

## Zoning of Aluminium among Different Crystallographic Sites in Zeolite Omega

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<sup>27</sup>Al Magic angle spinning n.m.r. demonstrates that the preferential incorporation of aluminium into six-membered rings of the framework of zeolite omega decreases during the growth of the crystal, giving rise to a gradient in the aluminium occupation of the crystallographic sites.

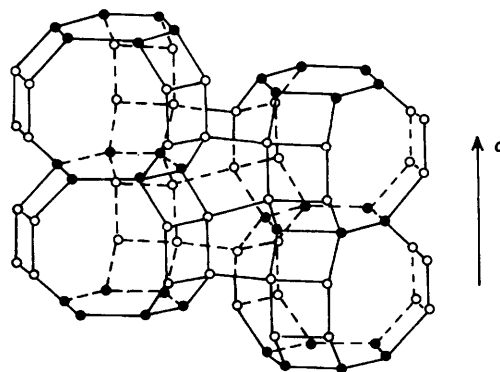
The occurrence of compositional zoning in synthetic zeolites is well known. For example the gradients of the Si/Al ratio from core to rim are negative for ZSM-5<sup>1</sup> and positive for zeolite beta.<sup>2</sup> In both cases the preferential incorporation of one of the elements in the first stages of crystallization increases the concentration of the other element in the growth medium, and hence its concentration on the outer parts of the crystallite.

We report here a different type of zoning, which concerns the distribution of the AlO<sub>4</sub><sup>-</sup> tetrahedra among the different crystallographic sites of zeolite omega.

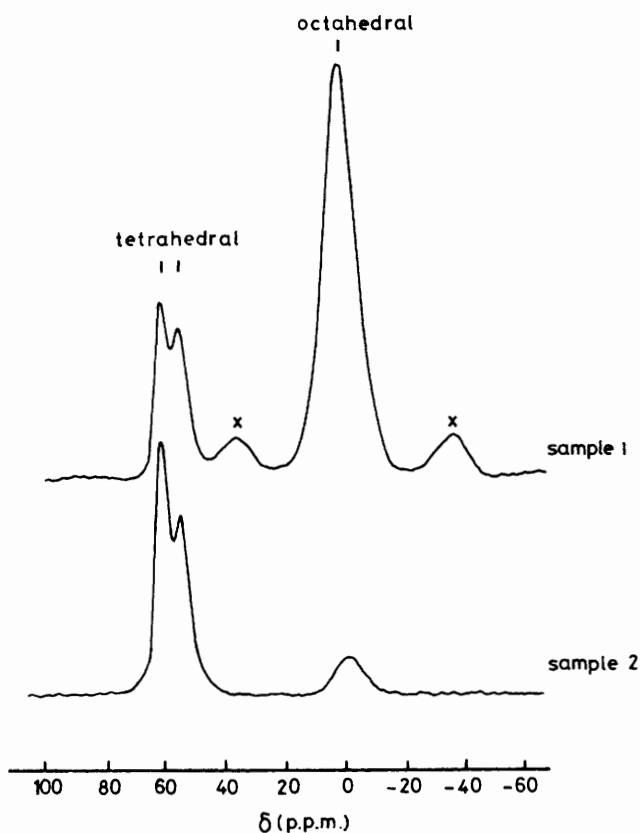
The framework of zeolite omega is composed of tetrahedra located in two types of geometrical environment: sites A in four-membered rings, and sites B in six-membered rings<sup>3</sup> (Figure 1). <sup>27</sup>Al N.m.r. allows us to differentiate the aluminium atoms located in these two types of sites.<sup>3,4</sup> A quantitative estimate of the AlO<sub>4</sub><sup>-</sup> tetrahedra occupying each kind of site is possible, provided that the spectra are registered at high field and using short radiofrequency pulses.<sup>5-8</sup> The literature values for the ratio Al<sub>A</sub>/Al<sub>B</sub> deduced from this treatment range from 0.9 to 1.6, depending on the mode of preparation of the samples.<sup>3,4,9</sup> Sites A outnumber sites B by a factor of 2 and thus random distribution of the aluminium atoms between the two types of sites corresponds to an Al<sub>A</sub>/Al<sub>B</sub> ratio of 2. Hence the lower experimental values of the Al<sub>A</sub>/Al<sub>B</sub> ratio denote a preferential incorporation of aluminium in sites B.

The aim of the present work was to determine if any zoning of the Si-Al distribution between the two crystallographic sites exists inside the crystal. To this end, intermediate samples of product were collected during the hydrothermal conversion of kaolinite into zeolite omega, and were analysed by <sup>27</sup>Al magic-angle-spinning (m.a.s.) n.m.r. spectroscopy. The spectra were recorded at 104.27 MHz with a Bruker MSL 400 spectrometer. The spinning rate was 4.0 kHz, and 100 free

induction decays were accumulated per sample at a recycle time of 2 s. Radiofrequency pulses of 2 μs (*ca.* π/6) were used in order to ensure quantitative line intensities. The procedures of the synthesis, the sampling, and the characterization of the solids are detailed elsewhere.<sup>10,11</sup> The molar composition of the parent medium was 2.6(0.94Na·0.06TMA)<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·8.8SiO<sub>2</sub>·165H<sub>2</sub>O (TMA = tetramethylammonium). The synthesis was carried out at 115 °C under autogeneous pressure in a 500 ml stainless-steel stirred reactor allowing periodic sampling. The solid fraction was recovered by filtration, washed with deionized water and dried at 75 °C. Samples collected at 50 and 90% conversion (as determined by powder X-ray diffraction) are referred to here as samples 1 and 2, respectively. Habit and size of the crystals of zeolite



**Figure 1.** Structure (*P6<sub>3</sub>/mmc*) of zeolite omega: open circles: sites A (24 per unit cell), located in the four-membered rings; filled circles: sites B (12 per unit cell), located in the six-membered rings.



**Figure 2.**  $^{27}\text{Al}$  m.a.s. n.m.r. spectra at 104.27 MHz; chemical shifts in p.p.m. from  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ; crosses indicate spinning sidebands of the 0 p.p.m. signal of kaolinite.

were determined by scanning electron microscopy. In sample 1 zeolite crystals appeared as cylinders 1.4  $\mu\text{m}$  in length and 1.6  $\mu\text{m}$  in diameter. In sample 2 they have grown to hexagonal prisms of 5.5  $\mu\text{m}$  in length, with double apothem 1.8  $\mu\text{m}$ . In both samples zeolite omega and unchanged kaolinite were the only solid phases present.

The  $^{27}\text{Al}$  m.a.s. n.m.r. spectra of the two samples are given in Figure 2. The two peaks in the 50–65 p.p.m. region due to the tetrahedral aluminium can be attributed to the sole zeolitic

product: they are not perturbed by the peak at 0 p.p.m. due to the octahedral Al of the kaolinite. The  $\text{Al}_A/\text{Al}_B$  ratio deduced by deconvolution of the two Lorenz curves increases from 1.10 in sample 1 to 1.25 in sample 2; this represents clear evidence for a gradient of Al distribution between sites A and B in the crystal.

The preferential incorporation of aluminium in site B is thus more effective in the earlier stages of the crystallization; the distribution approaches randomness in the later stages.

Distributional zoning results most probably from changes in the synthesis medium during crystallization. This suggests that not only the chemical composition but also the nature of the growth units is being modified. More detailed studies are required to rationalize the factors directing Al incorporation. Nevertheless it may be expected that the outcome of such studies will be of paramount importance for the application of zeolites as catalysts, since both the strength of the acid sites and the thermal and hydrothermal stabilities of the solid are influenced by the location of the aluminium atoms.<sup>12,13</sup>

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