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On the Structures of X- and Y-Type Zeolites. Structural Changes Within the Cavities of Na-X During Dehydration

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Abstract. Samples of partially dehydrated and dehydrated Na-X were examined structurally by X-ray diffraction methods, revealing the progressive structural changes which occur as water is removed. In general, the total number of Na atoms in the small pore region remains unchanged by dehydration (*ca.* 18 per unit cell), as does the total number (non-mobile) in the 12-ring and site III regions (*ca.* 39). The site II population, however, is more than doubled by dehydration, from about 12 to about 25 Na, accounting for most of the loss from the mobile phase. The 12-ring sites, which in hydrated samples appear to comprise pairs of centrosymmetrically related $[Na(H_2O)_2]^+$ units, rearrange during dehydration, with site III becoming an important location of Na atoms. At intermediate levels of dehydration, the remaining localized water molecules in the 12-ring region are found in a variety of associations with Na atoms, including perhaps as $[Na(H_2O)_5]^+$ units whose Na atom occupies site III. In a sample containing H_3O^+ ions as well as Na^+ as counter ions, site II was found to have a very low occupancy.

Key words: Zeolite X, crystal structure, faujasite, dehydration.

1. Introduction

In an earlier paper [1], preliminary results were presented from X-ray powder diffraction studies of a series of samples of Na-X with different water contents. It was demonstrated that despite the disorder of supercage sites, the observed patterns of structural occupancies could be explained in terms of particular types of Na—H_2O networks linked to the framework atoms of the 12-rings. In a second paper [2], the interpretation of this nonframework structural disorder and variability was taken further, with descriptions of results for the structures of samples of well-hydrated Na-X (220–265 water molecules per unit cell). Simple overcrowding prevents full occupancy of 12-ring sites, and the observed occupancies were interpreted in terms of just two $[Na(H_2O)_2]^+$ units per 12-ring, centrosymmetrically related but having a tendency to be linked to different types of framework atoms in different 12-rings. It was also demonstrated [2] that the same general structural model for supercage disorder could be applied to the single crystal data of Olson [3] and Smolin *et al.* [4].

Comparison [2] of the powder diffraction results for samples A, B and C (265 H_2O per cell) with the results of the single-crystal studies (220–240 H_2O per cell) begins to reveal the effects of dehydration on the arrangement of the nonframework sites. The present paper extends this work to less-hydrated samples G (*ca.* 139 H_2O), E (*ca.* 100 H_2O), F (*ca.* 26 H_2O) and D (*ca.* 0 H_2O), revealing the progressive structural changes which occur on further dehydration.

Samples D, E, F were mentioned briefly in [2] without details of their nonframework sites. Preliminary results were presented in MSc or PhD reports as follows: D [5], E [6], F and G [7].

2. Experimental

Samples D, E, F were individually prepared by different workers [5–7] from Linde 13-X zeolite. The samples were treated with NaCl solution before dehydration to maximise sodium

Table I. Comparison of occupancies[a] of nonframework sites

Atom	Sites[b]	Wyckoff position	Hydrated Na-X[2]				Original sample[c]		Dehydrated Na-X			
			A	B	C	Mean	G		E	F	D	Mean (Na)
Small-pore region:												
Na	I	16(c)	10	6	3		4(1)		4(2)	—	3(3)	
Na	I′, U	32(e)	15	5	12		15(3)		16(7)	10(1)	21(4)	
H_2O	II′, I′, U	32(e)	18	18	16		6(3)		—	—	—	
H_2O	U′	96(g), 48(f)	33	32	35		35(4)		16(8)	8(1)	—	
Sub totals:												
Na			25	11	15	17	19		20	10	24	18
H_2O			51	50	51	51	41		16	8	—	
Site II region:												
Na	II	32(e)	11	15	10	12	4(2)		24(4)	31(1)	20(3)	25
H_2O	IIA[d], IIB	32(e), 96(g)	23	—	24	16	4(2)		9(4)	6(1)	—	
Sub totals (small pore and site II regions):												
Na						29	23		44	41	44	43
H_2O						67	45		25	14	—	
12-ring region:												
Na	IIIA	96(h)	23	—	—		21(3)		22(6)	10(1)	—	
H_2O	IIIA′	96(g)	40	—	—		—		—	—	—	
Na	IIIB	96(g)	20	39	31		24(6)		—	—	24(8)	
H_2O	IIIB′	192(i)	36	52	71		42(8)		37(14)	15[e](2)	—	
Sub totals (12-ring region):												
Na			43	39	31	38	45		22	25	24	24
H_2O			76	52	71	66	42		37	—	—	
Site III region:							(i)	(ii)				
Na	III	48(f)					—	14(2)	13(6)	13(1)	23(3)	16
H_3O^+	III	48(f)					14(2)	—	—	—	—	
H_2O	III*	48(f)					12(2)	12(2)	14(6)	—	—	
Sub totals (Na in 12-ring and site III regions):						38	45	59	35	38	47	40
Totals.												
(a) see above		Na				67	68	82	79	79	91	
		H_2O				133	113	99	76	14	—	
(b) mobile phase(est.)		Na				20	7	$7H^+$	4	2	—	
		H_2O				120	42	42?	24	12	—	
(a) + (b)		Na				87	75	82	83	81	91	85
		H_2O				253	155	141	100	26	—	
Analysis		Na				86	79(+7H^+)		86	85	86	86
		H_2O				265	139		?	?	?	

[a] Number of occupied sites per unit cell; e.s.d. in parentheses. For further details of samples A, B, C see [2].

[b] Where an atom occurs in more than one site, the sites are listed in order of importance.

[c] See text for discussion of the two alternative interpretations. [d] Site IIA is sometimes designated II*. [e] Na in IIIB′.

content [2]. A small quantity of each sample was placed in a powder-diffraction capillary and dehydrated by heating slowly to 350–400°C under a vacuum of 10^{-5} torr, subsequently maintaining these conditions for several hours. Varying the severity of the conditions generated samples with varying water contents. The tubes were then sealed and stored for several days to ensure equilibrium conditions. The powder diffraction pattern of each sample was recorded photographically using CuKα radiation.

Sample G was taken straight from the original batch of untreated Linde 13-X which had equilibrated in the arbitrary conditions of humidity and temperature of the laboratory. Chemical analysis [2] prior to dehydration revealed that each of the four samples possessed 85–86 cations per unit cell, although untreated sample G was deficient in Na by 7 atoms per cell (see Table I). The water content of sample G, determined by weight loss at 900°C, was 139 H_2O per cell. The water contents of the dehydrated samples were revealed by the X-ray structural analyses. The structures were analysed in the space group *Fd*3*m*. The unit cell constants a_0/Å for each sample were found to be: D, 25.02(2); E, 25.01(3); F, 25.03(1); G, 24.85(1).

Table II. Coordinates[a] of framework and supercage sites

Site	Wyckoff positions	Coord.	Samples				
			A	G	E	F	D
T	192(i); x, y, z	x	0.2136(2)	0.2104(3)	0.2153(11)	0.2144(3)	0.2131(7)
		y	0.1280(3)	0.1243(5)	0.1338(10)	0.1276(4)	0.1242(9)
		z	0.3007(2)	0.3029(4)	0.3052(8)	0.3035(3)	0.3033(6)
01	96(h); $x, \frac{1}{4}, \frac{1}{4}+x$	x	0.1049(3)	0.1081(10)	0.0982(8)	0.1126(6)	0.1033(15)
02	96(g); x, x, z	x	0.0026(3)	0.0002(5)	0.0030(10)	−0.0019(4)	−0.0001(12)
		z	0.1335(4)	0.1308(10)	0.1354(18)	0.1314(5)	0.1431(19)
03	96(g); x, x, z	x	0.0691(3)	0.0681(7)	0.0713(18)	0.0726(6)	0.0731(12)
		z	−0.0346(5)	−0.0395(11)	−0.0510(33)	−0.0252(9)	−0.0366(17)
04	96(g); x, x, z	x	0.0684(5)	0.0731(11)	0.0596(15)	0.0691(5)	0.0614(19)
		z	0.3357(6)	0.3345(13)	0.3330(17)	0.3256(5)	0.3323(23)
IIIA	96(h); $x, \frac{1}{4}, \frac{1}{4}+x$	x	0.176(1)	0.176(2)	0.156(5)	0.172(2)	–
IIIA′	96(g); x, x, z	x	0.162(f)	–	–	–	–
		z	0.416(1)	–	–	–	–
IIIB	96(g); x, x, z	x	0.162(f)	0.197(4)	–	–	0.210[b]
		z	0.416(1)	0.414(4)	–	–	0.430[b]
IIIB′	192(i); x, y, z	x	0.209(1)	0.178(4)	0.199(9)	0.176(3)	–
		y	0.379(2)	0.352(5)	0.387(10)	0.390(3)	–
		z	0.474(2)	0.449(3)	0.477(12)	0.450(3)	–
III	48(f); $\frac{1}{8}, \frac{1}{8}, z$	z	–	0.437(5)	0.402(12)	0.39(2)	0.346(5)
III*	48(f); $\frac{1}{8}, \frac{1}{8}, z$	z	–	0.525(6)	0.573(12)	–	–
Residual[c] (%)			2	2.3	4.6	2.2	12

[a] Fractional coordinates; e.s.d. in parentheses refer to last significant figure quoted. Coordinates for the small pore and site II regions are available from the authors. [b] Mean coordinates of two adjacent sites.

[c] $100\Sigma|\Delta F|/\Sigma|F_o|$, where $\Delta F = F_o - F_c$ and F_o and F_c are observed and calculated structure factors.

X-ray intensities were digitized microdensitometrically and processed as described briefly in the following (full details are given in [2] which also gives an objective assessment of the accuracy of the method, including a comparison with single-crystal results for similar samples). The intensity data for the nonunique reflections were resolved into component *hkl* contributions by treating the framework sites as conventional heavy atoms.★ Difference Fourier methods then revealed the nonframework sites and least-squares refinement provided partial occupancy parameters (Table I) and atomic coordinates (Table II) for the interstitial Na and H_2O species. The resolution and refinement steps were repeated cyclically until the self-consistent structures given in the tables were obtained. Final residues (Table II) are in the range 2–5% except for sample D (12%). Selected interatomic distances are given in (Table III). Consideration was given to employing the Rietveld method of refinement [8] to the present problem. The procedure for applying the Rietveld method with X-ray powder data has been described by Thompson [9] but he points out that the Rietveld method is of little value as a direct means of structure solution; the complete crystal structure must be known

Table III Geometry[a] of nonframework sites

Sample	Sample A [2]	Original sample G	Dehydrated samples			
			E	F	D	Mean
Site I:						
Na(I)—O3	2.6	2.6	2.8	–	2.7	2.8
Site I′:						
Na(I′)—O3	2.5	2.4	2.6	2.0	2.3	2.3
Na(I′)—H_2O(II′)	2.6	3.2	–	–	–	–
Na(I′)—H_2O(U′)	2.1	2.4	2.9	3.2	–	3.1
H_2O(II′)—O2	2.9	2.6	–	–	–	–
H_2O(U′)—O3	3.0	3.4	3.9	3.3	–	3.6
Site U.						
Na(U)—H_2O(U′)	2.5	2.2	–	–	–	–
Site II:						
Na(II)—O2	2.9	2.5	2.3	2.5	2.4	2.4
Na(II)—H_2O(IIA)	1.4	3.1	2.4	2.2	–	2.3
Site IIIA:						
Na(IIIA)—O1	2.5	2.4	2.0	2.1	–	2.1
Na(IIIA)—H_2O(IIIA′)	2.2	(2.6)[b, c]	–	–	–	
H_2O(IIIA′)—O4	2.1	–	–	–	–	
H_2O(IIIA′)—O1	3.0	–	–	–	–	
Site IIIB:						
Na(IIIB)—O4	2.1	2.1	–	–	2.6[f]	
Na(IIIB)—H_2O(IIIB′)	2.1	2.7	–	–	–	
H_2O(IIIB′)—O1	2.7	2.4	2.6	(2.0)[e]	–	
H_2O(IIIB′)—O4	2.6	2.5	2.2	(3.1)[e]	–	
Site III:						
Na(III)—O4	–	3.1	2.9	2.6	2.3[g]	2.6
Na(III)—H_2O(IIIB′)	–	(1.9)[c]	2.8	–	–	
Na(III)—H_2O(III*)	–	2.2	4.3[d]	–	–	
12-ring diameter:						
O1...O1	10.2	10.0	10.7	9.7	10.4	
O4...O4	9.5	9.7	9.4	10.0	9.5	

[a] Distances in Å; e.s.d. *ca.* 0.1 Å; 1 Å = 10^{-10} m.
[b] Na(IIIA)—H_2O(IIIB′).
[c] If appropriate equivalent positions are occupied simultaneously.
[d] E.s.d. *ca.* 0.5 Å.
[e] Na in IIIB′.
[f] Mean for two adjacent IIIB sites.
[g] Na(III)—O3 = 2.4 Å.

★ There is an unfortunate typographical error in Equation (4) of [2]. Equation (4) should read

$$F_o^2(h_1k_1l_1) = I_o(N) \Big/ \left(g_1 + \sum_{2}^{n} g_i C_i^2\right)$$

at the start of the work. In cases where it is not completely known, as in the present work, Thompson recommends 'pattern stripping' and Fourier techniques. This is essentially the approach employed in the present work.

Lists of structure factors, intensity data, less important coordinates and interatomic distances, and other details, can be supplied by the authors.

3. Results and Discussion

In Table I, which compares the observed partial occupancies of the non-framework sites, the samples are presented in order to diminishing water content. In the small-pore region, including site I, the total number of Na atoms appears to be unchanged by dehydration (a mean of 17 Na per unit cell for hydrated samples, 19 for sample G, a mean of 18 for dehydrated samples). In the site II region the Na occupancy at least doubles on dehydration (means of 12 Na for hydrated samples, 25 for dehydrated samples). We noticed this doubling of site II occupancy when comparing samples A, B, C with single-crystal samples of hydrated Na-X [2]. The increasing occupancy of site II appears to begin early in the dehydration process, because the single crystal samples have lost only 25–45 water molecules per unit cell compared with samples A, B, C. In the site II region, sample G does not exhibit the same behaviour as the other samples. This may be because it is deficient in Na by 7 atoms per cell according to the analytical results, the balance of 86 cations being hydrated protons. This sample is discussed further below.

The aspects of primary interest in the present work are the changes which occur in the 12-ring region upon dehydration. These can be assessed from the data in Tables I–III and

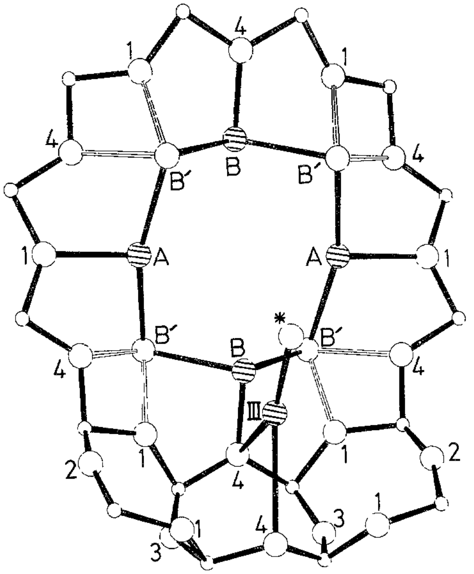

Fig. 1. Summary diagram of 12-ring sites in sample G (prepared by computer using ORTEP [16]). Not all sites shown are necessarily occupied simultaneously (see text). Small circles: Si, Al; large open circles: oxygen atoms labelled to identify site type; large hatched circles: Na. Labels A, B, B',* denote sites IIIA, IIIB, IIIB', III*. The centre of the 12-ring is a centre of symmetry. Interatomic distances are given in Table III.

Figures 1 and 2. Once again, as in [2], we stress how nominally similar samples show considerable structural individuality. As suggested in [2], however, a definite general pattern of behaviour does emerge: dehydration does appear to populate site II, for example. There is also evidence of greater utilisation of sites near the 4-rings of the sodalite cages, i.e. in the site III region. In samples D, E, F the material in site III must be identified as Na if the total count of Na in the samples is to agree with the analytical results. Table I reveals that the build-up of Na on site III is accompanied by a loss of Na from sites in the 12-ring region, although the total occupancy of the 12-ring and site III sites by Na appears to remain constant (means of 38 Na for the hydrated samples A, B, C and 40 for the dehydrated samples D, E, F; this is not the case for sample G). Three samples of Na-X were studied by Hseu [10]. We shall refer to them with the labels used by Mortier [11]. Hseu's most hydrated single-crystal (sample e) was observed to have a small-pore content of 20 Na : 44 H_2O much as in sample G of the present work (19 Na : 41 H_2O) and in the single-crystal samples of Olson [3] and Smolin *et al.* [4] (average, 17 Na : 43 H_2O). The remaining sites in Hseu's sample e more closely resemble those of our sample E (Table I) than those of the samples mentioned above, suggesting considerable dehydration, although he did not report occupancy of site III; in all, Hseu located 72 H_2O. Site III is also unobserved or overlooked in his other samples: g ('hydrated') and f ('dehydrated'). Hseu located a total of 25 H_2O throughout sample g, which resembles our sample E in the small-pore region and F elsewhere. To obtain a reasonable Na-count for his sample f, to match the analytical result of 81 Na per cell, Hseu assigned 36 Na to the small-pore region ($+2H_2O$). If we reapportion these occupancies as 20 Na + 18 H_2O (giving approximately the Na-content observed in all other samples) and also suppose there are 16 Na in site III as in other dehydrated samples (Table I), the required Na-count is maintained. In general, Hseu's samples appear to be more dehydrated than was thought. The slightly Na-deficient sample of Aldridge and Pope [12] (called a by Mortier [11]) warrants similar comments. The latter sample together with Hseu's three samples all show considerable site II occupancy by Na, again suggesting dehydration.

Figure 1 is a summary of the occupied sites in the 12-ring and site III regions of sample G; it shows that sample G retains water in the 12-ring region. We stress that in any given 12-ring it is unlikely that all the sites shown in Figure 1 will be occupied simultaneously. Recalling

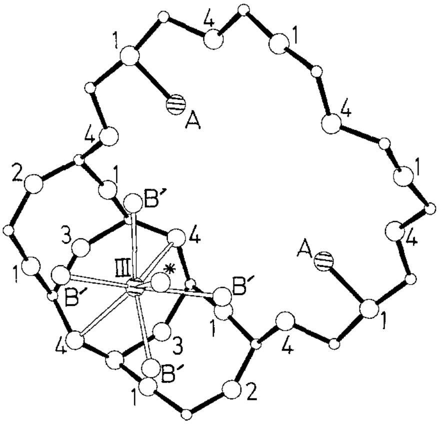

Fig. 2. Summary diagram of 12-ring sites in sample E, detailed as for Figure 1.

the results for sample A [2], we might expect each of the sixteen 12-rings per unit cell in sample G to be occupied by one centrosymmetrically placed pair of $[Na(H_2O)_2]^+$ units per 12-ring. More than the 32 Na atoms required for such a distribution is indeed found in sites IIIA and IIIB of sample G (Table I) but rather less than the required 64 H_2O are observed in site IIIB′. In sample G it is likely, therefore, that some 12-rings are deficient in H_2O and that the filling of the 12-rings is much less orderly than in hydrated samples like A. The atomic coordinates of sites IIIB and IIIB′ in sample G are rather different from those of sample A (Table II); the differences are such that the water molecules IIIB′ in sample G occupy positions were they can be coordinated to either of the two Na sites (Figure 1), providing scope for a variety of possible Na—H_2O arrangements in different 12-rings. The presence of H_3O^+ ions could permit further possibilities. Table I also shows alternative interpretations of the site III region which arise when we recall that sample G has an overall deficiency of 7 Na^+ ions. The second alternative (ii) of interpreting site III in sample G as Na is preferred, and supported by the existence (at almost equal occupancy) of site III* (= H_2O) at a distance of 2.2 Å from site III (Figure 1). The problems encountered in the interpretation of the observed sites in sample G suggest the need for a systematic study of NaH-X systems with a variety of Na/H ratios, in order to obtain a clearer picture of the role played by the H_3O^+ ions.

The role of site IIIB′ in sample E can only be in association with site III because site IIIB is absent and site IIIA is too far away (Figure 2). At this intermediate stage of dehydration, the site III region is revealed as a staging post for a fragment $[Na(H_2O)_5]^+$ of the mobile hydrated cation $[Na(H_2O)_6]^+$. The Na atom of this cation inevitably moves from the mobile phase to the framework walls as it is stripped of its hydration sphere. Within experimental error the observed occupancies match the required stoichiometry $Na(H_2O)_5$ of the fragment [13(6)Na : 51(15)H_2O]. In samples F and D, possessing yet fewer water molecules, all the sites observed in the 12-ring and site III regions must be attributed to Na to achieve an Na-count in agreement with the analytical results. Nevertheless, as noted above, the total number of Na atoms in this part of the structure remains fairly constant in all samples, except G. This leads to the general finding, for the samples fully loaded with Na, that dehydration brings about a loss of *ca.* 20 Na from the mobile phase and a gain of most of this number by site II.

At the bottom of Table I the atom counts based on the structural model described in this paper are shown to be in good agreement with the analytical results.

The present work provides data on the distribution of Na^+ ions amongst the available sites and its changes during dehydration, but the factors determining this distribution are less clear, although Dempsey's ionic model [13] makes a major contribution to their understanding. To investigate these factors further, we propose to develop a computer model, along the lines of that for sodalites, [14] which incorporates covalency as well as ionicity by employing the bond strength versus bond length equations of Brown and Shannon [15].

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