Investigation of the Dealumination of High Silica Zeolite A (ZK-4) by ^{29}Si Magic-angle-spinning N.M.R. Spectroscopy

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The high-field (11.7 T) ^{29}Si magic-angle-spinning n.m.r. spectrum of the completely siliceous analogue of zeolite A, prepared by hydrothermally dealuminating zeolite ZK-4, which consists of a single sharp resonance at −112.9 p.p.m. from Me_4Si is indicative of the removal of all the lattice aluminium and retention of the crystalline framework; powder *X*-ray diffraction measurements confirm that this novel material retains the framework topology of zeolite A.

In recent years ^{29}Si magic-angle-spinning (m.a.s.) n.m.r. spectroscopy has greatly contributed to the understanding of the structure of zeolites.[1] ^{29}Si M.a.s. n.m.r. spectroscopy can detect the relative amounts of the five structural groups, $Si(OAl)_n(OSi)_{4-n}$ (n = 0, 1, 2, 3, or 4), which may be present in a zeolite. In the case of zeolite A (Si/Al = 1.0) the ^{29}Si m.a.s. n.m.r. spectrum[1,2] consists of a single sharp resonance centred at δ *ca.* −89 p.p.m. from Me_4Si which is assigned to $Si(OAl)_4$. Zeolite ZK-4 has the same framework topology as zeolite A but has a Si/Al ratio of greater than unity.[3] The ^{29}Si m.a.s. n.m.r. spectrum[4] of zeolite ZK-4 consists of up to five peaks depending upon the Si/Al ratio and was instrumental in confirming the ordering in zeolite A as being $Si(OAl)_4$.[4]

More recently[5] we have shown that the ^{29}Si m.a.s. n.m.r. spectra of zeolites are greatly simplified following dealumination. Lines become very narrow and the line-broadening in low-Si/Al-ratio zeolites may be deduced as being due to the disorder in the aluminium distribution amongst second and further nearest neighbours. The increased resolution in dealuminated zeolites permits the observation of crystallographic inequivalent sites and suggests in some cases that previous ^{29}Si peak assignments are incorrect and that a detailed interpretation of some zeolite spectra is complex.

Zeolite A, commonly used as a molecular sieve, sorbent, and ion exchanger, and considered the 'prototype' zeolite might be considered impossible to produce in completely siliceous form owing to its high aluminium content, framework topology, and thermal and hydrothermal instability. We have found that by starting with highly siliceous zeolite ZK-4, prepared as previously described,[3] a completely siliceous analogue of zeolite A can be prepared by hydrothermal dealumination which retains exactly the framework topology of zeolite A.

^{29}Si M.a.s. n.m.r. spectra were obtained at 99.3 MHz using a home-built probe[6] on a narrow-bore Bruker AM-500 spectrometer (see acknowledgements) and are presented here with appropriate line broadening without resolution enhancement. Hydrothermal dealumination of zeolites has previously been described.[7] Dealumination of zeolite ZK-4 in this case was carried out hydrothermally by passing water vapour at atmospheric pressure over the hydrogen form of the zeolite sample maintained at 700 °C for 48 h, the temperature being monitored by a thermocouple inserted into the sample. Powder *X*-ray diffraction (X.r.d.) patterns were obtained on a Rigaku *X*-ray diffractometer.

Figure 1(A—C) shows the ^{29}Si m.a.s. n.m.r. spectra of zeolite A, the untreated zeolite ZK-4, and the product formed by hydrothermal dealumination carried out at 700 °C for 48 h. Figure 1(D—F) shows little change in the X.r.d. pattern upon dealumination, indicating that the framework structure is unchanged, although there is evidence of some amorphous material indicated by the variation in background. The cell dimension of the completely siliceous form is 23.68 Å compared to 24.61 Å for zeolite A itself and a theoretical value of 23.73 Å calculated from data by Gramlich and Meier.[8] The single peak in Figure 1(A) is assigned to $Si(OAl)_4$. The high-field peak in Figure 1(B) can be assigned to $Si(OSi)_4$, while the neighbouring peak is due to $Si(OSi)_3(OAl)$, the next peak is from the $Si(OSi)_2(OAl)_2$, and so forth. The sole peak at δ *ca.* −112.9 p.p.m. from Me_4Si in the spectrum of

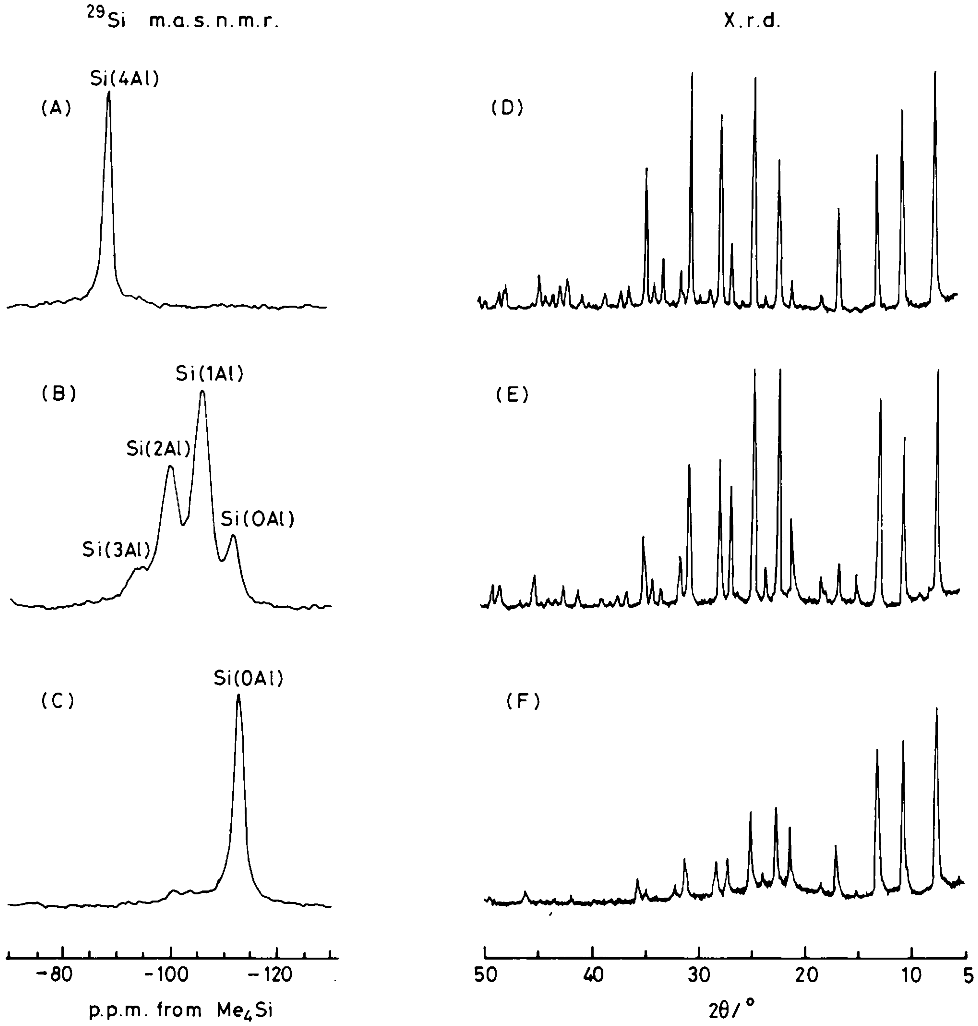

Figure 1. ^{29}Si M.a.s. n.m.r. spectra of (A) zeolite A, (B) zeolite ZK-4, (C) completely siliceous zeolite A, and (D—F) the corresponding powder X.r.d. patterns.

dealuminated ZK-4 (Figure 1C) is of course due to $Si(OSi)_4$. This high chemical shift for the highly siliceous analogue of zeolite A is due to silicon in the strained double four-membered rings in the zeolite A framework which result in large T–O–T angles. The very narrow line (*ca.* 1.8 p.p.m.) is indicative of the removal of *all* the lattice aluminium and retention of a crystalline framework as confirmed by the X.r.d. measurements.

We are currently investigating the sorptive properties and *X*-ray-determined structure of this novel material.

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