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ON THE SIMILARITY OF THE HIGH-RESOLUTION SOLID-STATE ^{29}Si AND ^{27}Al SPECTRA OF SILICALITE AND DEALUMINATED ZEOLITE ZSM-5

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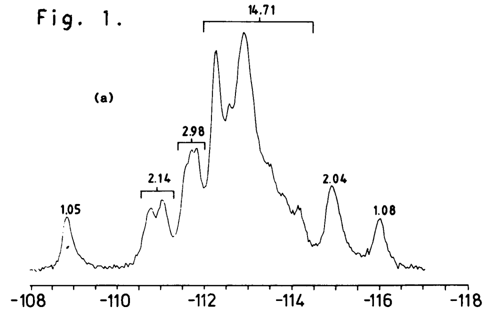
On dealuminating a sample of zeolite ZSM-5 (Si/Al ratio of 33.3 initially, 119 finally) at 540°C using silicon tetrachloride vapour, the ^{29}Si magic-angle-spinning NMR spectrum develops fine structure akin to that seen in the spectrum of silicalite, while the ^{27}Al spectrum confirms that Al has been removed from tetrahedral sites. This lends further support to the view that the framework structures of ZSM-5 and silicalite are closely similar.

If it is true, as now seems possible,[1)] that zeolite ZSM-5 and silicalite possess essentially the same framework structure; and if, in particular, silicalite contains tetrahedrally bonded aluminium and the difference between the two materials devolves upon their Si/Al ratios, it ought to be possible to generate, by dealumination,[2)] the rich fine structure in the ^{29}Si magic-angle-spinning (MAS) NMR spectrum which we have shown[1,3)] to be attributable to different, crystallographically non-equivalent $Si(OSi)_4$ groupings in the silicalite framework. As the practical repercussions of this proposed experiment are likely to be of considerable interest, we decided, along with our collaborators (Fyfe et al.[4)]) to conduct two separate, independent but similar sets of investigations, the results of which we now briefly report in tandem.

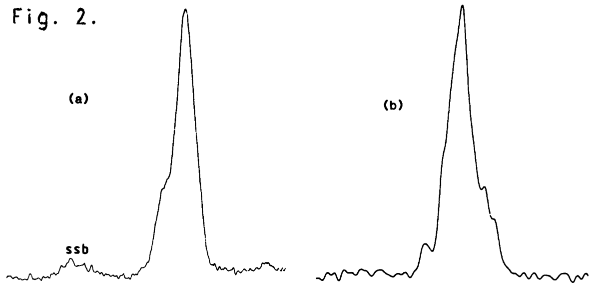
The parent ZSM-5 (kindly provided by Dr. M. Barlow) has a stoichiometry of $Na_{0.2}(NH_4)_{2.6}Al_{2.8}Si_{93.2}O_{192}$ corresponding to a Si/Al ratio of 33.3. The dehydrated sample was dealuminated at 540°C for 80h with dry nitrogen saturated, at room temperature, with $SiCl_4$. After thermal treatment the sample was washed with distilled water and dried at 100 °C in air. X-ray diffraction, high-resolution electron microscopy and IR spectroscopy showed it to be highly crystalline; and

Fig. 1.



^{29}Si MASNMR spectra of silicalite (Si/Al>1000) at 11.74T. Relative areas of signals (total normalized to 24) are indicated.

Fig. 2.



^{29}Si MASNMR spectra of zeolite ZSM-5.
(a) Parent material at 9.40T; (b) ZSM-5 dealuminated with SiCl$_4$ vapour. 4.70T spectrum.

the Si/Al ratio was found to be 119 by X-ray fluorescence. ^{29}Si and ^{27}Al MASNMR spectra were measured in the magnetic fields of 4.70, 9.40, and 11.74T (corresponding to ^{1}H frequencies of 200, 400, and 500MHz, respectively). Magic-angle rotors were spun at 3.6 KHz.

The spectrum at 11.74T of one of the high purity (Si/Al > 1000) silicalite samples (prepared by Dr. B. Nay, B.P. Sunbury) is shown in Fig.1a. It displays a little more detail than the silicalite spectrum recorded at 9.4T, which we have discussed fully elsewhere.$^{3)}$ Fig.2a gives the ^{29}Si MASNMR spectrum of the parent ZSM-5. The large peak (FWHM ≈ 7 ppm) centered at -113 ppm from TMS and the smaller signal at -105 ppm are due to Si(OSi)$_4$ and Si(OSi)$_3$(OAl) groupings respectively. The partial removal of Al from the ZSM-5 framework reveals non-equivalent tetrahedral Si(OSi)$_4$ sites owing to the significant reduction of the long-range chemical shift effect of residual Al atoms on the ^{29}Si spectra.

The key point emphasized in this communication is that silicalite and dealuminated ZSM-5 are structurally near-identical. These conclusions have been independently arrived at by Fyfe et al.$^{4,5)}$

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5) C.A. Fyfe, G.C. Gobbi, and G.J. Kennedy, to be published.

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