Does the Mode of Preparation of an Aluminosilicate Influence the Short-range Si,Al Ordering?

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Summary Magic-angle-spinning ^{29}Si n.m.r. spectroscopy shows that 3:1 ordering (three AlO_4^{5-} and one SiO_4^{4-} surrounding each SiO_4^{4-} tetrahedron) occurs in zeolite A irrespective of the method of preparation, whereas in sodalite and cancrinite which also have Si, Al ratios close to unity, either 4:0 or 3:1 ordering may occur.

Until very recently it was thought that in zeolite A (idealised formula $M^+_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$) each Si atom is linked, *via* oxygen bridges, to four Al atoms and *vice versa*. Thus 4:0 ordering of SiO_4^{4-} and AlO_4^{5-} tetrahedra was thought to prevail. Three independent techniques[1,2] (electron diffraction, high-resolution solid-state ^{29}Si n.m.r. spectroscopy, and profile analysis of neutron diffraction of powders) have, however, revealed that each silicate tetrahedron is surrounded by *three* aluminate tetrahedra and *one other* silicate tetrahedron, and *vice versa* (3:1 ordering). Subsequent high-resolution magic-angle-spinning n.m.r. studies[3–5] have shown that in the synthetic zeolite Losod[5] ($Na_{12}Al_{12}Si_{12}O_{48}\cdot 18H_2O$) the Si, Al ordering is also 3:1, while several other zeolites and feldspars show, unambiguously, 4:0 ordering. Clearly Al–O–Al linkages (which *must* be present whenever 3:1 ordering prevails in an aluminosilicate with a Si/Al ratio of unity) are sometimes adopted, contrary to what has hitherto been believed in zeolite and aluminosilicate chemistry according to the precepts of Loewenstein's rule.[6] The question now arises as to whether, for a given structural type with a fixed topology, preparative conditions may be altered so as to lead either to 4:0 or to 3:1 ordering.

Zeolite Na-A (Linde 4A), $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$, may be prepared in two quite different ways. In the Charnell[7] method, which yields crystals 100—140 µm in diameter, sodium metasilicate reacts with sodium aluminate in triethanolamine—water solution at 75—95 °C. Component solutions are carefully filtered before mixing so as to limit the number of crystal seeds. Crystallization time is 2—3 weeks. Crystals of Na-A can also be produced[8] from kaolinite, $Al_2Si_2O_5(OH)_4$, a sheet silicate in which each SiO_4^{4-} tetrahedron is attached to three other SiO_4^{4-} tetrahedra in one plane and to an octahedrally co-ordinated Al in an adjacent plane. Kaolinite is first converted into metakaolinite, an amorphous material, by thermal treatment (calcination) at about 600 °C. Metakaolinite is then treated with aqueous sodium hydroxide at 100 °C. We have examined samples of Na-A made from kaolinites from Georgia and from Cornwall. The two methods of preparation of Na-A are non-topochemical and non-topotactic.[9]

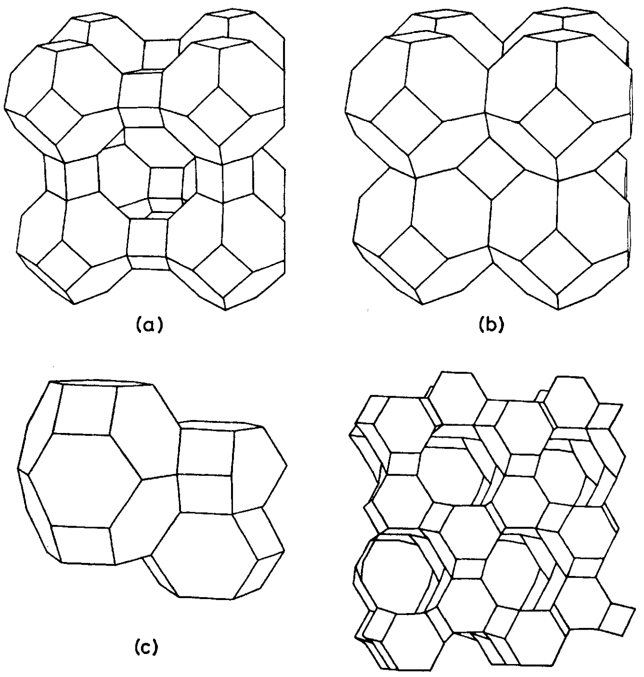

Figure 1. Aluminosilicate frameworks of the zeolites studied. Si and Al atoms are located at vertices of polyhedra. For clarity, oxygen atoms, through which Si and Al are joined, and the cations are not shown. (a) Na-A; (b) sodalite; (c) Losod; (d) cancrinite.

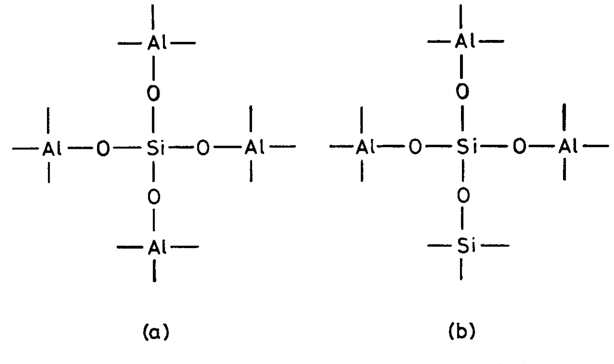

Figure 2. Even though the co-ordination of the Si is invariant (and equal to four, with tetrahedral symmetry), depending upon their mode of preparation both cancrinite and sodalite can adopt either 4:0 (a) or 3:1 (b) ordering. Zeolite A exhibits 3:1 ordering irrespective of whether it is prepared from kaolinite or by mixing solutions of aluminate and silicate.

The n.m.r. results show that the ^{29}Si isotropic chemical shifts are identical within experimental error (−88·9 ± 0·3 p.p.m. from Me_4Si) showing that 3:1 ordering is also adopted in the kaolinite-derived Na-A.

In sodalite ($Na_6Al_6Si_6O_{24}.6H_2O$), however, which is structurally very similar to zeolite A, Engelhardt reported[10] that the ^{29}Si chemical shift is −83·5 p.p.m. indicating a 4:0 ordering scheme, whereas in the several samples studied by us the shifts were −86·7 ± 0·3 p.p.m., so that the ordering is 3:1. Furthermore, in samples of synthetic cancrinite hydrate ($Na_6Al_6Si_6O_{24}.6H_2O$) of different origin we have found either 4:0 ordering (chemical shift −81·8 ± 0·3 p.p.m.) or 3:1 ordering (−87·2 ± 0·3 p.p.m.) (Figure 2).

The mode of preparation is, therefore, important in governing the nature of the short-range Si, Al ordering adopted for a given Al content within a given structural topology at least for sodalite and cancrinite, and may be of great significance for the physical and chemical properties, particularly the acidity, of the respective materials.

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