On the Siting of Aluminium in Zeolite Omega

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Two crystallographically non-equivalent and unequally populated tetrahedral aluminium sites are identified by magic-angle-spinning ^{27}Al n.m.r. spectroscopy in the parent zeolite (Si/Al = 4.24 ± 0.05); after treatment with $SiCl_4$ at 500 °C relatively mobile, 6-co-ordinated aluminium is generated (most of it released from one of the tetrahedral sites) and there is evidence for some realumination of the tetrahedral framework.

Tetrahedrally bonded aluminium in zeolite structures is almost always[1] surrounded, *via* oxygen bridges, by four silicons also in tetrahedral sites [this is usually designated Al(4Si)]. Silicon, on the other hand, may have five distinct, 'first shell' environments: $Si(OAl)_4$, $Si(OAl)_3(OSi)$, $Si(OAl)_2(OSi)_2$, $Si(OAl)(OSi)_3$, and $Si(OSi)_4$, usually designated Si(*n*Al), with $n = 4, 3, 2 \ldots 0$, all of which may be identified[2] by magic-angle-spinning ^{29}Si n.m.r. spectroscopy, the signals falling in the ranges −80 to −120 p.p.m. from tetramethylsilane. Magic-angle-spinning ^{29}Si n.m.r. spectroscopy is also sensitive to other, 'second-order' differences in crystallographic environments, as shown by the richness of the silicalite spectrum[3] [nominally made up entirely of $Si(OSi)_4$] where nine distinct peaks and shoulders can be directly identified and even more can be detected by deconvolution.

In view of these facts, magic-angle-spinning ^{27}Al n.m.r. spectroscopy when applied to zeolites normally detects[4] a single signal, attributable to Al(4Si). This peak, depending upon the actual structure, falls within the range 51 to 65 p.p.m. from $Al(H_2O)_6^{3+}$, there being, only occasionally, partly-resolved fine structure. Using very high magnetic fields, however, we have found (see below) that magic-angle-spinning ^{27}Al n.m.r. spectroscopy is capable of resolving non-equivalent, tetrahedrally-bonded Al atoms, that differences in Al-population of these tetrahedral sites are readily measured, and that the nature of the solid-state reorganization and changes in aluminium siting can be charted.

The magic-angle-spinning ^{27}Al n.m.r. spectra were taken at 130.32 MHz on the Bruker AM-500 multinuclear spectrometer operating at the highest currently available persistent magnetic field of 11.74 Tesla. Other details of the technique are given elsewhere.[2–4] The starting material was commercial zeolite omega (Union Carbide) with Si/Al = 4.24 ± 0.05 determined by *X*-ray fluorescence by Dr. A. E. Comyns. The unit cell composition was $Na_{4.87}(TMA)_{2.00}Al_{6.87}Si_{29.13}O_{72}\cdot 21H_2O$, where TMA denotes the tetramethylammonium cation. *X*-Ray data were collected on a Philips APD10 automatic powder diffractometer with vertical goniometer and high-temperature stage. Samples were sedimented from a slurry with acetone and heated in a nitrogen flow gradually to 300 °C over three hours; diffractograms were collected at the final temperature at the rate of 1° 2θ per minute. The diffractograms of the heated dehydrated samples were superior to those from hydrated ones. 55 peaks were indexed for zeolite omega with no trace of crystalline impurities. [Our assignments for the peaks at d = 3.78 Å (311) and d = 3.12 Å (411) differ from those originally given:[5] (002) and (500), respectively.] Refinement of the lattice parameters was based on 22 peaks assuming hexagonal symmetry and gave $a = b = 18.12 \pm 0.01$ Å, $c = 7.61 \pm 0.01$ Å.

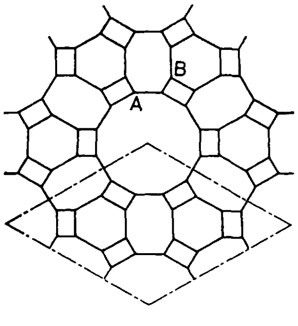

Figure 1. Projection drawing, viewed along [001], of the structure of zeolite omega (see ref. 6). There are two distinct tetrahedral sites, one more (A) and one less (B) accessible *via* large channels (10 Å diameter). Unit cell indicated.

The accepted model for the structure of zeolite omega[6] has 24 tetrahedral sites per unit cell located in the four-membered rings in the gmelinite columns and 12 sites per unit cell located in the six-membered rings (Figure 1). Figure 2(a) shows the ^{27}Al n.m.r. spectrum of zeolite omega. There are two distinct tetrahedral environments for aluminium atoms, but the distribution of Al betwen these site groups, which we term 1 and 2, is in the ratio of 4.56:1 (we have ensured that the spectra are quantitative). It follows, therefore, that site 1 contains 5.63 Al atoms per unit cell and site 2 1.24 Al atoms per unit cell.

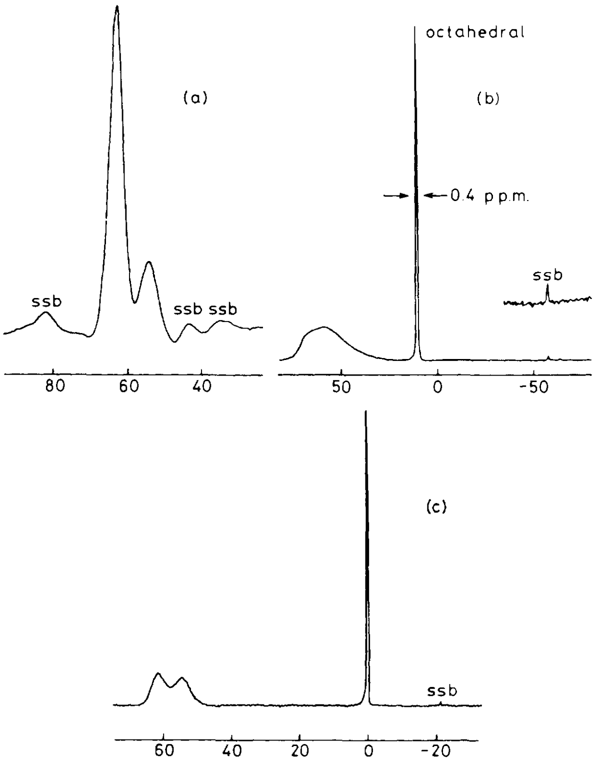

Figure 2. ^{27}Al Magic-angle-spinning n.m.r. spectra of zeolite omega. (a) Spectrum of the parent material at 130.32 MHz. 431 scans, 1 s recycle time. Chemical shifts are in p.p.m. from $Al(H_2O)_6^{3+}$. ssb denotes spinning sidebands. (b) Spectrum of dealuminated omega at 52.11 MHz. (c) Dealuminated omega at 130.32 MHz. ssb is a spinning sideband, whose distance from the signal at 0.31 p.p.m. indicates spinning rate of 2.86 kHz.

Dealumination was performed by treating dehydrated zeolite omega at 500 °C with dry nitrogen saturated, at room temperature, with $SiCl_4$ for 6 h. Aluminium was successively removed from the crystals in the form of volatile $AlCl_3$ and replaced by silicon on the tetrahedral sites.[7] After thermal treatment the sample was washed with distilled water and dried at 100 °C. *X*-Ray diffraction and i.r. spectra showed that the treated material is highly crystalline with unit cell parameters (again determined at 300 °C) $a = b = 18.18 \pm 0.01$ Å, $c = 7.61 \pm 0.01$ Å. The small expansion of the unit cell corresponds to an increase of unit cell volume by 0.7 per cent. *X*-Ray fluorescence gives $Si/Al = 4.50 \pm 0.05$ for the dealuminated material, signifying that the unit cell now contains 6.86 Al atoms. The magic-angle-spinning ^{27}Al n.m.r. spectra of the product are given in Figure 2(b) and (c). The very high field spectrum contains *three* signals: two corresponds to tetrahedrally co-ordinated Al and an extremely sharp signal attributable to octahedrally co-ordinated Al in the relative intensity ratio 3:3:2, respectively. (The octahedral peak, FWHM = 0.2 p.p.m., is the narrowest we have measured in the solid state.) This means that the *tetrahedral* Si/Al ratio is now 6.00. The octahedral Al is evidently quite mobile and in a highly symmetrical environment, which is consistent with the fact that zeolite omega has the widest intracrystalline channels (*ca.* 10 Å in free diameter) of any known zeolite. The intensity of the octahedral signal is one third that of the tetrahedral signal (one Al^{3+} ion balances the charge of *three* Al atoms in the framework). Note that the spectrum measured at the lower magnetic field of 4.70 Tesla [Figure 2(b)] features only one tetrahedral signal, demonstrating the advantages of high-magnetic-field solid-state n.m.r. spectroscopy. It is evident that the line-broadening influence of the second-order quadrupolar interaction, inversely proportional to the magnetic field strength, is reduced at 11.74 Tesla [Figure 2(c)].

The chemical composition of the product together with the magic-angle-spinning ^{27}Al n.m.r. spectra indicate that there are 2.57 Al atoms on site 1 and 2.57 Al atoms on site 2 in the dealuminated zeolite omega. This means that site 1 has been dealuminated by 54 per cent and also that site 2 has been enriched in Al. Crystallographically (see Figure 1) there are clearly two distinct tetrahedral sites, one more accessible and one less accessible to the 10 Å channels. It is tempting to assign the former as site 1 and the latter as site 2; but more work is required to confirm this assignment. The slight but real expansion of the unit cell is in line with the view that Al has been redistributed. Reinsertion of framework Al during stabilization of ammonium-exchanged zeolite Y has been proposed by Breck and Skeels[8] based on indirect i.r. evidence. Our work demonstrates that this can be observed directly, and that magic-angle-spinning ^{27}Al n.m.r. spectroscopy at very high magnetic fields is well equipped to determine the status and quantity of aluminium in the solid state. As such, it is of considerable promise in zeolite chemistry.

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