

Solid-state ^{29}Si N.M.R. and High-resolution Electron Microscopic Studies of a Silicate Analogue of Faujasite

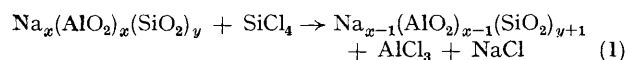
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Summary Reaction of synthetic zeolite Na-Y with SiCl_4 yields an essentially aluminium-free faujasite structure which is highly crystalline, and which, when studied by ^{29}Si n.m.r. spectroscopy with magic-angle-spinning, gives a spectrum consisting of a single, sharp peak characteristic of regular, Si(4 Si) lattice ordering.

ZEOLITES with high Si/Al ratios are known to be strong Brønsted acids and to possess remarkable catalytic activity. They were first prepared by repeated ammonium exchange followed by hydrothermal treatment and acid washing.¹ The synthesis of zeolite ZSM-5^{2,3} (with Si/Al ratio in the range 40–8000) was a major step forward in catalysis and the material was found to be very active in a number of reactions.^{4,5} Recently a new method of dealuminating synthetic faujasites by reaction with SiCl_4 vapour at elevated temperatures has been reported.⁶ We have examined the reaction and its product in some detail and found the highly siliceous analogue of faujasite to have rather striking properties.

Dehydrated Na-Y was treated at 560 °C with dry argon saturated (at room temperature) with SiCl_4 for 3 hours. Aluminium was successively substituted in the zeolitic matrix by silicon and removed from the crystals in the form of volatile AlCl_3 . Each step of the reaction, taking Na-Y with an Si/Al ratio of y/x as starting material, can be written as in equation (1). Part of the aluminium remains in the



solid as NaAlCl_4 , but more can be removed by washing the product with water, drying and repeating the treatment with SiCl_4 . Two successive treatments yielded material in which aluminium is no more than an impurity. In this respect the product is similar to the ZSM zeolites. It is highly crystalline to X-rays and in high-resolution electron microscopy (HREM), highly resistant to heat treatment, and with powder diffraction gives lines which are sharper than for the starting zeolite. The aluminium content can be varied by altering the duration of exposure to SiCl_4 . For complete dealumination the cubic unit cell constant contracts from 24.68 Å (Na-Y with Si/Al = 3.06) to 24.31 Å.

We have examined the starting Na-Y and the dealuminated final product by high-resolution ^{29}Si n.m.r. in the solid state (with magic-angle-spinning). Lippmaa *et al.*⁷ have demonstrated a regular dependence of the ^{29}Si chemical shifts on the number of AlO_4^{5-} tetrahedra linked, *via* oxygen bridges, to each SiO_4^{4-} tetrahedron. These shifts are practically independent of the type of cation present. For each distinct type of structural unit, represented as Si(n Al) where $n = 0, 1, 2, 3$ or 4, a distinct narrow range of chemical shift was found, with each aluminium substituent being responsible for a *ca.* 5 p.p.m. low-field shift. Thus Si(4 Al) corresponds with –82 p.p.m. shift from tetramethylsilane and Si(0 Al) in aluminium-free quartz with –107.4 p.p.m. This important discovery makes solid-state ^{29}Si n.m.r. spectroscopy a powerful tool of structural investigation, capable of tackling the enigmatic problem of Si,Al ordering in aluminosilicates.⁸

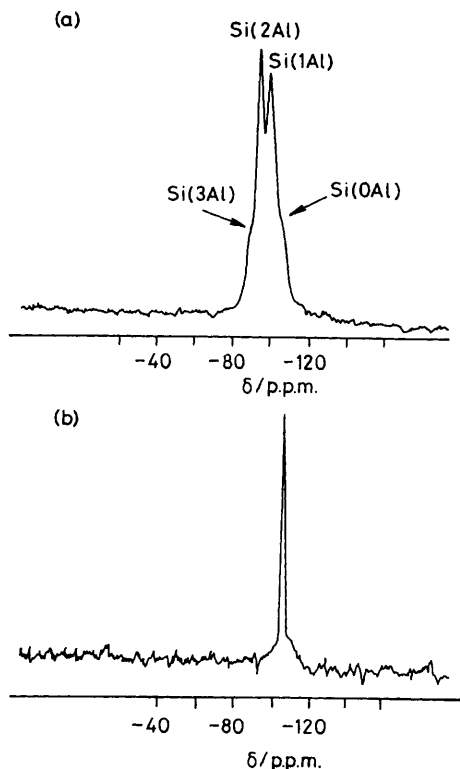


FIGURE 1. ^{29}Si N.m.r. spectra. (a) Parent Na-Y zeolite. (b) After treatment with SiCl_4 . Chemical shifts are given in p.p.m. from tetramethylsilane.

Figure 1(a) shows the ^{29}Si n.m.r. spectrum of zeolite Na-Y. The two main peaks correspond, from left to right, with Si(2 Al) and Si(1 Al) ordering of the aluminate and the silicate tetrahedra, in the approximate intensity ratio of 4:5. There are also slight humps corresponding to a small concentration of Si(3 Al) and Si(0 Al) structural units. The values of the four chemical shifts are -89.7 , -94.6 , -100.6 , and -105.5 , each ± 0.5 p.p.m. Figure 1(b) gives the spectrum for the material which has been dealuminated using silicon tetrachloride. There is only one sharp peak corresponding with the chemical shift of -107.4 ± 0.1 p.p.m. It is obvious that:

- (i) the peak represents Si(0 Al), *i.e.* Si(4 Si) ordering of tetrahedra, with a chemical shift precisely equal to that found by Lippmaa *et al.*⁷ in quartz;
- (ii) the peak is very narrow (*ca.* 0.5 p.p.m. at half-height) which indicates high homogeneity and crystallinity. This is

the best resolved ^{29}Si peak we have found in the course of our extensive measurements⁹ in solid silicates and aluminosilicates.

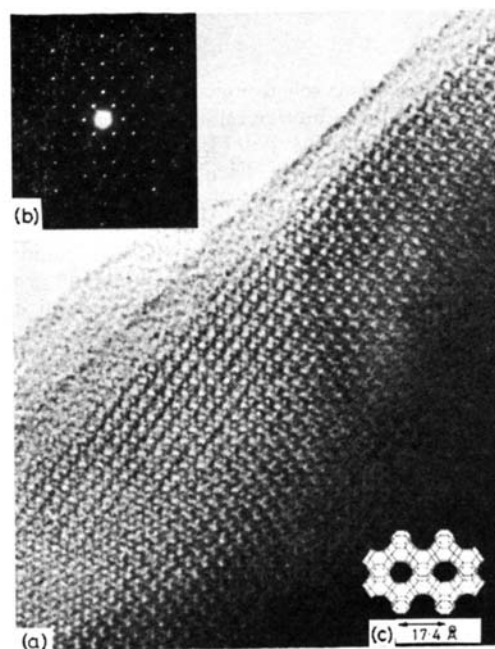


FIGURE 2. (a) High-resolution image of dealuminated synthetic faujasite along the $[110]_p$ zone axis. The image is exactly the same as for the parent Na-Y zeolite. (b) Selected area diffraction pattern corresponding to this zone axis. (c) $[110]$ projection of the framework.

We have further examined the dealuminated faujasite by HREM.¹⁰ Apart from its remarkable stability in the electron beam, much higher than for the parent Na-Y zeolite, it is seen (Figure 2) to possess a perfectly regular zeolitic framework. This novel material is likely to possess many unusual properties which are currently under investigation.

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