

^{27}Al MAS NMR Studies of a New Polyoxyaluminium Cluster and its Selective Transformation to Five-coordinate Aluminium in the Solid State

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Solid state ^{27}Al MAS NMR (MAS = magic angle spinning) studies of a new large polyoxyaluminium cluster cation provide insight into its structure, and show that thermal treatment at 850 °C yields a novel transitional aluminium oxide containing a metastable five-coordinate aluminium site.

Alumina sol–gels are precursors for a multitude of ceramic materials ranging from transparent matrices for laser-dye hosts to ceramic refractory fibres and heterogeneous catalyst supports.¹ These are often formed by thermal processing of simple precursors at high temperatures. In spite of the fact

that thermodynamics determines the ultimate ceramic phase, the molecular nature of the sol–gel should control the kinetic pathway that is followed. This raises the question of whether unique and interesting metastable phases can be formed from specific precursor materials.

Only one polyoxycation of aluminium has been isolated and well-characterized: $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Al_{13}), which has the well known Keggin ion structure.² This cluster cation is a ubiquitous component of many alumina sol-gels. Circumstantial evidence exists for many other clusters,³ but until recently their isolation and study was precluded by the complexity of these solutions.

In a previous paper, we identified two new larger polyoxycation clusters of aluminium in solution, dubbed AIP_2 and AIP_3 .⁴ We have shown that these are formed by the thermal treatment of Al_{13} in solution at 90 °C. The results of kinetic NMR analysis, together with quantitative NMR studies, have led us to propose that AIP_2 is produced by the dimerization of two Al_{12} units formed from the loss of an octahedron from Al_{13} . The resulting cluster, tentatively formulated as $\text{Al}_{24}\text{O}_{72}$, is remarkably stable in solution, but eventually transforms on further heating to AIP_3 . We found that AIP_2 (as well as AIP_3) has similar NMR features in solution to that of Al_{13} : namely, $\delta(\text{tet}) = 70.2$; $\delta(\text{oct}) = 10.0$. However, the broadening of the Al(4) resonance, coupled with the dramatic narrowing of the Al(6) signal compared to that of Al_{13} , shows that the local structure must be significantly different in this cluster.

In this communication, we present the first solid state MAS study of the sulfate salt of AIP_2 . These results support our original proposed structure. We find that unlike Al_{13} , AIP_2 undergoes solid state thermal transformation to a material containing a very large fraction of five-coordinate aluminium.

The AIP_2 cluster cation was prepared as described previously⁴ and separated by gel-permeation chromatography. The sulfate salt of AIP_2 was isolated as a microcrystalline powder from a solution containing the pure polyoxycation.

The solid state ^{27}Al MAS NMR 130.3 MHz spectrum of the sulfate salt of AIP_2 , Fig. 1, shows two peaks at δ 68.4 and 3.5 assigned to tetrahedral and octahedral Al, respectively. MAS averages the chemical shift anisotropy and dipole-dipole interactions to zero. The second-order quadrupole interaction, however, is not averaged but leads to a field-dependent shift from the isotropic value, which depends on the magnitude of the quadrupole coupling constant, Q_c . The observed chemical shifts of the tetrahedral resonance of AIP_2 at 104.2 and 93.8 MHz are δ 67.5 \pm 1 and 65.5 \pm 2, respectively. An extrapolation to infinite field yields an isotropic value of 70 ppm, identical to that in solution. A least-squares analysis of the data yields $Q_c = 2.2$ MHz, assuming $\eta = 0$.[†]

The Q_c value for the octahedral resonance could not be accurately determined using this method, as the line was broad at the lower field strengths. In addition, it is likely that a range of octahedral sites contribute to the observed peak, each with a different quadrupole coupling constant (and hence different second-order shift). Double rotation⁵ (DOR) ^{27}Al NMR was unable to resolve these sites. In solution, the linewidths ($1/\pi T_2$) are determined by the quadrupole coupling.⁶ Since we know Q_c for the tetrahedral site, we can, therefore, estimate the average Q_c for the octahedral site from the ratio of the linewidths of the octahedral and tetrahedral sites. These were determined to be 1665 and 320 Hz, respectively (solution NMR data at 90 °C).⁴ This gave an average $Q_c(6)$ of 5 MHz. By comparison with the values for Al_{13} [$Q_c(4) = 0.8$ MHz; $Q_c(6) = 10.2$ MHz],⁷ we find that $Q_c(4)$ has increased in AIP_2 , implying a destruction of the pure tetrahedral symmetry at this site. Conversely, $Q_c(6)$ has decreased substantially in AIP_2 , at least on average. These changes in structure appear to have a significant effect on further thermal transformations.

The NMR parameters provide further insight into the structure of this cluster. First, the radius, a , of AIP_2 can be estimated from the Stokes-Einstein-Debye equation:^{6,8} $\tau_c = 4\pi f \eta a^3 / 3kT$, where η is the viscosity, and f is the microviscosity coefficient. We determined τ_c from the linewidth for the

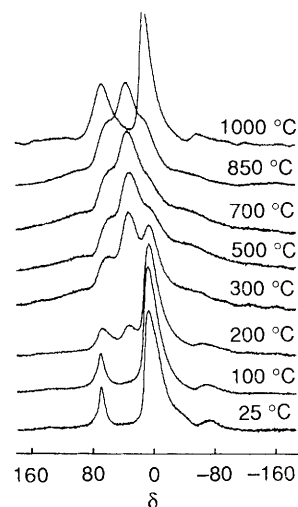


Fig. 1 (lower trace, 25 °C): ^{27}Al MAS NMR spectra at 11.7 T (130.3 MHz) of the sulfate salt of AIP_2 ; (upper traces): after calcination for 0.5 h at 100, 200, 300, 500, 700, 850 and 1000 °C. Spectra were accumulated with 4000 scans using a 2 μs pulse width, at a spinning rate of 9 kHz.

tetrahedral site, assuming pure quadrupolar relaxation with the measured $Q_c(4)$. With $\eta = 10^{-2}$ poise and $f = 0.6$,^{8,9} we find that the radius of AIP_2 is 7 Å. This is in good agreement with the average radius of 7.2 Å calculated from a model in which two Al_{12} clusters are dimerized to form an $\text{Al}_{24}\text{O}_{72}$ cluster. As a check on the validity of this approach, we used this same method for Al_{13} , with our value of $1/\pi T_2(4) = 20$ Hz at 90 °C, and $Q_c = 0.8$ MHz.⁷ This gave a calculated radius of 5.5 Å, in excellent agreement with the literature value of 5.4 Å.² Secondly, the established correlation between the ^{27}Al chemical shift, and the Al-O bond length suggests that the bond length (or angle) at the tetrahedral site has decreased substantially relative to that of Al_{13} .¹⁰ This is confirmed by our Fourier transform infrared (FT-IR) spectra of AIP_2 , which show $\nu(\text{AlO}_4)$ at 775 cm^{-1} , compared to that of 725 cm^{-1} for Al_{13} . The corrected solid state chemical shift for the AIP_2 tetrahedral site in comparison with other aluminates indicates that the average bond length is closer, for example, to that reported for zunyite, [$\delta = 72$, $d(\text{Al}-\text{O}_4) = 1.80$ Å]⁷ than in Al_{13} ($\delta = 62.9$, $d = 1.84$ Å).

Thermal treatment of AIP_2 in air produces dramatic changes in the MAS ^{27}Al NMR spectra, shown in Fig. 1. After thermal treatment at 200 °C for 0.5 h, a new peak is evident in the spectrum at δ 35, midway between the Al(4) and Al(6) resonances. Although an assignment to Al in a very highly distorted four-coordinate site cannot be ruled out, there is no precedent for such a large low-frequency shift in the absence of second-sphere coordination to heteroatoms (*e.g.*, Si). The signal, however, is well within the range reported for five-coordinate Al. Well-documented examples of this site in solid state oxides are few, but values reported for Al(5) in andalusite, barium aluminium glycolate and in $\text{Al}_2\text{Ge}_2\text{O}_7$ show an isotropic chemical shift between δ 30–37.^{11a,b} Signals attributed to Al(5) in less well-characterized materials have also been reported in this spectral region.¹² The δ 35 peak begins to dominate the spectrum after treatment at 300 °C: at 500–850 °C, the Al(6) resonance has collapsed, and the Al(5) signal accounts for almost all of the NMR spectral intensity. This coincides with a small weight loss (4%, broad endotherm) in the thermal analysis curve. Variable-speed spinning of the sample (up to 12 kHz) showed that the shoulders of this broad signal were due to residual Al(4,6) sites, and/or high order quadrupole structure in the Al(5) site, not spinning side bands. X-Ray diffraction (XRD) analysis indicated that the

[†] Even if $\eta = 1$, this would result at the most in an increase of 15% in e^2qQ/h .

material was quasi-amorphous. Between 850 and 1000 °C, this phase is converted into transitional alumina (the spinel phase of η -alumina), evidenced by the Al(4) and Al(6) resonances at δ 67 and 9, respectively, and confirmed by the powder XRD pattern of the calcined material.

This is the first example of the formation of Al(5) in the solid state from a specific precursor. It is also unusual in that it occurs in an aluminium oxide (in contrast to an aluminosilicate or phosphate) lattice. We also believe that AlP_2 may be the precursor to five-coordinate Al formed in other sol-gels on thermal treatment.¹² In our investigation of other aluminium polyoxycation sulfates such as $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8][\text{SO}_4]_2$ and the Al_{13} salt, we find that AlP_2 is unique in its propensity to form five-coordinate Al. A signal at δ 35 is also observed on thermal treatment of Al_{13} between 300–500 °C, as previously noted by others, albeit of much lower intensity.^{12a} This may be the result of partial transformation of Al_{13} to AlP_2 in the solid state at lower temperatures, since it is preceded by the appearance of a shoulder at δ 70 on the tetrahedral resonance of Al_{13} . Two factors appear to be responsible for the evolution of Al(5) in the present case: the specific bonding at the Al(4) and/or Al(6) sites, and the presence of an anion, which may partially stabilize the site.‡

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‡ The AlP_2 chloride salt also gives rise to a large proportion of Al(5) at δ 35 on thermal treatment, albeit slightly less than in the sulfate.