Location of Supercage Sodium Ions and Water Molecules in Hydrated NaX Zeolite

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Summary The positions of supercage sodium ions and co-ordinated water molecules in a hydrated NaX zeolite are determined using *X*-ray powder diffraction.

Although the structures of NaX-type zeolites have been examined before by *X*-ray diffraction techniques using both powder[1] and single crystal methods[2,3], considerable uncertainty exists as to the location of the supercage sodium ions and water molecules. Indeed, insufficient sodium ions have been located to account for typical analytical unit cell contents $Na_{86}[Al_{86}Si_{106}O_{384}]264H_2O$. As part of a wider study of zeolite catalysts, we have developed a procedure, using the *X*-ray powder method for determining the cation and water sites. Generally, the single crystal method is considered to be superior where precise structural information is required, but it has a serious disadvantage in studies of zeolite catalysts because it is seldom that they can be obtained as single crystals, and furthermore, the variability of the composition of these ion exchange materials makes it uncertain whether the single crystals obtained have the same composition as the bulk material. Additionally, there is a need to examine catalysts after use in reaction vessels and they are not normally single crystals.

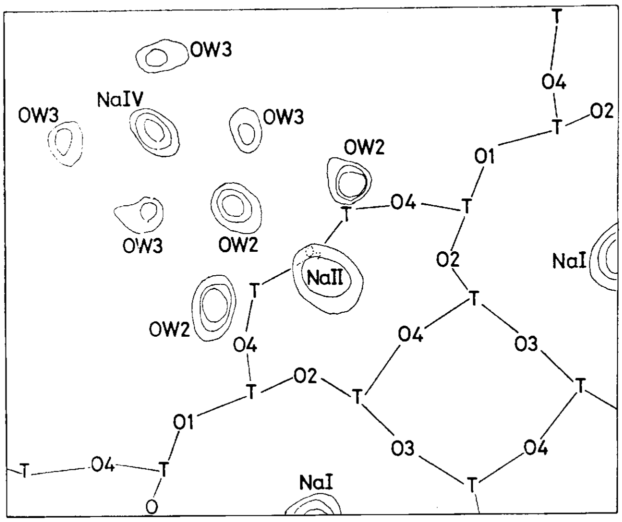

Figure 1. Environment of the site IV cation. Octahedral co-ordination to water is achieved by interaction with the four coplanar water molecules (shown) and with water molecules above and below the plane.

Our procedure utilises microdensitometrically collected photographic intensity data, which are prepared for input to the *X*-ray 72 program suite[4] by our own routine for unscrambling multi-indexed reflexions using a heavy-atom method based on the zeolite framework sites. The *X*-ray 72 suite is then used in the conventional way to determine the non-framework sites by Fourier methods, and to refine all structural parameters by least squares.

The Table summarises the cation and water sites found in our work and compares them with the results of previous work. The additional Na^+ sites we have found (designated sites IV and V) and their environments in the supercage are depicted in Figures 1 and 2. The octahedral co-ordination spheres of ligands around these sites clearly indicate the presence of $Na(H_2O)_6^+$ ions. The occupancies of the Na^+ sites IV and V and associated water molecules were refined individually and the results show, within experimental error, the correct proportions of Na^+ ions and H_2O molecules for the formulation $Na(H_2O)_6^+$. We find a total of 81 Na^+ ions per unit cell which is within experimental error of the 86 found by chemical analysis, whereas Olson,[2] for example, identified only 41. We have also found 151 out of the 265 water molecules in the unit cell. The Table shows that the 25 water molecules in the β cages (SII′) provide octahedral co-ordination for SI′ Na^+ ions and the 66 OW2, 16 OW3, and 44 OW4 waters in the supercages provide octahedral co-ordination for the SII, SIV, and SV Na^+ ions respectively. The nature of water in zeolites is still a vexed question; the most detailed studies, using the n.m.r. method at different water loadings, reveal four regions of supercage water and provide tentative assignments.[5] The non-localised water can almost certainly be associated with

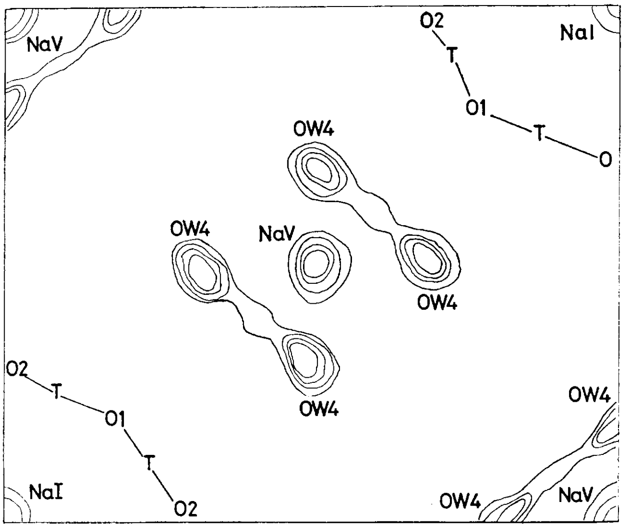

Figure 2. Environment of the site V cation. Octahedral co-ordination to water is achieved by interaction with the four coplanar water molecules (shown) and with water molecules above and below the plane.

TABLE

Summary of sodium ions and water molecules in a unit cell of hydrated NaX zeolites.

Comment	Site	Broussard and Schoemaker[1]	Olson[a]	Olson[b]	Hseu[3]	This study[c]	Co-ordinates
	I	16 Na^+	9 Na^+	9 Na^+	9 Na^+	9 Na^+	$x=y=z=0{\cdot}000$
	I′	0	8 Na^+; 12 H_2O	8 Na^+; 12 H_2O	11 Na^+ 12 H_2O	8 Na^+	$x=y=z=0{\cdot}070$
	II′	0	26 H_2O	26 H_2O	32 H_2O	25 H_2O	$x=y=z=0{\cdot}176$
	II	32 Na^+	24 Na^+ (IIa + IIb)	24 Na^+; 8 H_2O	22 Na^+	22 Na^+	$x=y=z=0{\cdot}245$
	II*	0	8 H_2O	0	6 H_2O	0	
	III′	0		31 Na^+ and/or H_2O (OW7 + OW10)	20 Na^+	32 Na^+	$x=y=0{\cdot}164.$ $z=0{\cdot}428$
	IV	0		0	0	3 Na^+	$x=y=z=0{\cdot}375$
	V	0		0	0	7 Na^+	$x=y=z=0{\cdot}500$
SII water	OW2	0		36 H_2O (OW5 + OW8 and OW9)		66 H_2O	$x=y=0{\cdot}313,$ $z=0{\cdot}213$
SIV water	OW3	0		0		16 H_2O	$x=y=0{\cdot}375,$ $z=0{\cdot}275$
SV water	OW4	0		28 H_2O	22 H_2O	44 H_2O	$x=y=0{\cdot}533,$ $z=0{\cdot}421$

[a] Olson's own interpretation: additional Na^+ and/or H_2O molecules were located (OW4—OW10 in ref. 2) but the nature of these sites was not clear to Olson. [b] Our re-interpretation of Olson's results. [c] Unit cell composition $Na_{86}[Al_{86}Si_{106}O_{384}]265\ H_2O$; $a_0 = 24{\cdot}924$ Å ($\pm 0{\cdot}01$ Å). Our work and that of refs. 1 and 3 uses space group *Fd3m*. Olson[2] employed the lower symmetry space group *Fd*3, but the differences in atomic co-ordinates resulting from the use of the different space groups is within our experimental error.

phase B[5] seen at higher loadings. Phases W and B′ total about 100 molecules of water (for Si/Al = *ca.* 1·1 and $\theta = 1$) and may be identified with waters co-ordinated to SII and SIV cations. In the n.m.r. work, phase W′, which was most strongly adsorbed, was assigned to defects in the structure but our work implies that this might be associated with a small number of SV Na^+ ions, hydration of which forms a hydrogen bonding network which probably enhances stability of the zeolite framework.

Olson[2] interpreted his data to indicate 193 out of 220 water molecules. In the light of our experience we have reinterpreted Olson's results to indicate 72 Na^+ ions and 98 water molecules (Table). The reduced number of localised water molecules in the re-interpreted Olson structures (98) compared with our 151, is balanced by the reduced total water content of Olson's sample (220) compared with our 265 molecules. What is most striking, however, is that Olson does not report electron density at sites IV and V, but his results do show some of the water molecules associated with site V (*i.e.*, our OW3 in the Table). These water molecules which we find form an extensive hydrogen bonding network with framework oxygen atoms, appear from Olson's results to form a stable octahedral cluster even in the absence of the site V Na^+ ion. It is possible that in Olson's crystal a proton is situated at site V, which would imply that Olson's zeolite may not have been completely charge balanced. The resulting species $H_{13}O_6^+$ has not previously been reported in zeolites although Chen[6] has suggested the existence of $H_9O_4^+$ species in dealuminated mordenites.

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