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On the Structures of X- and Y-type Zeolites. Structural Changes Within the Cavities of Na-Y During Dehydration and Contrasts with Na-X Systems

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Abstract. Samples of dehydrated and partially dehydrated Na-Y were examined by X-ray diffraction methods revealing the progressive structural changes which occur as water is removed and the different behaviour compared with Na-X. The differences between Na-Y and Na-X reflect the reduced Al content of Na-Y and the consequential lower average capability of each framework oxygen atom for balancing cation charges. In the small-pore region of Na-Y, the total number of Na atoms remains relatively constant during dehydration (*ca.* 15 per unit cell compared with *ca.* 18 in Na-X); unlike Na-X, Na-Y has no site I atoms. Significant dehydration of the small-pore region, and the change from low to high site II occupancy, do not occur until the total water content of the sample is less than that which pertains under atmospheric conditions. In the 12-ring region of Na-Y, $[Na(H_2O)_2]^+$ units are observed at an intermediate level of dehydration, possibly linked by water molecules astride the site III region to networks in adjacent 12-rings. There is no build-up, as in Na-X, of Na at site III, and site IIIB (= III′) is (at least partially) occupied by H_2O rather than Na. Further dehydration progressively removes H_2O but there is little rearrangement of Na atom positions, except the build-up in site II which accounts for much of the loss of Na from the mobile phase.

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

1. Introduction

In earlier papers [1–3] it was demonstrated that the partial occupancies observed for non-framework sites in hydrated [2] and partially dehydrated [3] Na-X can be interpreted in terms of networks of Na^+ ions and water molecules economically packed inside the sodalite cages and the regions of the supercages close to the framework atoms. Although individual samples show structural variability, even when analytically similar, certain general structural features were observed to recur. In the supercages of the hydrated samples [2], occupancies obtained from both powder diffraction and single-crystal X-ray studies suggested networks of $[Na(H_2O)_2]^+$ units in the 12-ring regions. In samples fully loaded with water, these units comprise the whole of the nonmobile supercage contents apart from about 12 Na^+ per unit cell in site II and associated water. In the single-crystal samples [4, 5] which possessed 25–45 fewer water molecules per unit cell, localised atoms in the region of site III were observed, and an Na^+ population of site II approaching full occupancy. In less-hydrated samples, [3] the mobile phase (probably consisting of $[Na(H_2O)_6]^+$ ions) is dispersed as water is lost, and Na^+ appears at site III with vestigial fragments of the hexaaquo ions. With further dehydration, water is gradually lost from all sites throughout the structure, with some rearrangement of Na^+ positions, but site III remains important. The present work investigates the structural changes which occur in Na-Y upon dehydration, thus extending the studies of Na-X samples to samples with about 30 fewer Na atoms per unit cell and enhanced potential as catalysts [6].

The earlier work on dehydrated Na-Y by Eulenberger *et al.* [7] established high site II occupancy, and this seemed to be the norm for all samples when Hesu's studies [8] suggested similar occupancies in hydrated as well as dehydrated samples. However, later work suggests otherwise. Probably the most recent X-ray study of hydrated Na-Y is that of Costenoble *et al.* [9] who incorporate in their calculations much of the material in the supercages and the sodalite cages by means of special scattering functions assuming the material to be randomly distributed in spheres simulating the zeolitic cavities. Amongst the localised sites they report is site II with an occupancy of 10 Na^+ per unit cell, much as in hydrated Na-X (see above). Soria, Cano *et al.* [10, 11] also report low site II occupancy in hydrated samples of Na-Y but emphasise the change to high occupancy upon dehydration. None of these studies of fully exchanged Na-Y samples led to a clear interpretation of localised non-framework sites and of the changes which occur on dehydration, except that of the behaviour of site II.

A preliminary report of the present work has appeared in Thesis form [12].

2. Experimental

The three samples Y2, Y3, and Y4 employed in this study originate from a batch supplied by the Davison Division of W. R. Grace Inc. (Baltimore, Maryland, U.S.A.). Sample Y3 was of intermediate water content and representative of the original batch of starting material after equilibration at laboratory temperature and humidity. To prepare samples Y2 and Y4, a quantity from the original batch was first treated with NaCl solution to maximise the Na content [2], then stored at room temperature in contact with water vapour in a desiccator containing saturated $Ca(NO_3)_2$ solution [12]. Some of the fully hydrated Na-Y so produced was sieved through a 200 mesh sieve to facilitate loading into powder-diffraction capillaries. A portion of the sieved material was allowed to dehydrate partially in air before loading into a capillary and sealing, producing sample Y2; a weighed portion of this partially dehydrated material was retained for analysis. A second portion of the sieved material, mounted in a capillary, was dehydrated [12] by heating slowly to about 400 °C under a vacuum of 10^{-5} torr, then maintaining these conditions for 48 h. Sealing the tube produced sample Y4.

Chemical analysis [2] of samples Y2 and Y3 revealed their water contents as 168 and 72 molecules per unit cell, respectively. Powder diffraction patterns were recorded photographically using $CuK\alpha$ radiation and intensities were digitised microdensitometrically. The crystal structures were analysed in the space group $Fd3m$, and the unit cell constants $a_0/Å$ for each sample were found to be: Y2, 24.61 (1); Y3, 24.63 (1); Y4, 24.78 (2). Full details of the method of structure determination are given in earlier papers [2, 3]. The partial occupancy parameters for the non-framework sites are presented in Table I; selected atomic coordinates and interatomic distances are given in Tables II and III. Lists of structure factors and intensity data, and fuller lists of coordinates, interatomic distances and other crystallographic details, can be supplied by the authors.

3. Results and Discussion

Table I lists the observed partial occupancies of the nonframework sites in samples Y2, Y3, Y4, comparing them where possible with the results for a sample, designated Y1, which is the fully hydrated Na-Y sample studied by Costenoble, Mortier and Uytterhoeven [9]. Thus samples Y1 through 4 are labelled and listed in order of diminishing water content. None of the samples are found to have scattering material in site I, in contrast to the behaviour of Na-X which almost invariably has significant occupancy of site I [2, 3]. All the Na-Y samples are also similar in their site I′ occupancies (mean, 15 Na^+ per cell) and the water contents of their

Table I. Comparison of occupancies[a] of nonframework sites in Na-Y

Atom	Sites[b]	Wyckoff position	Hydrated sample Y1 [9]	UMIST samples			Mean (Na) for samples indicated
				Y2	Y3[f]	Y4	
a_0/Å			24.70(1)	24.61(1)	24.63(1)	24.78(2)	
Small-pore region:							
Na	I	16(c)	0	0	0	0	0
Na	I′, U	32(e)	17(1)	14(2)	14(2)	13(3)	15(Y1–4)
H_2O	II′	32(e)	13(1)	22(2)	18(3)	–	
H_2O	U′	32(e)	–	12(2)	13(3)	–	
H_2O	liq[c]	–	24	–	–	–	
Sub totals:							
Na			17	14	14	13	15(Y1–4)
H_2O			37	34	31	–	
Site II region:							
Na	II	32(e)	10(2)	10(2)	11(3)	28(2)	10(Y1–3)
H_2O	IIA = II*		–	–	–	–	
Sub totals (small pore and site II regions):							
Na			27	24	25	41	25(Y1–3)
H_2O			37	34	31	–	
12-ring region:							
Na	IIIA	96(h)	–	13(2)	20(4)	–	17(Y2–3)
H_2O	IIIA′	96(g)	–	25(3)	15(6)	–	
Na, H_2O	IIIB	96(g)	–	19(4)[e]	15(7)[e]	13(4)	16(Y2–4)
H_2O	IIIB′	192(i)	–	44(6)	–	–	
Sub totals (12-ring region):							
Na			8[d]	23	28	13	
H_2O			90[d]	79	23	–	
Totals:							
(a) see above		Na	35	47	53	54	
		H_2O	127	113	54	–	
(b) mobile phase (est.)		Na	22[d]	9	3	–	
		H_2O	132[d]	54	18	–	
(a) + (b)		Na	57	56	56	54	56(Y1–4)
		H_2O	259	167	72	–	
Analysis		Na	57	56	56	56	56(Y1–4)
		H_2O	268	168	72	–	

[a] Number of occupied sites per unit cell; e.s.d. in parenthesis.

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

[c] 'Liquid' in small-pore 'sphere' (see [9]).

[d] 'Liquid' in supercage 'spheres'; [9] reports a total of 252 H_2O equivalents, which here are apportioned as marked with [d] (see text).

[e] Occupancies apportioned equally between Na and H_2O (see text).

[f] Original starting material.

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

Site	Wyckoff positions	Coord.	Samples		
			Y2	Y3	Y4
T	192(i); x, y, z	x	0.2140(3)	0.2128(5)	0.2138(4)
		y	0.1284(4)	0.1277(7)	0.1270(7)
		z	0.3033(2)	0.3026(4)	0.3023(4)
O1	96(h); $x, \frac{1}{4}, \frac{1}{4}+x$	x	0.1050(7)	0.1073(18)	0.1081(14)
O2	96(g); x, x, z	x	-0.0011(6)	-0.0043(11)	-0.0031(11)
		z	0.1435(10)	0.1397(19)	0.1373(17)
O3	96(g); x, x, z	x	0.0716(5)	0.0731(8)	0.0719(7)
		z	-0.0351(7)	-0.0348(12)	-0.0316(11)
O4	96(g); x, x, z	x	0.0703(5)	0.0720(10)	0.0742(9)
		z	0.3231(7)	0.3238(13)	0.3213(9)
IIIA	96(h); $x, \frac{1}{4}, \frac{1}{4}+x$	x	0.175(2)	0.186(3)	-
IIIA′	96(g); x, x, z	x	0.146(2)	0.147(7)	-
		z	0.421(3)	0.466(10)	-
IIIB	96(g); x, x, z	x	0.199(3)	0.192(7)	0.150(5)
		z	0.422(5)	0.426(12)	0.409(6)
IIIB′	192(i); x, y, z	x	0.244(2)	-	-
		y	0.382(3)	-	-
		z	0.453(3)	-	-
Residual[b] (%)			3.1	7.0	4.8

[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] $100\Sigma|\Delta F|/\Sigma|F_0|$ where $\Delta F = F_o - F_c$ and F_o and F_c are observed and calculated structure factors.

small-pore regions are consistent when the 24 H_2O associated with the 'liquid scattering function' used [9] to analyse sample Y1 are taken into account. The Na content of the small pore region in Na-X [2, 3] is a little higher (*ca.* 18 Na^+ per cell) and likewise hydrated Na-X samples have more water in the small pore region (41–51 H_2O per cell compared with 31–37 in Na-Y). These observations are presumably a consequence of the reduced Al content of Na-Y, the more siliceous material being the less hydrophilic as pointed out by Chen [13]. The associated lower average capability of each framework oxygen atom in Na-Y to balance cation charges is also likely to be a factor. The present study is in agreement with the earlier work reported in the introduction concerning the change in site II occupancy from low to high upon dehydration. We add, however, that this change and water loss from the small pore region occur at water contents less than that which pertains under ambient conditions (Table I).

Further into the supercage of sample Y1, all scattering material was represented by 'liquid scattering functions' [9]. The present work, however, sought localized material. Sample Y2 has four localized sites in the 12-ring or site II regions. One of the most plausible arrangements of these is shown in Figure 1, and is in keeping with the observed occupancies. Of the sixteen 12-rings per unit cell about half of them (within experimental error) can have the centrosymmetrically related pairs of $[Na(H_2O)_2]^+$ units shown (cf. Figure 2 of [2]). The remaining 12-rings (not shown) can have two species in site IIIB. The novel feature of sample Y2 is the pair of IIIB′ species close enough together astride site III to be hydrogen bonded together (2.5 Å: see Table III). Such pairs of IIIB′ species can also be close enough to a site IIIA′ atom (2.4 Å) and a site IIIB atom of an adjacent 12-ring (2.7 Å) to be linked as shown in Figure 1. Such an arrangement of bridging water molecules is comparable with that proposed

Table III. Geometry[a] of nonframework sites

Sample	Y1 [9]	Y2	Y3	Y4	Mean (for samples indicated)
Site I′:					
Na(I′)–O3	2.5	2.7	2.7	2.1	2.6 (Y1–3)
Na(I′)–H_2O(II′)	2.6	2.3	2.4	–	2.4 (Y1–3)
Na(I′)–H_2O(U′)	–	2.4[b]	2.5[b]	–	2.5 (Y2–3)
H_2O(II′)–O2	2.8	3.1	3.0	–	3.0 (Y1–3)
H_2O(U′)–O3	–	3.4	3.2	–	3.3 (Y2–3)
Site II:					
Na(II)–O2	2.8	2.5	2.6	2.5	2.6 (Y1–4)
Site IIIA:					
Na(IIIA)–O1	–	2.4	2.7	–	2.6 (Y2–3)
Na(IIIA)–H_2O(IIIA′)	–	2.7	2.8	–	2.8 (Y2–3)
H_2O(IIIA′)–O4	–	2.7	3.7	–	–
H_2O(IIIA′)–O1	–	3.2	3.8	–	–
H_2O(IIIA′)–IIIB	–	–	3.3	–	–
Site IIIB (= Na/H_2O):					
IIIB–O4	–	2.5	2.6	2.4	2.5 (Y2–4)
IIIB–H_2O(IIIB′)	–	2.7	–	–	–
H_2O(IIIB′)–O1	–	3.6	–	–	–
H_2O(IIIB′)–O4	–	3.5	–	–	–
H_2O(IIIB′)–H_2O(IIIA′)	–	2.4	–	–	–
H_2O(IIIB′)–H_2O(IIIB′)	–	2.5	–	–	–
12-ring diam:					
O1...O1		10.1	9.9	9.9	
O4...O4		10.0	10.0	10.3	

[a] Distances in Å; e.s.d. ≈0.1 Å; 1 Å = 10^{-10} m. [b] Mean of two.

by Shen, Zettlemoyer and Klier [14] for partially hydrated Na-Y samples, after IR studies. In sample Y3, the starting material, site IIIA is again occupied and assigned to Na^+, but site IIIA′ has neither the right occupancy nor the right coordinates (see Tables I and II) to form a normal $[Na(H_2O)_2]^+$ unit. A sensible arrangement taking account of the observed occupancies and incorporating site IIIB is shown in Figure 2. (For distances see Table III.) Once again it is a network astride site III. In fully dehydrated sample Y4, site IIIB must be assigned as Na^+ to achieve an Na-count in agreement with the analytical results; all the Na atoms in Y4 are localized. Partially hydrated samples Y2 and Y3 can be expected to possess supercages partly filled by a mobile phase probably composed of $[Na(H_2O)_6]^+$ ions, as was supposed for Na-X [2, 3]. Identifying site IIIB in Y2 and Y3 as Na^+ leaves insufficient Na for such a mobile phase. As is discussed below, it is better to consider site IIIB in samples Y2 and Y3 as available to both Na and H_2O. With water in site IIIB of sample Y3 (Figure 2) the bridging arrangement linking O1 and O4 is again similar to that suggested by the IR studies of Shen, Zettlemoyer and Klier [14].

The lower part of Table I includes an attempt to match the crystallographic and the analytical results for each sample. For sample Y1, the contents of the supercage (besides site II) were found to comprise 252 species [9], which we shall assume can be either Na or H_2O, because to a first approximation the scattering powers of Na^+ and H_2O are the same. The puzzle is: how do we apportion these 252 species between the four entries marked by footnote d in Table I? Fortunately there is a unique solution to this problem. If the four entries

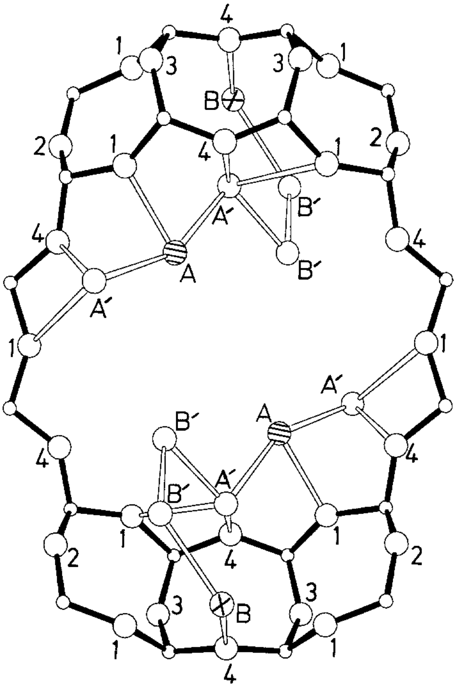

Fig. 1. Sample Y2. About half the 12-rings possess this arrangement; atoms B belong to the remaining 12 rings (see text). Diagram prepared by computer using ORTEP [15]. Small circles: Si, Al; large open circles: oxygen atoms labelled to identify site type; large hatched circles: Na; large crossed circles: Na, H_2O. Labels A, A′, B, B′ denote sites IIIA, IIIA′, IIIB, IIIB′. The centre of the 12-ring is a centre of symmetry. Interatomic distances are given in Table III.

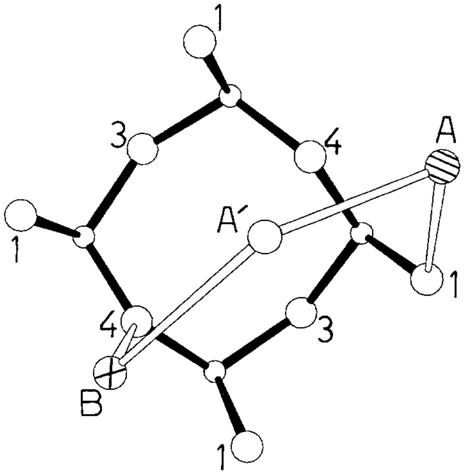

Fig. 2. Sample Y3. A possible arrangement of 12-ring sites near the 4-ring of a sodalite unit. Details as for Figure 1.

are, in order, A, B, C, D, then A + B + C + D = 252; we also have D = 6C, if the supercage species are $[Na(H_2O)_6]^+$ ions, and 27 + A + C = 57 if the total Na-count is to match the analytical result. Our model for the 12-ring region of hydrated Na-X [2] supposes space for about 96 species, thus $A + B \simeq 96$; the present work on sample Y2 supports this. There is a unique solution to these four equations relating A, B, C, and D: $96 + 7C \simeq 252$, so $C \simeq 156/7 = 22$, D = 132, A = 8, B = 90 as given in Table I. A somewhat similar approach may be used to apportion the occupancies of site IIIB in samples Y2 and Y3 between Na and H_2O, but the experimental error is such that equal apportionment between Na and H_2O is adequate; the lower entries in Table I are assigned on this basis. The final agreement with the analytical results is good for all samples.

On the above basis, Na-Y possesses fewer Na^+ ions in the 12-ring region than found in the 12-ring region of Na-X, again in keeping with the reduced Al content of Na-Y and the consequential lower average capability of each framework oxygen atom for balancing cation charges. The present work suggests that this effect persists into the inner regions of the structure (no site I in Na-Y, for example). As in Na-X [2, 3], the mobile phase appears to contain about 20 $[Na(H_2O)_6]^+$ ions in fully hydrated samples. These fragment on dehydration with inevitable migration of the Na^+ ions to the framework walls (especially site II), but whereas in Na-X [3], Na occupancy of site III becomes important, in Na-Y it does not and Na occupancy in the 12-ring region shows a greater variability.

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