

## Aluminium Partitioning in Zeolite L

J. M. Newsam

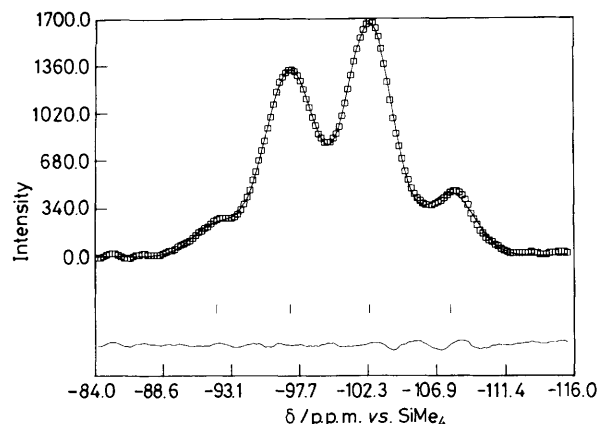
*Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801, U.S.A.*

Powder neutron diffraction has been used to measure directly the silicon–aluminium partitioning between the two tetrahedral sites in zeolite L; the similar environments of the two sites prevent simple measurement of this partitioning by  $^{29}\text{Si}$  n.m.r. spectroscopy, but enable its use as a probe of framework composition.

Local aluminium ordering and partitioning effects are important in defining the properties of aluminosilicate zeolites, particularly relative acid site strengths. Aluminium *distributions*, at least within the first co-ordination shell, are measured directly by  $^{29}\text{Si}$  n.m.r. spectroscopy.<sup>1</sup> Aluminium *partitioning* over, for example, two inequivalent T-sites (T = tetrahedral species, Si, Al, or Ga *etc.*) can be measured by  $^{27}\text{Al}$  n.m.r.<sup>2</sup> or, in certain instances, by detailed analysis of  $^{29}\text{Si}$  n.m.r. spectra,<sup>3</sup> although these measurements require that the chemical shifts for Al (or Si) at the two T-sites differ significantly. The expectation Al–O and Si–O bonds differ by some 0.14 Å<sup>4</sup> enabling precise structural studies to yield aluminium ordering/partitioning parameters if it is assumed that the mean T–O bond length varies linearly with relative aluminium population. Although of necessity widely used, the accuracy of this measurement is limited by, for example,

thermal libration effects and by the dependence of the observed bond lengths on the local framework geometry.<sup>5</sup> For X-rays, silicon and aluminium have near-identical scattering powers, making direct distinction between them impractical in all but the most precise analyses of data from single crystals.<sup>6</sup> The differing neutron scattering lengths of silicon [4.1491 fermi ( $\times 10^{-15}$  m)] and aluminium (3.449 fm) do allow a direct distinction between the two in single crystal studies<sup>7</sup> but no attempt has been made to exploit this difference in measuring aluminium partitioning in a synthetic zeolite. We have now used full profile analyses both of the powder neutron diffraction profile to measure the aluminium partitioning in zeolite L (both directly and from bond length considerations), and of the  $^{29}\text{Si}$  n.m.r. spectrum to measure the framework composition.

The powder neutron diffraction profile of a dehydrated



**Figure 1.** Observed ( $\square$ ), calculated (continuous line), and difference (lower)  $^{29}\text{Si}$  n.m.r. spectral profiles for aluminosilicate zeolite L. The spectrum was fitted as a sum of four gaussian terms and the optimized central peak positions are indicated by the vertical bars.

sample of a potassium zeolite L,  $\text{K}_9\text{Al}_6\text{Si}_{27}\text{O}_{72}$  was recorded at ambient temperature on the powder diffractometer of the Missouri University Research Reactor. An approximate structural model was taken from Barrer and Villiger<sup>8</sup> and the parameters describing the framework and five nonframework potassium cation sites were then optimized, iteratively, by full-matrix least-squares profile analysis.<sup>9</sup> The partitioning of aluminium over the two tetrahedral sites was treated as a variable, the total aluminium population being constrained so as to satisfy the known chemical composition. This direct measurement of the partition factor,  $P = F_{\text{T4}}/F_{\text{T6}}$  [where  $F_{\text{T4}}$  is the fractional aluminium occupancy of site T4 or Si(1)], yielded a value of  $P = 1.4(3)$ . The partition factor calculated from the mean bond lengths to Si(1) and Si(2) of 1.650(4) and 1.636(3) Å, respectively, is 1.4(2), in good agreement. The aluminium is located preferentially in the Si(1), T4 sites, in contrast both to the random partitioning found in gallosilicate zeolite L<sup>10,11</sup> and to the aluminium preference for the Si(2), T6 sites indicated by the earlier powder X-ray diffraction results.<sup>8,12</sup> The mean T–O–T angles for the two sites, 142.0(3)° and 142.9(2)° respectively, are similar, consistent with structural results from several other LTL-framework zeolites.<sup>11</sup>

The similar geometries of the two T-sites imply that the corresponding  $^{29}\text{Si}$  n.m.r. chemical shifts will be similar. The  $^{29}\text{Si}$  n.m.r. spectrum (Figure 1)<sup>11</sup> was digitized on a Summagraphics Bit Pad One and fitted as a sum of four gaussian terms

whose intensities, central positions, and half-widths were each taken as independent variables. Treating the spectrum in this way as a single site case gives an excellent fit to the data (Figure 1). Further, the framework Si:Al ratio calculated from the optimized intensities as  $(\text{Si}:\text{Al}) = 4 \sum I_n / \sum n I_n$ ;  $n = 0-3$ , is 2.89, in good agreement with the ICPES chemical analysis result, 2.87.<sup>11</sup> Thus although the similar environments of the two T-sites prevent the direct use of  $^{29}\text{Si}$  or  $^{27}\text{Al}$  n.m.r. spectroscopy to measure the aluminium partitioning, they allow importantly the use of  $^{29}\text{Si}$  n.m.r. spectra as a measure of framework composition.

A key component in the successful application of full profile analysis to powder diffraction data is the ability to calculate precise peak positions from the crystallographic unit cell parameters. Improved descriptions of the geometrical and compositional dependencies of the  $^{29}\text{Si}$  chemical shifts<sup>13</sup> promise to enable full profile analysis methods to be extended to fitting the  $^{29}\text{Si}$  n.m.r. spectra of even highly complex zeolites.

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