The Direct Observation of Cation Hydrolysis in Lanthanum Zeolite-Y by Neutron Diffraction

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Neutron diffraction studies on a partially dehydrated sample of lanthanum zeolite-Y (Si/Al = 2.61) reveal the locations of the hydrogen atoms, thus providing direct evidence for the cation hydrolysis and Brønsted acidity that account, in part, for the catalytic activity of this faujasite zeolite.

Synthetic analogues of the mineral faujasite exhibit catalytic activity in a wide range of chemical reactions including the cracking, hydrocracking, and isomerisation of hydrocarbons,[1] processes that are facilitated by Brønsted acid sites.[2] For reactions that proceed *via* alkylcarbenium ion intermediates, the Brønsted acidity can be generated by heat treatment of the NH_4^+-substituted zeolite,[3] but cation hydrolysis involving rare-earth ions is also an important method of generating acid sites in commercial catalysts. The role of the rare-earth ion appears to be twofold: to confer thermal stability on the aluminosilicate framework and to generate protons by hydrolysis of the rare-earth hydrate according to equation (1).

$$La(H_2O)_x^{3+} \rightarrow La(H_2O)_{x-1}(OH)^{2+} + H^+ \qquad (1)$$

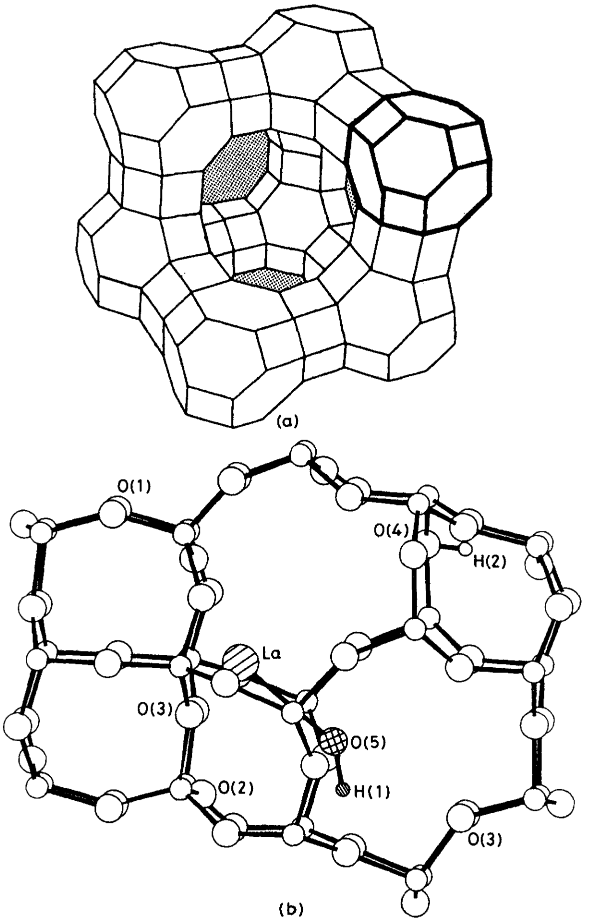

Figure 1. (a): A view of the framework structure of zeolite-Y: the truncated octahedron shown in (b) is indicated by thicker lines. (b): the truncated octahedral element in La–Y, showing one of the hexagonal prismatic linkages to the adjacent element. Site SI′, here shown occupied by La, is in the hexagonal window forming the outer end of this prism.

Evidence for hydrolysis comes from i.r. spectroscopy, where O–H stretching frequencies can be ascribed to OH groups attached to both the cation and the aluminosilicate framework.[4] For samples of La-Y dehydrated at 600 °C, *X*-ray studies[5] indicate the presence of La^{3+} ions at SI′ sites (Figure 1) with residual water providing oxygen bridges to adjacent lanthanum ions; thermal analysis[6] indicates the retention of *ca.* one water molecule per La^{3+} ion at this temperature. In this communication, we present direct evidence, obtained by neutron diffraction, for cation hydrolysis in lanthanum zeolite-Y.

A polycrystalline sample of La-Y, Si/Al = 2.61, was prepared by ion exchange[7] from a sodium derivative at 75 °C and then dehydrated at 600 °C. Neutron diffraction data were collected at 5 K on the high resolution, powder diffractometer, D1A, at I.L.L. Grenoble, and analysed by the Rietveld method[8] using the POWDER system[9] on a DEC-10 computer at the S.E.R.C. regional computing centre, Edinburgh. A combination of least-squares refinements and Fourier calculations in space group $Fd\bar{3}m$[10] located lanthanum ions at site SI′ and unexchanged sodium ions at SI′ and SII_b, in agreement with previous *X*-ray work.[5] The total cation occupancy is in excellent agreement with 67% ion exchange.[7] Our results also confirm the presence of non-framework oxygen atoms, O(5), bonded to lanthanum, as reported previously. Furthermore, the advantage of using neutrons rather than *X*-rays is demonstrated in the present work by our detection of the protons from the residual water molecules. Our difference Fourier calculations reveal a single proton attached to O(5) at a distance of 0.99 Å, and protons attached to framework oxygen O(4) at a distance of *ca.* 1.2 Å [Figure 1(b)]. The hydrogen and oxygen occupancy factors confirm that hydrolysis of the lanthanum hydrate has taken place according to equation (2) with *x* between 1 and 2. The final profile

$$La(H_2O)_x^{3+} \rightarrow La(OH)_x^{(3-x)+} + xH^+ \qquad (2)$$

R-factor[8] is 11.5%.

The identification of hydrogen in the Fourier maps is quite unambiguous because it is the only element present that has a negative scattering amplitude. The influence of the cations upon the silicon, aluminium–oxygen (T–O) bond lengths is seen in the lengthening of the bonds T–O(2) and T–O(3) (Table 1), but this effect is not apparent from the influence of hydrogen on the T–O(4) bond length, presumably because only a small fraction of the O(4) atoms are protonated. The

Table 1. Some important bond lengths in lanthanum zeolite-Y (Å).

T[a]–O(1)	1.606(9)	La–O(2)	3 × 2.937(11)
T–O(2)	1.676(9)	La–O(3)	3 × 2.411(11)
T–O(3)	1.631(9)	La–O(5)	2.62(2)
T–O(4)	1.618(11)		

[a] T = Si,Al

reluctance of the lanthanum compound to lose all its adsorbed water is readily understood in view of the exceptionally low co-ordination numbers offered by the zeolite framework, and the hydrolysis reaction reflects an attempt to achieve better charge compensation at the trivalent cation site. Our results suggest that this is achieved by means of terminal, rather than bridging, OH^- ligands, as was deduced[5] from *X*-ray work.

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