

# Inorganic aluminium precursors in the synthesis of mullite – an investigation

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A variety of inorganic aluminium sols were investigated for their reactivity with colloidal silica to form polycrystalline mullite. Nuclear magnetic resonance (NMR) spectroscopy was used on the precursor aluminium sols to ascertain the co-ordination and reactivity of the species present. Differential thermal and thermogravimetric analysis and X-ray diffraction were used to analyse the products of the fired xerogels. Commercial reactants produced diphasic materials with little or no mullite formed at 1000 °C. A monomeric/dimeric sol produced in house however, showed a sharp exotherm at 920 °C and crystalline mullite formation at this temperature.

## 1. Introduction

Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is recognized as a highly promising ceramic for high-temperature structural applications, and as such it has been extensively studied over the last decade. Its properties such as high creep resistance, low density, low thermal conductivity and high temperature chemical stability can only be exploited if high purity densifiable powders with a small crystallite size can be readily produced and at the moment such powders are not commercially available.

The major problem in achieving crystalline single phase mullite, is to achieve a homogeneous mixing of alumina and silica in the precursor material or xerogel. Hoffman and Roy [1] postulated that differences in the homogeneity on the nano-scale produced monophasic and diphasic xerogels which in the organo-metallic sol-gel synthesis was related to the rate of hydrolysis. Monophasic gels showed a sharp exotherm at 980 °C which was attributed to mullite crystallization from an amorphous precursor, while diphasic gels showed no such exotherm, instead a silica substituted spinel phase was produced at lower temperatures which transforms to mullite at 1380 °C. These observations were reproduced in later publications [2–4].

The colloidal sol-gel approach, which is entirely inorganic, has shown benefits over organic routes in respect of commercially cheaper processing and producing products which more readily densify at lower temperatures [5–7]. However, in recent publications [7–10], the use of boehmite sols and colloidal silicas has produced only diphasic gels and subsequent mullite formation at only 1400 °C. These products however, have improved densification properties over the monophasic products.

Recently, the concentration of penta-coordinate  $\text{Al}^{3+}$  at inhomogeneous boundaries in the gel, has been shown to be critical to the amount of mullite crystallization that occurs at 980 °C in monophasic precursors [11]. Entirely 4 and 6 co-ordinate diphasic gels showed no mullite formation at this temperature.

This paper therefore, explores the inorganic sol-gel approach to the synthesis of mullite using a variety of aluminium precursors, and studies the reactivity with a specific silica sol, using solution  $^{27}\text{Al}$  NMR to investigate the amount, reactivity and nature of the aluminium species present.

## 2. Experimental procedure

### 2.1. Alumina precursor materials

The commercial precursor/sol materials used were degussa 'aluminumoxide C' flame hydrolysed powder (99.6% alumina), Condea 'disperal' pseudo boehmite powder (74% alumina) and Hoersch aluminium chloride 'Locron P' (47.5% alumina). In addition, a novel inorganic alumina sol was made by extracting the anions from a 2 M aluminium nitrate solution (Aldrich 99%), using an organic tertiary alkyl amine dissolved in a suitable dense solvent. The resulting sol was dried to a glassy transparent gel, redispersed in distilled water and filtered to  $< 0.2 \mu\text{m}$ . The final sol was completely transparent with a  $\text{NO}_3^- : \text{Al}^{3+}$  ratio of 0.9.

### 2.2. The preparation of mullite xerogels

The commercial source for the silica sol was Monsanto's Syton D30 colloidal silica (summer grade), which was always acidified to pH 3–4 with nitric acid before adding to any alumina precursor, in order to

avoid gellation. Mixed sols were made to a concentration of  $\sim 250 \text{ g l}^{-1}$  total oxide by slowly adding filtered and pH adjusted alumina precursor to the silica. The mixed sols were then evaporated to glassy gels at  $60^\circ\text{C}$  and then calcined to various temperatures in an atmospheric muffle furnace.

The novel  $\text{Al}^{3+}$  sol was also mixed as above and spray dried on a Niro mobile minor spray drier to yield  $5\text{--}15 \mu\text{m}$  gel particles.

### 2.3. Characterization techniques

Differential thermal and thermogravimetric analysis (DTA/TGA) of the samples was performed to determine the phase changes as well as the weight loss of gel samples using a Polymer Laboratories thermal analyser (Model STA1500). Flowing air was used as the normal atmosphere and the temperature was ramped at a rate of  $10^\circ\text{C}$  per min.

X-ray powder diffraction (XRD) patterns for samples treated at various temperatures were recorded in the region of  $2\theta = 5\text{--}120^\circ$  with a step scan of  $0.1^\circ$  per min on a Philips diffractometer (Model PW1710) using  $\text{CuK}\alpha$  radiation. Cell parameters were calculated and further refined using linear regression procedures (Philips APD 1700 software) applied to the measured peak positions of all major reflections up to  $2\theta = 90^\circ$ . Nuclear magnetic resonance spectroscopy (NMR) was performed on a Bruker ACP 400 spectrometer with a 9.1 T superconducting magnet and a probe tuned to the  $^{27}\text{Al}$  isotope.

### 3. Results and discussion

With particle sizes in the range of  $50\text{--}100 \text{ nm}$ , the Condea and Degussa based colloidal gels were thought likely to be the most diphasic or inhomogeneous and were therefore characterized first. As expected, the X-ray diffraction (XRD) patterns of these two xerogels showed no mullite formation at temperatures below  $1000^\circ\text{C}$ , the Degussa mixture being almost completely amorphous, whilst the Condea mixture showed strong reflections characteristic of the spinel phase. Heating the Condea based gel to  $1400^\circ\text{C}$  however, produced crystalline orthorhombic mullite with a slight amorphous silica background.

XRD patterns of the chlorhydrate based xerogel however, showed a more interesting development. At  $800^\circ\text{C}$ , small peaks due to mullite formation were seen, along with the spinel phase and amorphous silica. At  $1000^\circ\text{C}$ , Fig. 1, approximately 20% of the phase is mullite and the spinel reflections have intensified, but no further increase in the mullite percentage is seen until  $1400^\circ\text{C}$ , as is the case in the more colloidal gels.

The DTA/TGA analysis of the chlorhydrate mixed gel is shown in Fig. 2. This shows the presence of an exotherm at  $800^\circ\text{C}$  due to the 20% mullite formation seen in the XRD pattern, and a small exotherm at  $980^\circ\text{C}$  probably due to the crystallization of a silica substituted spinel phase.

This behaviour of the chlorhydrate precursor material suggests that it contains two or more species

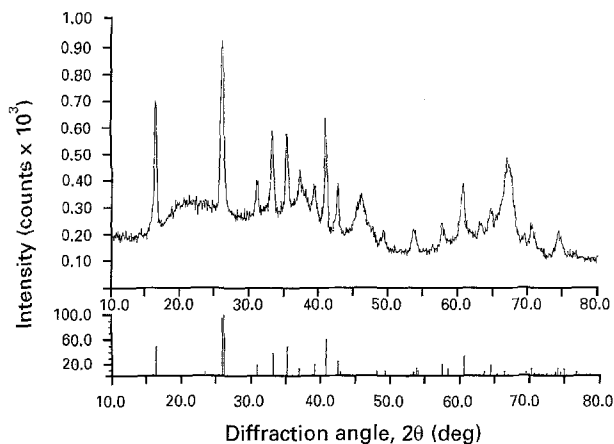


Figure 1 XRD pattern of the chlorhydrate based xerogel at  $1000^\circ\text{C}$ . For comparison purposes the JCPDS card 15-776 for  $\text{Al}_6\text{Si}_2\text{O}_{13}$  is also shown.

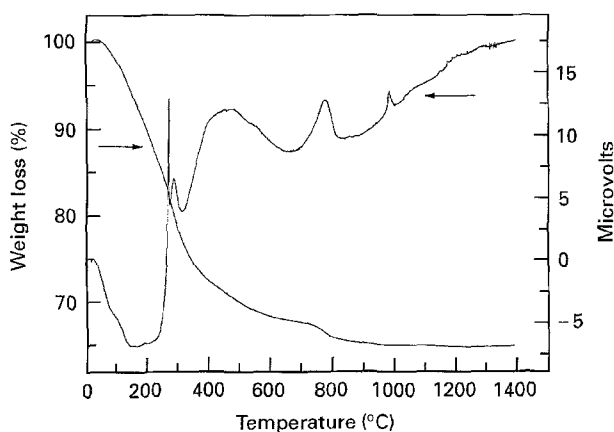


Figure 2 DTA/TGA of the chlorhydrate based gel dried to  $105^\circ\text{C}$ .

with greatly different reactivities towards the formation of mullite. In order to investigate this, solution NMR was performed on the precursor chlorhydrate sol. A typical spectra on the  $^{27}\text{Al}$  isotope is shown in Fig. 3. This shows the presence of six co-ordinate Al at 0 ppm, a five co-ordinated species at 11 ppm and a four co-ordinated species at 63 ppm. The former is indicative of monomeric hexa-aquo  $\text{Al}^{3+}$ , whilst the latter two are characteristic of the keggion ion structure  $[\text{Al}_{13}(\text{OH})_{24}\text{O}_4(\text{H}_2\text{O})_{12}]^{7+}$ , where the four co-ordinated species is a single  $\text{Al}(\text{OH})_4^-$  unit at the cage centre surrounded by the five co-ordinated species on the cage shell. Considerable work on aluminium hydrate solutions [12] using infra red/Raman spectroscopy and turbidity measurements has indicated that the method of production influences the proportion of monomeric, polymeric  $\text{Al}_{13}$ , aggregated polymeric  $[\text{Al}_{13}]_n$  and colloidal species. In nitrate based alumina hydrate solutions at pH 4–6, the Keggin ion above is believed to be predominant but in chloride based solutions as in the chlorhydrate used in this study, it has been shown that considerable further aggregation occurs resulting in large unreactive polymers. This explains the partial formation of mullite at low temperature (the monomeric and unaggregated species reacting), while the majority of the chlorhydrate

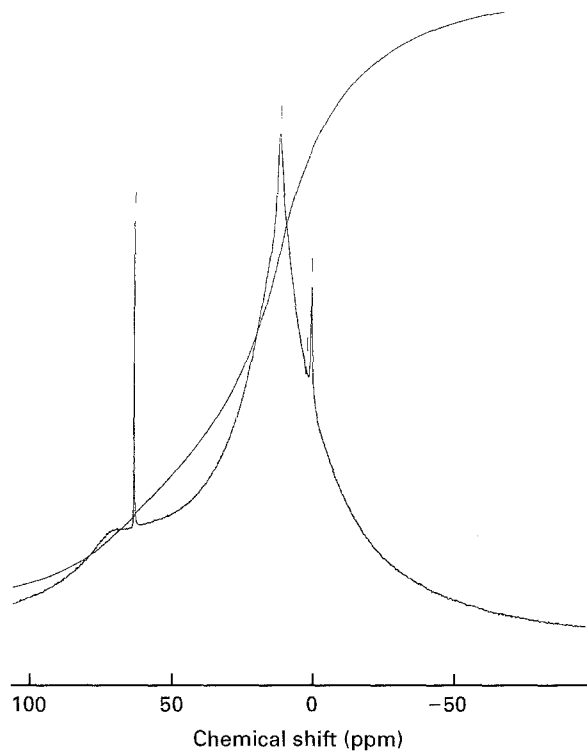


Figure 3  $^{27}\text{Al}$  solution NMR of the commercial aluminium chloride hydrate.

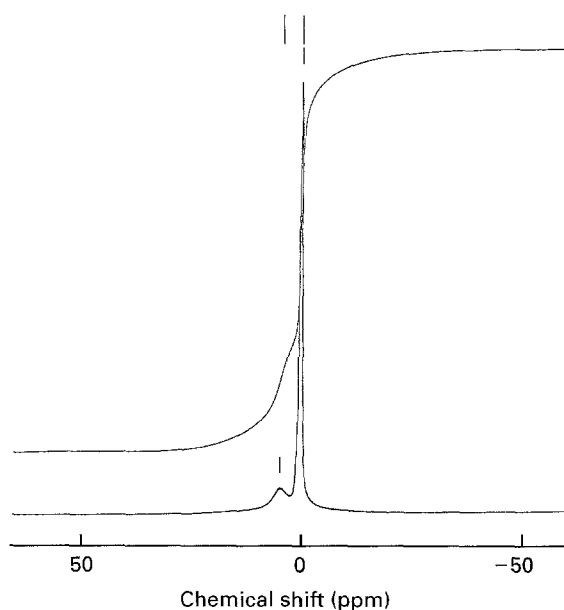


Figure 4  $^{27}\text{Al}$  solution NMR of the nitrate based alumina sol.

species remained unreactive until  $1400^\circ\text{C}$ . With this in mind, a nitrate based partially hydrolysed aluminium solution was made in our laboratory to see if the low temperature reactivity of the chloride system could be expanded. The resulting sol was completely transparent and photon correlation spectroscopy failed to determine a particle size  $< 5\text{ nm}$ , the resolution limit of the instrument.

An NMR spectra of the nitrate based sol is shown in Fig. 4. This consists of two distinct six co-ordinated species, the major (60%) one at 0.6 ppm and the other (40%) at 4.9 ppm. The major species present is mono-

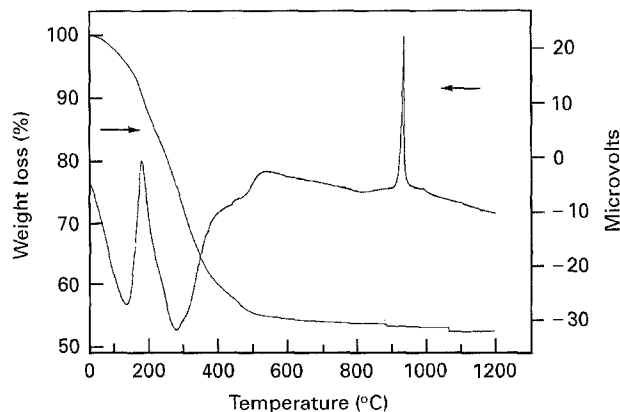


Figure 5 DTA/TGA of the spray-dried alumina-silica gel dried to  $105^\circ\text{C}$ .

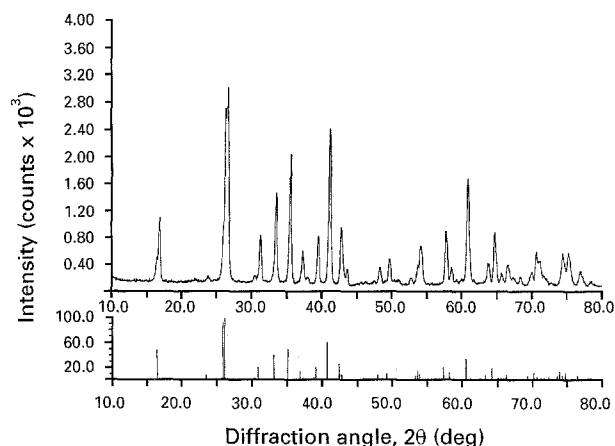


Figure 6 XRD pattern of spray-dried gel calcined to  $1000^\circ\text{C}$ . For comparison purposes the JCPDS card for  $\text{Al}_6\text{Si}_2\text{O}_{13}$  (no 15-776) is also shown.

meric hexa-aquo  $\text{Al}^{3+}$  which is in dynamic equilibrium with the partially hydrolysed dimeric species  $[\text{Al}_2(\mu\text{-OH})_2(\text{OH})_n(\text{H}_2\text{O})_{8-n}]^{[4-n]+}$ . This is entirely different to the chloride sol used, with the absence of any polymeric ions and should therefore produce a more reactive and homogeneous xerogel. The XRD pattern of the xerogel produced using this sol, fired to  $1000^\circ\text{C}$ , however, showed equal concentrations of mullite, spinel and cristobalite, indicating increased reactivity but slight inhomogeneity of the bulk gel. This is probably due to segregation of the silica and alumina on slow drying. It was decided therefore, to increase the homogeneity of the gel by spray-drying the mixed sol, a process which effectively freezes the sols *in situ* to produce 5–15  $\mu\text{m}$  particles.

DTA/TGA of the spray dried-product is shown in Fig. 5. This shows endotherms at  $150^\circ\text{C}$  and  $300^\circ\text{C}$  and a corresponding weight loss due to water and nitrate loss respectively, and a large, very sharp exotherm at  $920^\circ\text{C}$ , which in the absence of any weight loss/gain indicates crystallization. No other exotherms or weight losses are seen upto  $1500^\circ\text{C}$ . The XRD pattern of the xerogel at  $1000^\circ\text{C}$ , Fig. 6, shows single phase crystalline mullite indicating complete transformation of the xerogel to mullite at  $920^\circ\text{C}$ .

#### 4. Conclusions

Using solution NMR as an investigative tool, it has been possible to gain an understanding of the nature and reactivity of aluminium species present in inorganic sols and thereby produce in house a sol which has a greatly improved homogeneity and reactivity towards the formation of mullite over commercial reactants. This investigation has also shown that the homogeneity of a given reactive aluminium species is of paramount importance in the crystallization of mullite and the need for pentacoordinate aluminium as a precursor is not a pre-requisite in the inorganic sol-gel approach.

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