

Alumination of Highly Siliceous Zeolites

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^{27}Al Magic angle spinning n.m.r. and i.r. spectroscopy show that introduction of 4- and 6-co-ordinated aluminium occurs during treatment of highly-siliceous ZSM-5/silicalite with AlCl_3 vapour at elevated temperatures.

Catalytic and other properties of zeolites are strongly dependent on their aluminium content, and it is therefore desirable to be able to vary the latter while retaining the topology and crystallinity of the parent structure. The aluminium content of zeolites can be *decreased* by heat treatment of their ammonium-exchanged forms (this process is known as ultra-stabilization), by acid washing, and by using a number of reagents such as ethylene diaminetetra-acetic acid, chlorine gas, acetylacetone, or phosgene, but it has not been possible hitherto (so far as we are aware) to *increase* the Al content after completion of synthesis. † We report a successful reversal of the recently discovered¹ reaction of zeolites with silicon tetrachloride vapour. We have used ^{27}Al magic angle spinning n.m.r. (m.a.s. n.m.r.) and i.r. spectroscopy to show that when highly siliceous zeolite ZSM-5 (silicalite) is treated with AlCl_3 vapour at elevated temperatures, aluminium is isomorphously substituted for silicon in the zeolitic framework and also enters 6-co-ordinated (octahedral) intrazeolitic positions.

Our parent material was commercial silicalite (Union Carbide) with Si:Al > 400, and was shown to be highly crystalline by X-ray diffraction and i.r. spectroscopy. About

3 g of the zeolite was carefully dehydrated in a flow of dry nitrogen in a vertical quartz tube placed inside a furnace at 400 °C for 12 h. The stream of nitrogen was then diverted through a bed of solid AlCl_3 maintained at 180 °C. The temperature of the zeolite was slowly increased to 500 °C and the gas flow continued for 2 h, and then increased again to 600 °C, at which temperature it was kept for 10 h in flowing $\text{N}_2(\text{AlCl}_3)$. The zeolite was then purged with dry nitrogen for 4

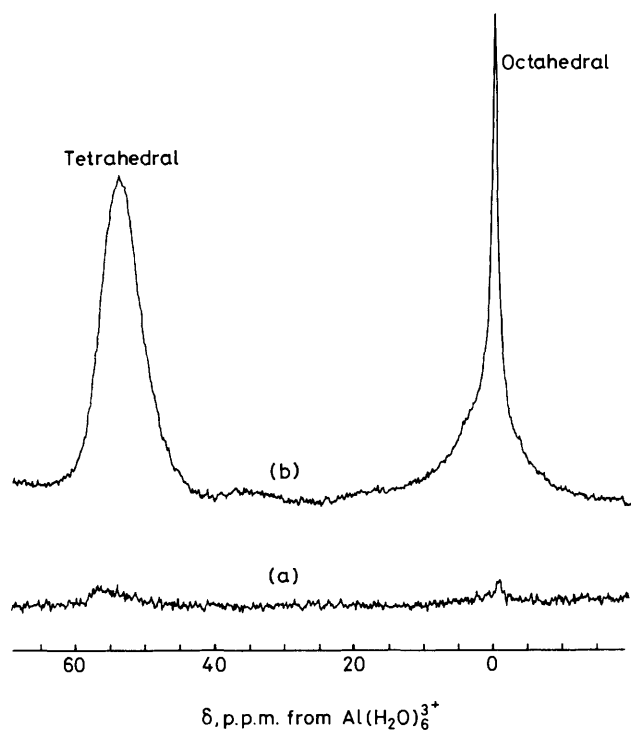


Figure 1. ^{27}Al M.a.s. n.m.r. spectra at 104.22 MHz of the parent and the aluminated ZSM-5/silicalite. 500 Scans with no line broadening. (a) Parent material with Si:Al > 400; (b) aluminated material (see text) with Si:Al ca. 50.

† Dessau and Kerr (U.S. Patent 4388215, 1984) have reported that the catalytic activity of zeolites is enhanced by treatment with aluminium chloride, but do not address the question of framework substitution.

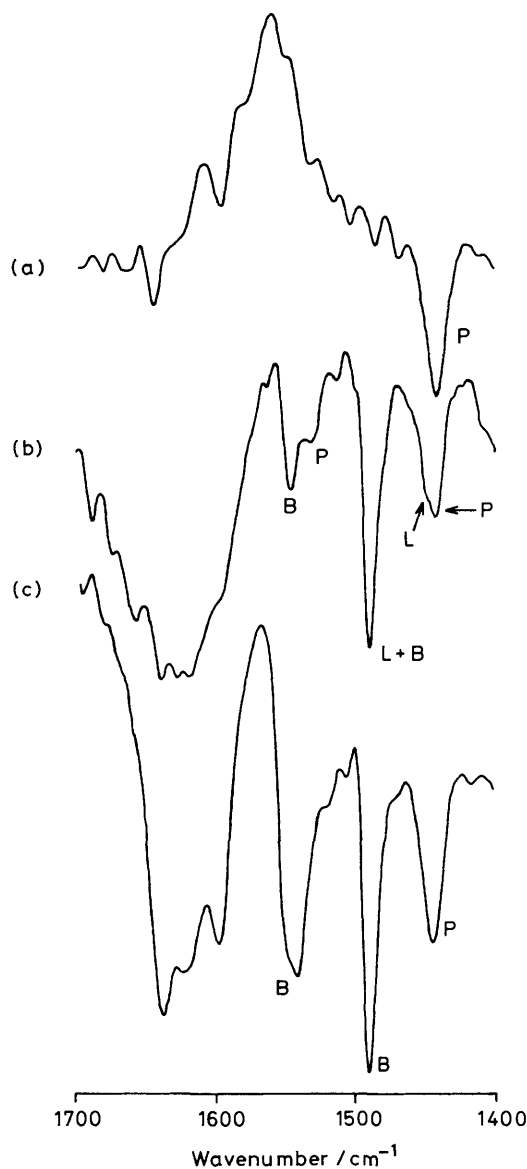


Figure 2. I.r. spectra in the ring vibration region of pyridine equilibrated with dehydrated zeolite samples (see text). (a) Parent ZSM-5/silicalite; (b) AlCl_3 -treated sample; (c) H-ZSM-5 with Si:Al = 33.3. B, L, and P denote signals due to the Brønsted and Lewis acidity and to physisorbed pyridine, respectively.

h at the final temperature, cooled, and washed with deionised water. The product was highly crystalline.

^{27}Al M.a.s. n.m.r. measurements were carried out at 104.22 MHz using a Bruker MSL-400 spectrometer equipped with a magic-angle probe. Samples were spun in cylindrical zirconia spinners at ca. 3.5 kHz without cross-polarization or decoupling. 60° Pulses were used with a 0.3 s recycle time. Chemical shifts were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Other details of the technique are given elsewhere.²

It is by now amply established² that ^{27}Al m.a.s. n.m.r. spectroscopy is sensitive to the co-ordination, quantity, and location of aluminium atoms in solid aluminosilicalites. Figure 1(a) gives the spectrum of the parent material. As reported previously³ very small amounts of 4-co-ordinated Al are present, but the signal (at ca. 55 p.p.m.) can be observed only when a very large number of scans are accumulated. The spectrum does not change when the recycle time is increased, which means that the intensity is relaxation-independent. N.m.r. spectroscopy also detects small amounts of 6-co-ordinated (octahedral) aluminium in the parent sample. In the aluminated silicalite the situation is dramatically changed [see Figure 1(b)]. Firstly, the tetrahedral signal becomes significant after a very few scans. Clearly the amount of tetrahedral aluminium has been considerably increased. Secondly, there is an octahedral signal with approximately 1/3 of the intensity of the tetrahedral one. The narrowness of the peak at 0 p.p.m. indicates that the 6-co-ordinated Al is highly mobile, such as in the hydrated Al^{3+} cation. Moreover, the intensity of this signal does not decrease on prolonged washing of the sample with water, which indicates that 6-co-ordinated Al, albeit mobile, neutralizes the framework charge created in the course of alumination and cannot therefore leave the zeolite crystals. (Note that *one* 6-co-ordinated Al^{3+} cation neutralizes the charge of *three* 4-co-ordinated framework aluminium atoms.) These observations are consistent with reaction (1), where $(\text{SiO}_2)_x$ symbolises the highly siliceous parent material. This amounts to the reversal of the reaction of dealumination of the zeolite with SiCl_4 vapour.¹ The Si:Al ratio of the product, as determined by energy-dispersive X-ray analysis, is ca. 50. It is also possible that AlCl_3 vapour reacts with the surface hydroxy groups in the parent zeolite and structural faults involving nests of four hydroxy groups, although 4-co-ordinated Al is created only in the latter case.



Pyridine vapour was admitted at room temperature into an evacuated i.r. cell with KBr windows containing a self-supporting wafer of dehydrated zeolite and placed in the path of the beam of a Perkin-Elmer 599 infrared spectrometer (equipped with a data station). Equilibration was attained in ca. 90 min, whereupon the system was evacuated and the i.r. spectra acquired. A comparison of Figures 2(a) and (b) shows⁴ that both Brønsted and Lewis acidity (the latter presumably due to 6-co-ordinated Al) appear in the spectrum of AlCl_3 -treated sample, making it similar to that of H-ZSM-5 given in Figure 2(c). Above 150°C physisorbed pyridine is lost. The protons required for Brønsted acidity are presumably produced by hydrolysis of the aluminium hexahydrate species.

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