A Study of Si,Al Ordering and Cation Positions in the Zeolites Sodium ZK-4 and Sodium Y by Neutron Diffraction

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Neutron diffraction measurements on the zeolites sodium ZK-4 (Si/Al = 1.65) and sodium Y (Si/Al = 2.61) show that there is no long range ordering of Si and Al, in contrast to results on sodium A and sodium X; the depopulation of the 8-ring sodium site in ZK-4 accounts for its ability to sorb linear hydrocarbons.

Current interest in zeolites has led to the application of several sophisticated physico-chemical methods to the study of their structural properties, particularly the investigation of Si,Al ordering. Important advances have been made using high resolution, ^{29}Si magic-angle spinning n.m.r. (m.a.s. n.m.r.),[1,2] powder neutron diffraction,[3,4] and high resolution

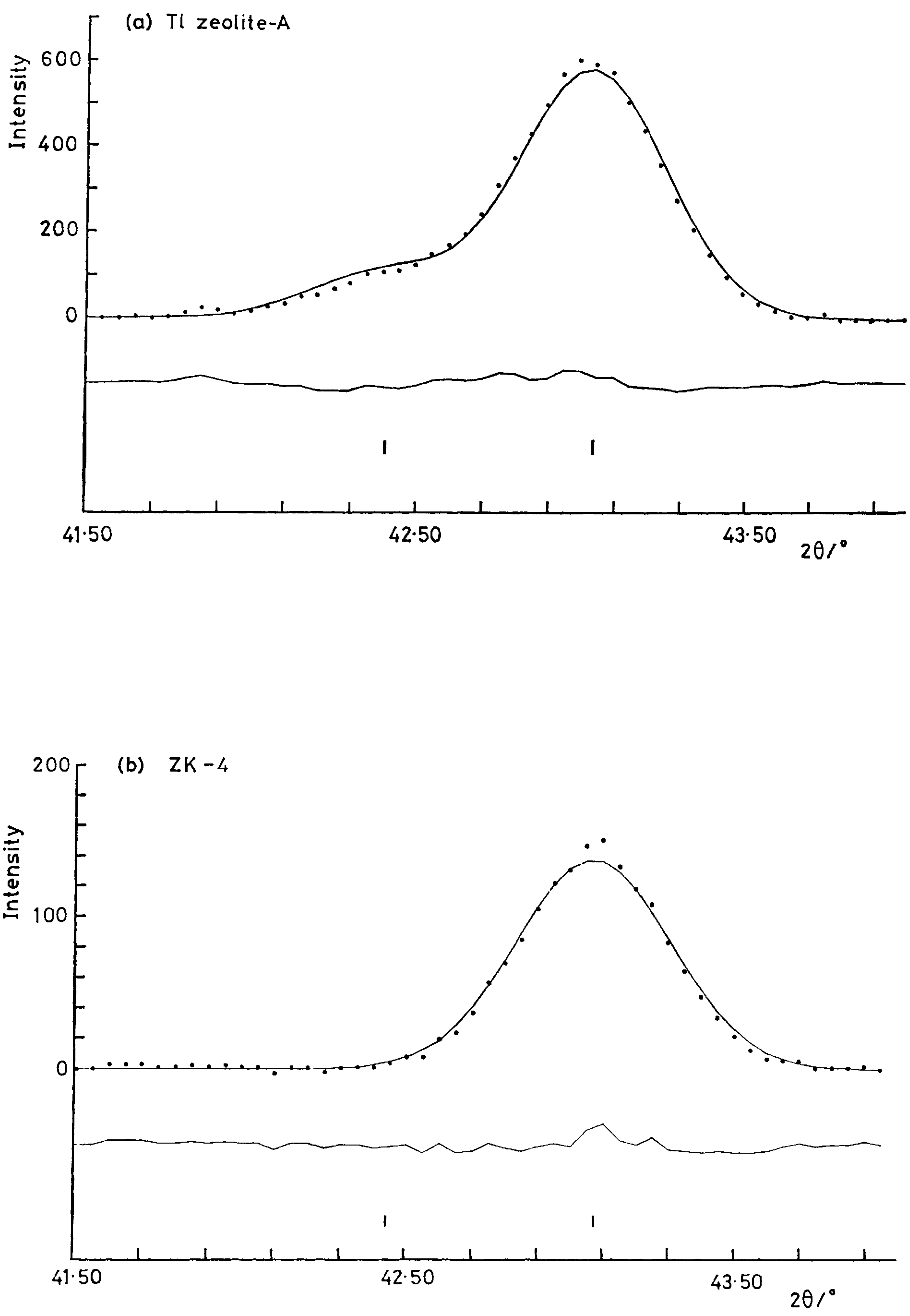

Figure 1. A part of the observed (dots) and calculated (smooth curve) diffraction patterns in (a) thallium zeolite-A and (b) sodium ZK-4. Note the absence of the superlattice reflection at *ca.* 42.4° in (b).

electron microscopy,[5] with attention largely focused on the simple cubic zeolites based on connected, truncated octahedra, *i.e.* zeolite-A and faujasite (zeolites-X and -Y). In the former case, alternation of Si and Al, in accordance with Loewenstein's rules,[6] is observed for Si/Al ratios close to unity[7,8,9] and the space group is *Fm*3*c*. In synthetic faujasites, there is again a marked tendency for ordering of Si and Al, when the Si/Al ratio is low; for example, Olsen showed[10] that there was Si and Al alternation, in space group *Fd*3, for zeolite-X with Si/Al = 1.18, and m.a.s.n.m.r. results[11] confirm that alternation is pronounced. For faujasite samples with higher Si/Al ratios (up to *ca.* 2.5), further ordered arrangements have been proposed on the basis of m.a.s.n.m.r. results.[11,12] In this paper, we present the results of an independent, neutron diffraction study of polycrystalline, sodium ZK-4 (a variant of zeolite-A with a high Si/Al ratio, in this instance 1.65) and polycrystalline, sodium zeolite-Y (Si/Al = 2.61). Single crystals of sufficient size for *X*-ray work cannot be prepared conveniently at these compositions.

Sodium ZK-4 was prepared by the method of Kerr,[13] and the Si/Al ratio determined[11,12,14] by m.a.s.n.m.r. The most striking feature of the neutron powder pattern, obtained on a high resolution diffractometer D1A at I.L.L., Grenoble using a mean neutron wavelength of 2.98 Å, is the absence of the superlattice reflections arising from the doubling of the cubic unit cell from *ca.* 12.3 Å to *ca.* 24.6 Å (Figure 1).

The smaller unit cell at this composition is also confirmed by electron diffraction. The implication of this result is that silicon and aluminium are no longer located preferentially on alternate tetrahedral sites, even though local ordering in conformity with Loewenstein's rules[6] is probably still present. Monte Carlo calculations predict that this situation can occur for Si/Al ratios greater than 1.7.[15] A good refinement of the data is obtained using the 12.3 Å cell in space group *Pm*3*m*, and the mean Si,Al–O bond length (1.643 Å) is in good agreement with the weighted average of Si–O and Al–O bond lengths (1.652 Å) at this composition. A similar conclusion can be drawn from the results on our zeolite-Y sample. No alternation of Si and Al can be detected in our refinements and all the tetrahedral sites appear to be equivalent, increasing the symmetry from *Fd*3 to *Fd*3*m*; in this instance the lattice parameter remains the same (*ca.* 24.6 Å). The mean Si,Al–O bond length (1.640 Å) is again in good agreement with the weighted average (1.639 Å).

The neutron refinements on ZK-4 and Y also provide interesting information concerning the location of the exchangeable cations in these structures. An obvious consequence of increasing the Si/Al ratio is that the number of exchangeable cations is reduced. Our measurements show that in ZK-4 the 8-ring site is preferentially depopulated, a possibility previously advanced[16] in order to account for the ability of sodium ZK-4, but not sodium-A, to sorb long chain hydrocarbons such as n-hexane.[13] In zeolite-Y, we find that site SI′ is partially vacated, in agreement with a previous examination using neutrons.[4]

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