor-

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[1] $R_p = 100\Sigma|y_{obs} - (1/c)y_{calc}|/\Sigma|y_{obs}|$. $R_{pw} = 100[\Sigma w(y_{obs} - (1/c)y_{calc})^2/\Sigma w(y_{obs})^2]^{1/2}$ where w is the weight at each 2θ step and y_{obs} and y_{calc} are the observed and calculated intensities at that point. c is the scale factor.

dinates from the $Fm\bar{3}c$ refinement were transformed to $F432$ generating 10 atom positions. Isotropic refinement converged at $R_{pw} = 16.24\%$ with 39 parameters refining, compared with 27 parameters at the same stage in the $Fm\bar{3}c$ refinement. Attempts to refine anisotropic temperature factors for the framework sites caused the refinement to diverge. It was concluded that $F432$ did not successfully model the symmetry loss and the refinement was abandoned.

The final parameters for the refinements in $Fm\bar{3}c$ and $Pm\bar{3}m$ are given in Table I. Table II gives the bond lengths and angles from the $Fm\bar{3}c$ refinement.

A Hamilton statistical test (*26*) was carried out to test the significance of the values of R_{pw} obtained in the $Pm\bar{3}m$ refinement (14.25%) and $Fm\bar{3}c$ refinement (13.6%) using the hypothesis that $Pm\bar{3}m$ was the correct space group. The number of independent observations was 3040 (i.e., the number of data points collected, and the dimension of the problem [13] was the number of parameters in the $Fm\bar{3}c$ refinement [46] minus the number in the $Pm\bar{3}m$ refinement [33]. The test showed that the hypothesis could be rejected at the 95% significance level.

Figure 3 shows the observed and calculated diffraction traces for the $Fm\bar{3}c$ model. It can be seen that there are some differences between observed and calculated intensity at low angles. However, there is no evidence in the diffraction pattern for any impurity, and moreover, it is not possible for these differences to arise because the sample is a mixture of Na zeolite A and Ca zeolite A: the cell parameters for these materials are different and this would be easily detected. On the final difference ($F_o - F_c$) Fourier map the only significant feature was a peak at the origin. This is reminiscent of the Al atom found recently by Pluth and Smith (*11*) in their study of a dehydrated Ca-zeolite A. In their study this Al is coordinated to four oxygen atoms at ($x = y = z$

TABLE I

FINAL PARAMETERS FOR THE REFINEMENTS OF Ca_5Na_2–A IN $Fm\bar{3}c$ AND $Pm\bar{3}m$

	Refinement in $Fm\bar{3}c$		Refinement in $Pm\bar{3}m$
	Si(1)	Al(1)	M(Si, Al)
Position	96(*i*)	96(*i*)	24(*k*)
Population	96	96	24
x	0.0	0.0	0.0
y	0.09245(40)	0.18853(50)	0.18275(26)
z	0.18516(76)	0.08958(56)	0.37262(29)
β_{11}	14(3)	7(3)	45(3)
β_{22}	0(2)	24(3)	9(2)
β_{33}	11(2)	8(2)	68(3)
β_{12}, β_{13}	0	0	0
β_{23}	0(1)	4(2)	0(3)
	Ca(1)		Ca(1)
Position	64(*g*)		8(*g*)
Population	40		5
x, y, z	0.08935(29)		0.17923(58)
$\beta_{11}, \beta_{22}, \beta_{33}$	19(1)		76(15)
$\beta_{12}, \beta_{13}, \beta_{23}$	7(1)		21(5)
	Na(1)		Na(1)
Position	64(*g*)		8(*g*)
Population	16		2
x, y, z	0.10937(63)		0.22064(139)
$\beta_{11}, \beta_{22}, \beta_{23}$	24(5)		82(15)
$\beta_{12}, \beta_{13}, \beta_{23}$	−14(4)		−41(15)
	O(1)		O(1)
Position	96(*i*)		12(*h*)
Population	96		12
x	0.0		0.0
y	0.10926(14)		0.21802(27)
z	0.24706(38)		0.5
β_{11}	15(1)		49(3)
β_{22}	14(1)		55(3)
β_{33}	8(1)		36(3)
β_{12}, β_{13}	0		0
β_{23}	4(2)		0
	O(2)		O(2)
Position	96(*i*)		12(*i*)
Population	96		12
x	0.0		0.0
y	0.14027(35)		0.28245(16)
z	0.14212(33)		0.28245(16)
β_{11}	41(1)		162(6)
β_{22}	10(2)		30(2)
β_{33}	5(2)		30(2)
β_{12}, β_{13}	0		0
β_{23}	6(1)		24(2)
	O(3)		O(3)
Position	192(*j*)		24(*m*)
Population	192		24
x	0.05424(20)		0.11199(16)
y	0.05801(22)		0.11199(16)
z	0.16930(11)		0.33906(22)
β_{11}	9(1)		49(1)
β_{22}	15(1)		49(1)
β_{33}	16(1)		61(2)
β_{12}	6(1)		17(2)
β_{13}	2(1)		−3(1)
β_{23}	−2(1)		−3(1)

Note. Anisotropic displacement factor given as $10^4 \exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR ZEOLITE Ca_5Na_2–A IN $Fm\bar{3}c$

Si(1)–O(1)	1.581(15)	O(1)–Si(1)–O(2)	116.8(7)
Si(1)–O(2)	1.586(14)	O(1)–Si(1)–O(3)	111.5(5)
Si(1)–O(3), O(3^{III})	1.631(8)	O(2)–Si(1)–O(3)	103.1(5)
Al(1)–O(1^{VI})	1.660(20)	O(3)–Si(1)–O(3^{III})	110.1(6)
Al(1)–O(2)	1.758(18)	O(1^{VI})–Al(1)–O(2)	115.5(8)
Al(1)–O(3^{II}), O(3^{IV})	1.740(10)	O(1^{VI})–Al(1)–O(3^{II})	114.0(7)
Ca(1)–O(3), O(3^{I}), O(3^{II})	2.287(8)	O(2)–Al(1)–O(3^{II})	100.6(7)
Ca(1)–O(2), O(2^{I}), O(2^{II})	2.849(9)	O(3^{II})–Al(1)–O(3^{IV})	110.5(8)
Na(1)–O(3), O(3^{I}), O(3^{II})	2.373(16)	Si(1)–O(1)–Al(1^{V})	147.8(6)
Na(1)–O(2), O(2^{I}), O(3^{II})	2.916(16)	Si(1)–O(2)–Al(1)	174.5(9)
		Si(1)–O(3)–Al(1^{I})	140.6(7)

Note. Symmetry code for table: I: z, x, y, II: y, z, x, III: $-x, y, z$, IV: $-y, z, x$, V: $-x, z, -y + \frac{1}{2}$, VI: $x, -z + \frac{1}{2}, y$.

= 0.0411). Since we could not find any evidence of these atoms, or any other peaks with sensible coordinations to this origin position, we have not included it in the refinement.

Discussion

Exchangeable Cation Positions

In the previous determinations of Ca-containing samples of zeolite A (*11, 13, 14*) most if not all of the exchangeable cations were located on the threefold axis at different distances from the 6 ring. We have also found an elongated ellipsoid (here of nuclear scattering density) along the [111] direction. However, for our sample the maximum of this ellipsoid is located just inside, rather than outside the β cage (Fig. 2). We have interpreted this result as implying that the Ca^{2+} ions are located just inside the β cage whereas the Na^+ ions are just outside. Given that the number of Ca^{2+} and Na^+ ions per unit cell and the scattering length

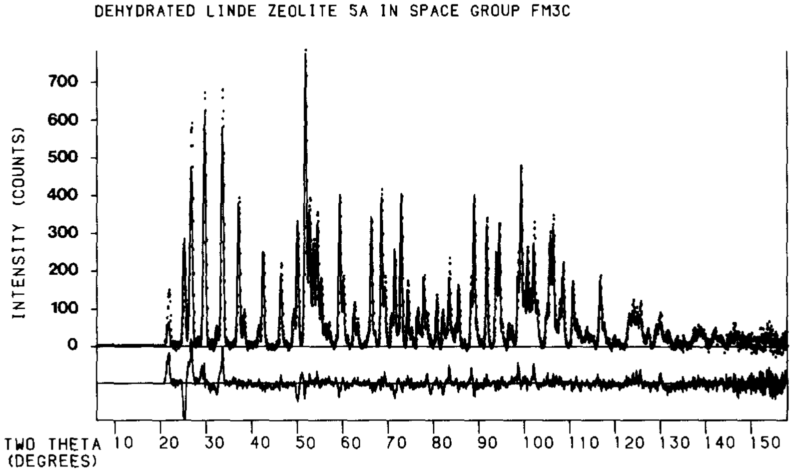

FIG. 3. Observed (. . .) and calculated (—) neutron diffraction profiles, together with difference plot, for dehydrated zeolite 5A in space group $Fm\bar{3}c$.

for each atom is known, and that all the cations reside in the 6 ring on the threefold axis, it is a straightforward calculation to find the Ca/Na distribution that agrees with the observed scattering density. The solution of this problem yielded 40 Ca^{2+} ions on the β-cage site and 16 Na^+ ions on the α-cage site. A difference Fourier map showed no residual scattering density and therefore the occupancy of these sites was fixed to the above values. However, it should be noted that these two cation positions are about equidistant, 2.287 (8) and 2.373 (16) Å, from the 6 ring (in agreement with the similar ionic radii for Na^+ and Ca^{2+}) on either side of it and it is possible that the different interpretation of these sites by ourselves and Seff and Shoemaker (*13*) arises because there is statistical occupancy by both kinds of atom in both positions. We prefer the former description since the Na^+ ion positions are then consistent with those found in similar studies of zeolite 3A (*6*) and 4A (*4*).

In accordance with the previous study of Ca_4Na_4–A (*13*) we have concluded that all exchangeable cations are located in the 6-ring sites; there are no Ca^{2+} ions in the 8 ring, whereas Firor and Seff (*14*) found one-sixth of the Ca^{2+} ions in Ca_6–A were in 8-ring sites and were considered to be "near zero coordinate." If this is the case it would imply that the molecular sieving properties of 5A were critically dependent upon the complete removal of all Na^+ ions. Moreover in recent redeterminations of the Sr_6–A and Ca_6–A structures Pluth and Smith (*9, 11*) have shown that all the cations are in 6-ring sites. This must cast some doubts on the previous structure determination of Ca_6–A (*14*).

Framework Distortions

Comparison has been made between the 6-ring shapes and dimensions for zeolites 3A (*6*), 4A (*4*), and 5A, and the results are given in Table III. Table III(a) gives the bond angles for the framework atoms in the 6 rings and Table III(b) gives the calculated distances from the centroid of the 6 ring (denoted CEN in the table) to the O(2) and O(3) framework oxygen sites. Close examination of these tables has shown that the 6 rings in zeolite 5A are severely distorted by the presence of the Ca^{2+} ions. Comparison of the Si(1)–O(3)–Al(1) angle for 3A, 4A, and 5A shown in Table III(a) and the CEN–O(3) distance in Table III(b) indicates that with a change in cation from large monovalent (K^+ in 3A) to small divalent Ca^{2+} in 5A) the O(3) atom is pulled in towards the 6-ring centroid. This distortion involves the Si(1) and Al(1) tetrahedra rotating in opposite directions. The predicted effect of this on the

TABLE III

COMPARISON OF THE DISTORTION IN THE 6 RINGS OF LINDE ZEOLITES 3A, 4A, AND 5A

(a) Bond angles

	Si(1)–O(3)–Al(1)	Si(1)–O(2)–Al(1)	O(2)–Si(1)–O(3)	O(3)–Al(1)–O(2)
3A (*6*)	146.1 (5)	170.1 (6)	107.1 (4)	105.0 (4)
4A (*24*)	144.6 (3)	164.4 (4)	107.3 (2)	105.9 (3)
5A	140.6 (7)	174.5 (9)	103.1 (5)	100.6 (7)

(b) Bond lengths from the centroid of the 6 ring to the oxygen atoms

	CEN–O(3)	CEN–O(2)
3A (*6*)	2.3538 (72)	2.8921 (72)
4A (*24*)	2.3152 (34)	2.9200 (42)
5A	2.2801 (72)	2.8431 (101)

O(2) atom site is that, as the Si(1) and Al(1) tetrahedra rotate, O(2) moves further away from the 6-ring centroid. Examination of Table III(b) shows that this trend is indeed followed for 3A and 4A, but in the case of 5A the CEN–O(2) distance is unexpectedly short. Inspection of the Si(1)–O(2)–A(1), O(2)–Si(1)–O(3), and O(3)–Al(1)–O(2) bond angles shows firstly that Si(1)–O(2)–Al(1) is more linear than would have been expected, and secondly, the O(2)–Si(1)–O(3) and O(3)–Al(1)–O(2) angles are more acute than expected, confirming that O(2) has in fact moved *towards* the 6-ring centroid. The distortion of the 6-rings is therefore much more severe in 5A than in 3A or 4A. The O(2) site is most affected by this distortion and this probably accounts for the instability of the O(2) coordinates during refinement and the unexpectedly large temperature factor for O(2) (Table I).

Disorder in Zeolite 5A

The final value of R_{pw} for zeolite 5A is higher than the values obtained for previous refinements of zeolites 3A (*6*) and 4A (*4*) (R_{pw} = 13.6% for 5A, 10.2% for 3A, and 10.3 and 7.9% for samples of 4A having Si/Al = 1.09 and 1.03, respectively (*4, 27*). One possible explanation of this fact is that the structure of this sample of zeolite 5A had been damaged during the ion exchange process. However, this loss of crystallinity would be reflected in the diffraction trace as lower overall peak intensities coupled with peak broadening. Comparison with previous refinements showed that the overall peak intensities and the full width at half height of the peaks were similar for 3A (*6*), 4A (*6*) and 5A. It is considered instead that the poorer refinement is a consequence of effects produced by replacement of at least some of the monovalent ions by divalent ions in these structures.

There are two types of disorder. First, the Ca^{2+} and Na^+ ions are disordered over the 6-ring sites so that a given 6 ring might contain Ca^{2+} or Na^+ ions or indeed be completely empty. Second, the 6 rings in zeolite 5A are severely distorted whenever they are coordinated to a Ca^{2+} ion, i.e., there is positional disorder of the 6-ring oxygen atoms which depends upon the nature of the exchangeable cation. This results in high thermal parameters at least for O(2).

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