Cation Distribution in Zeolite Zinc/Sodium-Y by Resonant X-Ray Diffraction

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The distribution of extra-framework cations in zinc/sodium zeolite-Y has been determined by synchrotron X-ray powder diffraction using anomalous scattering methods.

The aluminosilicate zeolites are an important class of materials which find widespread use for ion-exchange, molecular sieving and catalytic applications.[1] In their dehydrated forms, they contain cations that are typically distributed over a number of partially occupied crystallographic sites, and the location of these cations can have a profound influence on the sorption and catalytic properties. In the case of zeolites containing only one type of extra-framework cation, their distribution can be determined uniquely from a single X-ray or neutron data set. Unfortunately, however, this is not possible for compounds containing more than one type of extra-framework cation. In the past this difficulty has been overcome by combining crystallographic information with chemical intuition concerning the site preferences of particular cations, but the recent development of anomalous scattering techniques with synchrotron radiation offers the possibility of determining cation distributions without recourse to qualitative chemical arguments. Such a strategy has recently been used to establish the cation distribution in 'Bi$_2$Sr$_2$CaCu$_2$O$_8$' superconductors.[2]

A partially zinc-exchanged sodium zeolite-Y of composition Na$_{0.07}$Zn$_{0.11}$(Al$_{0.28}$Si$_{0.72}$)O$_2$ (determined using inductively coupled plasma spectroscopy) was selected for study. No zinc-containing zeolite-Y materials have been previously studied by diffraction techniques, and this compound is of interest as a model for a new class of basic, alkene isomerisation catalysts.[3] A small quantity of the dry zeolite was sealed into a 0.7 mm diameter Lindemann tube under a helium atmosphere and the resulting sample was used for data collection at beam line X7A, NSLS (National Synchrotron Light Source), Brookhaven National Laboratory. Two diffraction patterns were obtained: the first one at a mean wavelength of 1.28564 Å (approximately 21 eV below the Zn K-edge) over the 2θ range 4.8–68.288° and the second at 0.79889 Å over the range 3–42.025°. The value of the real component of the anomalous scattering correction, f', for Zn
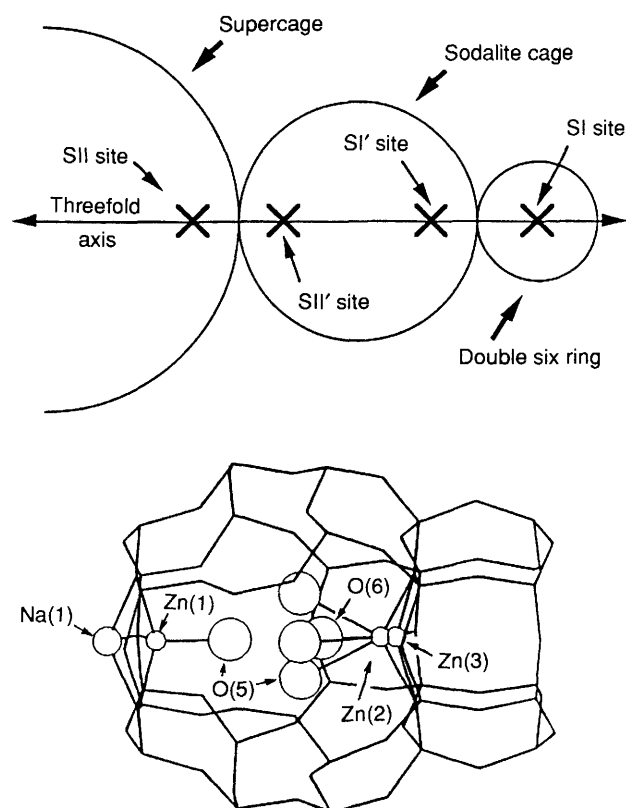

Fig. 1 A comparison of (top) a schematic view of the channel system found in faujasite framework zeolites showing the location of the commonly found extra-framework cation positions with (bottom) the structural model found for Zn/Na zeolite Y (see text). The crystallographic [111] direction runs across the figure.

Table 1 The structural model for Zn/Na zeolite Y[a]

	m	x	y	z	U_{iso}/Å^2	Frac.
T site	192i	−0.05250(7)	0.12446(7)	0.03663(8)	0.0104(4)	1.0
O(1)	96h	0.0	−0.1037(1)	0.1037(1)	0.026(2)	1.0
O(2)	96g	−0.0008(2)	−0.0008(2)	0.1463(2)	0.020(2)	1.0
O(3)	96g	0.0730(1)	0.0730(1)	−0.0273(2)	0.013(2)	1.0
O(4)	96g	0.0750(2)	0.0750(2)	0.3219(2)	0.023(2)	1.0
Na(1)	32e	0.2351(2)	0.2351(2)	0.2351(2)	0.013(4)	0.54(1)
Zn(1)	32e	0.2042(3)	0.2042(3)	0.2042(3)	0.013(4)	0.137(4)
Zn(2)	32e	0.062(1)	0.062(1)	0.062(1)	0.018(2)	0.23(5)
Zn(3)	32e	0.052(1)	0.052(1)	0.052(1)	0.018(2)	0.25(5)
O(5) (OH)	32e	0.158(2)	0.158(2)	0.158(2)	0.23(3)	0.41(4)
O(6) (OH)	32e	0.100(1)	0.100(1)	0.100(1)	0.23(3)	0.41(4)

[a] Space group $Fd3m$; lattice constant a = 24.6388(2) Å; agreement indices 0.799 Å data: R_{wp} 8.35%, R_p 6.66%, R_F 3.78%; 1.286 Å data: R_{wp} 13.29%, R_p 10.37%, R_F 6.72%; overall χ^2 = 1.671.

Table 2 Selected distances/Å

T–O(1)	1.633(2)
T–O(2)	1.662(2)
T–O(3)	1.672(2)
T–O(4)	1.635(2)
Average T–O distance	1.651
3 × Na(1)–O(2)	2.555(6)
3 × Na(1)–O(4)	2.992(5)
3 × Zn(1)–O(2)	2.162(6)
1 × Zn(1)–O(5)	1.95(8)
3 × Zn(2)–O(3)	2.23(2)
3 × Zn(2)–O(5)	2.59(5)
3 × Zn(3)–O(3)	2.091(2)
1 × Zn(3)–O(6)	2.05(6)
Short contacts	Zn(1)–Na(1) 1.32(1), Zn(2)–Zn(3) 0.42(1)

changes from −6 electrons to approximately zero between these two wavelengths.[4] This change in scattering contrast gives us the ability to determine uniquely the distribution of the two extra-framework cations over the available crystallographic sites.

Initially, the off-edge data set (0.8 Å) was analysed by the Rietveld method[5] in order to determine which of the possible cation sites were occupied and to locate any residual adsorbed water. At this stage it became clear that there were two additional sites which could be ascribed to residual water or hydroxide ions. The two data sets were then analysed jointly in a least-squares refinement, using the program GSAS,[6] to ascertain the nature of the cations at each of the occupied sites. This analysis indicated that none of the sites had both zinc and sodium present simultaneously, and a final refinement was therefore performed using both of the data sets with the newly determined distribution of zinc and sodium. The coordinates and occupancies resulting from this refinement are presented in Table 1 and a set of selected bond distances is presented in Table 2.

The T–O bond distances indicate that the structure of the aluminosilicate framework has been determined with accuracy and good precision, the average Si/Al–O bond length (1.651 Å) being in good agreement with that expected for a zeolite with a Si/Al ratio of 2.57 (1.639 Å) on the basis of previous studies of feldspars.[7] As expected, the shorter T–O bond lengths are associated with oxygen atoms that do not coordinate to cations (Table 2). Furthermore, the chemical composition obtained from the unconstrained refinement of the structure [Na$_{0.09}$Zn$_{0.10}$(Al$_{0.28}$Si$_{0.72}$)O$_2$] is in good agreement with that obtained from chemical analysis (see above).

The final structural model for the extra-framework cations is shown in Fig. 1.

The distribution of the extra-framework cations is similar to that found in other faujasites containing divalent transition metal ions,[8–17] except for the absence of cations at the octahedral SI site (the centre of the double six ring). The latter we attribute to the absence of ligand field stabilisation effects for Zn^{2+} compared with, for example, Ni^{2+} and Cu^{2+}. The presence of residual sodium at the SII sites is observed in many of these systems and in other related materials, La/Na-Y for example,[18] and has a marked influence on the dynamics of adsorbed hydrocarbons.[19] Our interpretation of the partial occupancy numbers of the extra-framework species (Table 2) requires local variations between sodalite cages. The SII and SII′ sites are mutually exclusive and are occupied by Na(1) and Zn(1), respectively, whilst the SI′ site accommodates either octahedrally or tetrahedrally coordinated zinc [Zn(2) and Zn(3), respectively]. O(5) completes the octahedron around Zn(2) and should therefore have a somewhat larger occupancy [i.e. 3 × the occupancy of Zn(2)] than that observed; the errors do not preclude this possibility. O(6) completes the tetrahedron around Zn(3); its occupancy should equal that of Zn(3) and is thus slightly overestimated in the refinement. We note that the occupancy of O(6) is also limited to 0.25 by short O(6)–O(6) contacts within the sodalite cages. A given sodalite cage would contain either one octahedral or one tetrahedral Zn at the SI′ site, and by implication, therefore, would contain either O(5) or O(6) oxygens.

The main uncertainty in our final model concerns the presence of the split zinc atom at the SI′ site. The introduction of this splitting leads to only a small improvement in the quality of the fit (R_F decreases by approximately 0.4% for the 0.8 Å data, and is little changed for the other data), but it is consistent with the observation of two water/hydroxide positions [O(5) and O(6)] associated with tetrahedral and octahedral zinc coordination at this site. Additionally, it reduces the temperature factor associated with the zinc from 0.031 to 0.018 Å^2, in line with that observed for the zinc at the SII′ position (0.013 Å^2).

This is, to the best of our knowledge, the first study of the cation distribution in zeolites to utilise anomalous scattering diffraction data. Such an approach, together with the combined use of X-ray and neutron diffraction data, offers a considerable improvement over the use of chemical intuition combined with experiment. Anomalous scattering powder diffraction data, both from laboratory and synchrotron sources, has previously been used to examine the cation distributions in simple materials;[20] we can now look forward to an increase in the use of the technique to study complex materials problems.

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