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CHEMICAL SHIFT DISPERSION DUE TO CRYSTALLOGRAPHIC INEQUIVALENCE AND IMPLICATIONS REGARDING THE INTERPRETATION OF THE HIGH-RESOLUTION ^{29}Si MAS NMR SPECTRA OF ZEOLITES

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The ^{29}Si MAS NMR spectra of dealuminated zeolites have been studied, where the chemical shift dispersion due to structurally distinct SiO_4 tetrahedra is comparable (or greater) in magnitude to first coordination sphere effects. The results suggest that some previous ^{29}Si peak assignments are incorrect and that a detailed interpretation of some zeolite spectra is complex.

We have recently1) shown that a limiting linebroadening mechanism precludes the observation of crystallographic inequivalence in the ^{29}Si MAS NMR spectra of most zeolites of low Si/Al ratios. This mechanism is due to a distribution of silicon environments resulting from the distribution of aluminium in second and further nearest neighbour coordination spheres. It follows directly from this that, for zeolites which are not perfectly ordered, the corresponding dealuminated isomorphs have the greatest potential for exhibiting narrow ^{29}Si NMR resonances. In fact for ZSM-5, it has been observed2) that the linewidths progressively decrease (and thus the resolution increases) as aluminium is withdrawn from the zeolite framework. Linewidths as low as 0.3 ppm for ^{29}Si at 79.5 MHz (22 Hz) have been recorded for highly dealuminated, crystalline samples. Relatively narrow peaks are also observed for zeolites and minerals which are perfectly ordered, since the long-range aluminium distribution for "equivalent" sites is identical.1) In the case of highly ordered aluminosilicates and very highly siliceous zeolites, the resolution of the ^{29}Si spectra allows a direct comparison of the NMR spectra with the gross structural data obtained by X-ray diffraction techniques.

The ^{29}Si MAS high-field NMR spectra of zeolites are considered, to a first approximation, to be split into five resonances by $\sim$ 5 ppm as previously described,3,4) due to the presence (or absence) of aluminium in the first coordination sphere of a SiO_4^{4-} tetrahedron. A given SiO_4^{4-} tetrahedron is linked, via oxygen bridges, to four, three, two, one or no AlO_4^{5-} tetrahedra, and these modes are denoted Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al), respectively. With second and further nearest neighbour interactions in all cases, and additional crystallographic inequivalence in some cases, many different environments are created and substantial linebroadening results. In some cases, as will be shown, a shift dispersion due to crystallographic inequivalence may be comparable in magnitude to the dispersion observed for first coordination sphere effects yielding deceptively 'simple' spectra.

^{29}Si MAS NMR spectra were obtained at 79.5 MHz using previously described[5)] equipment on a narrow-bore Bruker WH-400 spectrometer. Spectra are presented with appropriate linebroadening without resolution enhancement. Dealuminations were carried out hydrothermally using standard literature techniques.[6)]

The structure of Offretite, elucidated by Gard and Tait,[7)] consists of columns of 14 - hedral gmelinite cages, and of 11 - hedral cancrinite cages alternating with hexagonal prisms (double six-membered rings). There are two topologically distinct tetrahedral sites present in the unit cell of Offretite, 12 of one type (T_1) and 6 of another type (T_2). The T_1 sites are located in the hexagonal prisms, while the T_2 sites are in the single six rings of the 11 - hedral cancrinite cages. Figure 1A demonstrates the effect on the linewidths of the ^{29}Si spectra of Offretite upon dealumination. Inspection of the figure reveals that the ratio of the two peaks present at -109.8 ppm and -115.1 ppm for the highly siliceous material, are in the ratio of 2:1. These we attribute to the 12 T_1 sites and the 6 T_2 sites, respectively. A noteworthy feature of this spectrum is the large chemical shift dispersion ($\approx$ 5.3 ppm) for the two structurally inequivalent silicon tetrahedra, which is comparable in magnitude to the first nearest neighbour effect. Previous peak assignments[8)] in Offretites of lower Si/Al ratios are therefore suspect. The general implications are that the detailed interpretation of some zeolite spectra may be more complex than previously described.

In the past, the two highest-field resonances of Offretite were assigned to Si(0Al) units, with lower field resonances being assigned Si(1Al), Si(2Al), and Si(3Al), following the assignment of peaks in clinoptilolite.[3)] A revision was then suggested[8)] in which the assignment of one of the Si(0Al) peaks was changed to Si(1Al), giving 2 Si(1Al) peaks, and one of each of Si(0Al), Si(2Al), and Si(3Al). The criterion being agreement between the Si/Al ratios determined by ^{29}Si NMR and by chemical analysis. It was suggested[8)] that the two Si(1Al) signals were due to two crystallographically inequivalent sites, but intuitively, one would expect to find two inequivalent sites for each Si(nAl) unit. We suggest that the high-field peak in the lower Si/Al ratio material is due solely to Si(0Al) from T_2 sites, while the neighbouring peak contains contributions from Si(0Al) in T_1 sites <u>and</u> Si(1Al) in T_2 sites. Similarly, the next resonance is the sum of Si(1Al) in T_1 sites and Si(2Al) in T_2 sites, and so forth. This interpretation gives Si/Al = 5.4 which is in agreement with the Si/Al ratio from chemical analysis (Si/Al = 5.1) assuming that the random 2:1 distribution of silicon atoms over the two sites is maintained for all the Si(nAl) environments (small deviations from this would not be easily detected). A complete analysis of Offretite samples covering a range of Si/Al ratios will be reported.[9)] The linebroadening in the lower Si/Al ratio material is due to second and further nearest neighbour interactions.

Using electron diffraction and single crystal X-ray analysis, Bennett and Gard[10)] demonstrated that Offretite and Erionite had closely related but distinctly different structures. They differ from one another by their stacking sequences, i.e. the manner in which the hexagonal rings and the hexagonal prisms are arranged. The Erionite unit cell consists of 24 T_1 tetrahedra and 12 T_2 tetrahedra, consistent with Fig. 1B, which reveals that the relative intensities of the two peaks in dealuminated Erionite are in the ratio of 2:1 (24:12). We suggest that the assignment of peaks for Erionite is similar to Offretite. Again, note the relatively large (≈ 5.6 ppm) shift dispersion due to structurally distinct sites which yields degenerate peaks and a deceptively simple spectrum for the low Si/Al ratio Erionite. The Si/Al calculated from the assignment (Si/Al = 3.6) in the figure again is in agreement with that from chemical analysis (Si/Al = 3.6).

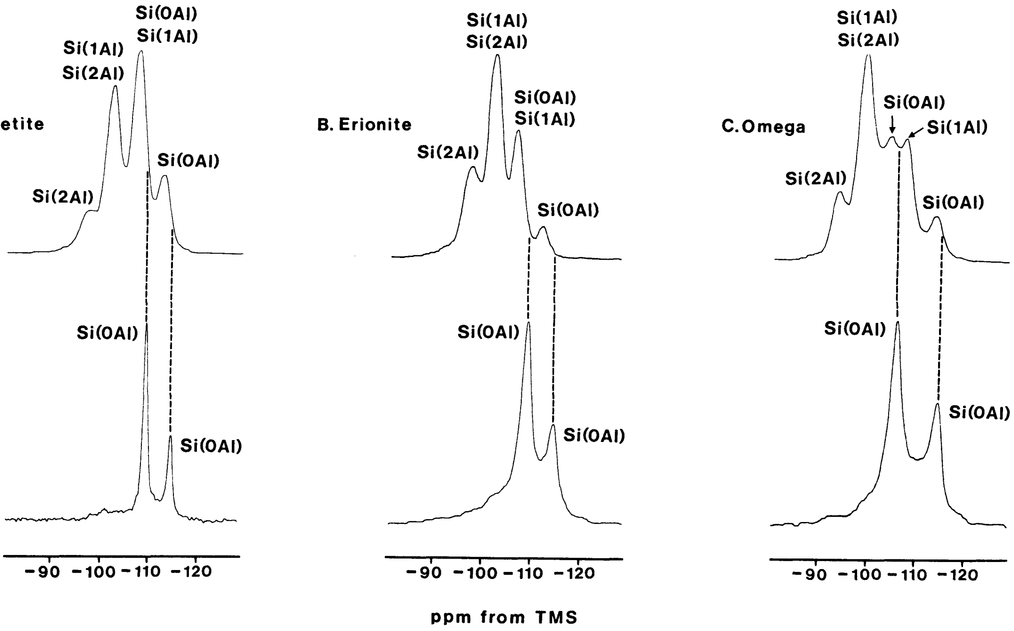

Fig.1. ^{29}Si (79.5 MHz) MAS NMR spectra of:

A. Low Si/Al Offretite (2154 scans, 20 Hz linebroadening) and High Si/Al Offretite (90 scans, 10 Hz linebroadening).

B. Low Si/Al Erionite (4544 scans, 10 Hz linebroadening) and High Si/Al Erionite (50 scans, 50 Hz linebroadening).

C. Low Si/Al Zeolite Omega (4215 scans, 25 Hz linebroadening) and High Si/Al Zeolite Omega (60 scans, 50 Hz linebroadening).

Zeolite Omega has the Mazzite[11)] type structure and its unit cell consists of 24 T_1 tetrahedra and 12 T_2 tetrahedra. The highly siliceous isomorph (Fig.1C) exhibits two ^{29}Si resonances in the ratio of 2:1 (24:12), which are separated by $\approx$ 8.5 ppm. This dispersion is quite large in comparison with Offretite ($\approx$ 5.3 ppm), Erionite ($\approx$ 5.6 ppm) and Silicalite ($\approx$ 7.1 ppm),[12)] and, in this case, it is larger than first coordination sphere effects. Consequently, two resonances at -103.5 ppm and -106.8 ppm are resolved and are assigned to Si(0Al) in T_1 sites and Si(1Al) in T_2 sites, respectively, suggesting the provisional assignment of the signals based on overlapping, additive contributions as shown (the same assignment based on different arguments has been proposed by Melchior and co-workers)[13)]. The ^{29}Si spectra of Omega are more complex and there are indications in the ^{27}Al spectra that substantial deviations from a statistical random distribution of aluminium[14,15)] can occur and these cases it will be difficult to unambiguously interpret them. Thus, the most thoroughly investigated cases of zeolites A, X and Y are deceptively simple in that they have single unique lattice sites. In other zeolites, crystallographic inequivalence will give multiple resonances and care must be taken in the interpretation of their ^{29}Si spectra.

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