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INVESTIGATION OF THE FACTORS AFFECTING THE ^{29}Si MAS NMR LINEWIDTHS OF ZEOLITES

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The study of ^{29}Si MAS NMR spectra of zeolites of both low and high Si/Al ratios has provided insight on the factors affecting the residual ^{29}Si linewidths of these materials. It is found that the residual linebroadening in low Si/Al ratio zeolites is due to the distribution of local environments of a particular Si(nAl) type, resulting from the distribution of aluminium atoms in second and further coordination spheres. This is complicated in some cases by a distribution of chemical shifts resulting from crystallographic inequivalence, each of which is subject to the above environmental broadening factors.

It has been shown$^{1)}$ that, in many cases the ^{29}Si NMR spectra of zeolitic systems exhibit five resonances which fall within reasonably well-defined chemical shift ranges. A given SiO_4^{4-} tetrahedron is linked, via oxygen bridges, to four, three, two, one or no AlO_4^{5-} tetrahedra, and these environments are denoted Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al), respectively. At high magnetic fields, the five absorptions may be clearly resolved and the spectra deconvoluted in terms of Gaussian curves. However, there appears to be a substantial residual linebroadening in the spectra - the linewidths generally being in the range of 2-7 ppm, even at high fields. In comparison, although the ^{13}C CP/MAS spectra of amorphous polymers are in this range, linewidths of $\approx$ 1 ppm may generally be obtained for crystalline organic compounds. The present work attempts to identify the contributing factors to the ^{29}Si linewidths of the NMR spectra of zeolites and also characterizes crystallographically inequivalent sites in their frameworks.

There are two likely contributing factors to linebroadening in the ^{29}Si spectra of crystalline zeolitic systems: unaveraged dipolar interactions and distribution of local Si environments due to siting of silicon and aluminium atoms. Excluded are: magnetic field inhomogeneity (used a high and extremely homogeneous magnetic field$^{2)}$ and unaveraged shift anisotropy due to missetting of the spinning axis (careful experimental technique in which KBr was used to set the spinning axis.$^{3)}$

Dipolar interactions to protons are possible, but very little improvement in the spectra is observed when proton decoupling is employed. Hydrogen nuclei in zeolites are present as water of hydration and to a small extent as hydroxyl groups, but they are isotropically mobile and not directly incorporated into the zeolite framework. A second dipolar interaction which may be of importance is that between silicon nuclei and aluminium nuclei in the lattice. Since ^{27}Al is a quadrupolar nucleus, the spins will not be quantized along the Zeeman field direction and thus, dipolar couplings to the aluminium nuclei are not averaged to zero by magic angle spinning.

To elucidate the nature of the involvement of the aluminium nuclei in the residual broadness of the ^{29}Si resonances observed at high fields, a variety of highly siliceous zeolites have been prepared by hydrothermal dealumination of the corresponding low Si/Al zeolites using standard literature techniques.$^{4)}$ Figure 1 shows the ^{29}Si MAS NMR spectra at 79.5 MHz of low Si/Al ratio (< 10:1) and the corresponding high Si/Al ratio forms (> 100:1) of the zeolites Mordenite and Offretite. A very marked narrowing of the resonances is observed in both cases upon dealumination, yielding spectra with linewidths of 1 ppm or less. This is characteristic of all highly siliceous systems investigated to date. Clearly, the linebroadening mechanism involves the presence of the aluminium atoms in the zeolite framework.

If the linebroadening were due to unaveraged Si - Al dipolar interactions, the effects on the absorptions due to Si(3Al), Si(2Al), Si(1Al), and Si(0Al) should decrease down the series indicated. In general, although there is some discrimination between the absorptions, they are in all cases quite broad. In addition, there is little change in the spectra between 200 MHz and 400 MHz while these dipolar interactions should be greatly reduced. Although the broadening is caused by the aluminium atoms, it must be by a less direct mechanism than direct spin-spin interactions between the nuclei.

An alternate mechanism is that a large number of silicon environments for each of the different Si(nAl) first coordination sphere absorptions is created by the distribution of aluminium atoms in the second and further nearest coordination spheres. This effect may be manifest both by proximity of different atoms and by distortions of bond angles and bond lengths. Experimental proof that the ^{29}Si chemical shifts are indeed sensitive to second and further nearest neighbour interactions can be seen directly from the spectra in Figs. 1 A-D, where there is a substantial upfield shift of the Si(0Al) signal upon removal of aluminium atoms. This mechanism also explains why narrowing is only observed during dealumination to very high Si/Al ratios, as the placing of a single aluminium atom may affect many silicon atoms, and final narrowing will only be achieved when it is removed from the zeolite framework.

If the linebroadening is indeed due to the distribution of aluminium in second and further nearest neighbour coordination spheres, then narrow ^{29}Si resonances are predicted for any perfect

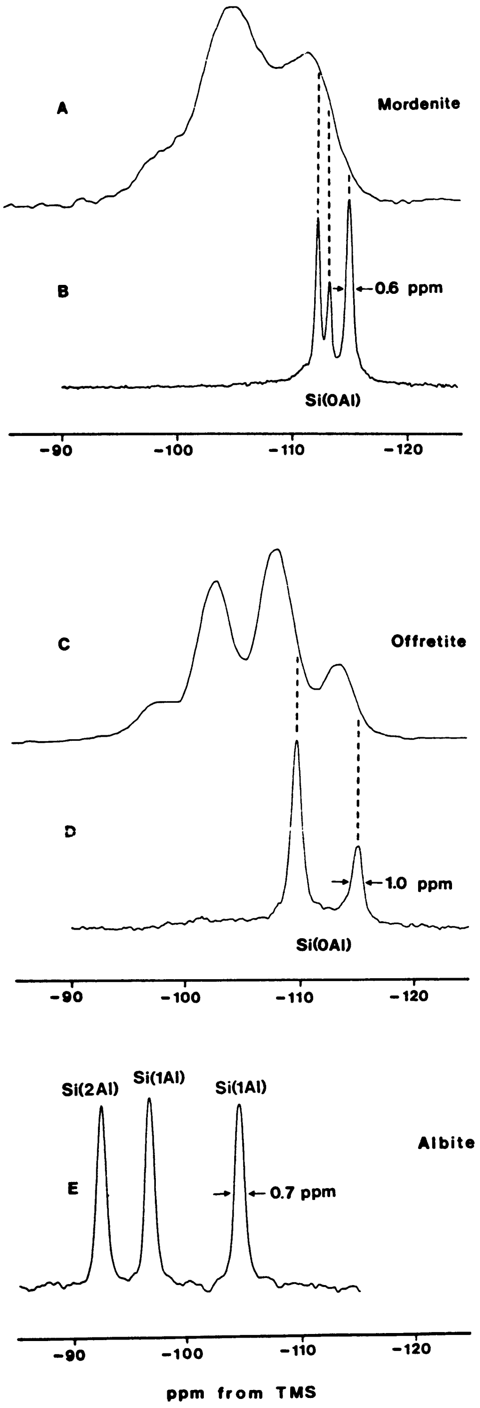

Fig. 1. ^{29}Si (79.5 MHz) MAS NMR spectra of:

A. Low Si/Al Mordenite (620 scans, 35 Hz linebroadening).

B. High Si/Al Mordenite (150 scans, 3 Hz linebroadening).

C. Low Si/Al Offretite (2154 scans, 20 Hz linebroadening).

D. High Si/Al Offretite (90 scans, 10 Hz linebroadening).

E. Albite (1180 scans, 25 Hz linebroadening).

ordered system, whatever the first coordination sphere environments may be. Thus, the sharp peak observed for zeolite A⁽⁶⁾ is considered to be due to the ordering which is perfect, and not particularly because the ordering is Si(4Al). Figure 1E presents a spectrum of high quality Albite, obtained to further test this hypothesis. The resonances are all relatively narrow ($\approx$ 0.7 ppm) and independent of the nature of the first coordination sphere.

An additional complication is also seen in Figs. 1 B,D which reveals the sensitivity of the ^{29}Si resonances to lattice effects, i.e. crystallographic inequivalence of the lattice sites. This effect has previously been observed in Silicalite,5) and the resulting shift dispersion may be quite large (up to 7-8 ppm). This distribution of shifts is an additional linebroadening mechanism and in some cases, e.g. Offretite Fig. 1D, can be of the same magnitude as the first coordination sphere effect. Two separate contributions are observed for the Si(0Al) peak at lower Si/Al ratios except they are substantially broadened by the effects described previously. In fact, the highest field peak is due to Si(0Al) but the next lowest peak in the low Si/Al ratios material must contain contributions from both Si(0Al) and Si(1Al) resonance. A complete assignment of all ^{29}Si NMR peaks, and a detailed description of the Offretite structure, will be reported.7)

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References

1) E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak, and G. Engelhardt, J. Am. Chem. Soc., 103, 4992 (1981).

2) C.A. Fyfe, G.C. Gobbi, J.S. Hartman, R.E. Lenkinski, J.H. O'Brien, E.R. Beange, and M.A.R. Smith, J. Magn. Reson., 47, 168 (1982).

3) J.S. Frye and G.E. Maciel, J. Magn. Reson., 43, 125 (1982).

4) C.V. McDaniel and P.K. Maher, "Zeolite Chemistry and Catalysis," ed by J.A. Rabo ACS Monograph 171, (1976), p.285.

5) C.A. Fyfe, G.C. Gobbi, J. Klinowski, J.M. Thomas, and S. Ramdas, Nature, 296, 530 (1982).

6) J. Klinowski, J.M. Thomas, C.A. Fyfe, and J.S. Hartman, J. Phys. Chem., 85, 2590 (1981).

7) C.A. Fyfe, G.C. Gobbi, W.J. Murphy, R.S. Ozubko, and D.A. Slack (in preparation).

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