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Water-soluble amorphous alumina-based ceramic precursors and alumosols: Structural and chemical characterization

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ABSTRACT

We examined the solid-state water-soluble amorphous precursors that are formed by partial thermal decomposition of $Al(NO_3)_3{\cdot}9H_2O$ (aluminum nitrate nonahydrate: ANN) using Raman and FTIR and solid-state magic-angle spinning NMR spectroscopy. We also studied the species formed in the aqueous alumosols formed by dissolution of the pre-ceramic precursors using ^{27}Al NMR spectroscopy. Species identified in the alumosols included the $Al^{3+}(H_2O)_6$ monomer, the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}(Al_{13})$ Keggin ion, and the Al_{30} polycation, $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$, as well as various other oligomers or nanoparticles containing IV-, V- and VI-coordinated Al^{3+} ions.

1. Introduction

Alumina-based ceramics provide a wide range of important refractory materials. As thin films, their unique dielectric and thermal properties lead to their use in microelectronics and as temperature-resistant protective coatings. They are incorporated as fibres in high-strength composites, and they have bioceramics applications. Traditional processing methods leading to bulk alumina ceramics usually involve high temperature sintering and forming steps followed by machining. These processes are expensive and they limit the shapes that can be achieved. The development of synthetic routes to 'alumosols', involving reactions in the liquid phase or dissolution of water-soluble precursors, has been of great interest [1–5]. Such methods lead to lower processing costs, simpler chemical handling, and thin films or complex shapes are easy to achieve. A key factor is the ability to make water-soluble precursors with an adjustable viscosity range that is suitable for a wide range of applications, that can be easily processed to yield dense alumina-based ceramics in near-net shape with minimal changes in the final geometry.

Various methods described to produce alumosols include reactions involving organometallic molecules in solution [1–4], or dissolution of solid aluminate precursors obtained by partial thermal decomposition of hydrated metal salts, such as aluminum nitrate nonahydrate (ANN: $Al(NO_3)_3{\cdot}9H_2O$) [5,6]. The formation of alumosols in this way involves heating to drive off water of crystallization and the bulk of the ligand species, so that a pre-determined weight loss occurs resulting in an X-ray amorphous material that is water-soluble. The degree of partial thermal decomposition critically determines the nature of the amorphous 'polymeric' solids produced and their ease of dissolution, as well as the viscosity of the resulting, and the drying characteristics of the alumosol pre-ceramic material. Complete removal of all H_2O and nitrate components from the ANN starting material results in anhydrous Al_2O_3 containing 13.6% of the initial mass (Table 1). Generally, weight loss values of 63–73% are found to be optimal for yielding water-soluble pre-ceramic precursors. It has been shown that partial decomposition of ANN to below ~27% retained mass (i.e., a weight loss of ~73%) yields an amorphous material that is no longer fully water-soluble [5]. It is important to study the chemistry and structure of the solid amorphous precursor in order to ascertain the factors that determine its solubility in aqueous solvents, and also the nature of the aluminate species that are present in solution.

A simple model has been suggested for the partial decomposition reaction to form a proposed O-bridged polymeric aluminate species that would give rise to the water-soluble ceramic precursors [5] (Fig. 1). In the proposed thermal decomposition model, it was suggested that some side groups (OH, NO_3) remain attached to the Al species in order to confer water solubility on the resulting polymer: this determines the minimum 27% retained mass value necessary for dissolution properties [5]. However, there are several problems with this proposal. First, the structural model depicts three-coordinated aluminate species forming linear polymer

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Table 1
Various compounds and chemical species/components that could contribute to the retained mass values (wt% relative to the starting ANN) of the water-soluble amorphous solid preceramic precursor, following loss of H_2O and NO/NO_2 species during partial thermal decomposition of the starting compound. The relevant retained mass values lie within the range 27–40%, that constitute water-soluble amorphous polymers that lead to useful ceramics after thermal processing.

Possible components and species remaining within amorphous precursor (normalized to 1 Al)	Description	Molecular weight	Retained mass (wt% relative to ANN)	wt% N	wt% H
$Al(NO_3)\cdot 9H_2O$	Starting material (ANN)	375	100	11.20	4.80
$Al(NO_3)\cdot 6H_2O$	Lose water of crystallization ($-3H_2O$): ANH	321	85.6	13.08	3.74
Potential formulations of solid amorphous pre-ceramic aluminate ‘polymers’ after removal of various combinations of H_2O/NO_x species from ANH (normalized to 1 Al)					
$Al(H_2O)_5(OH)(NO_3)_2$	$-HNO_3$	258	68.8	10.85	4.26
$Al(H_2O)_4(OH)_2\cdot(NO_3)$	$-2HNO_3$	195	52.0	7.18	5.13
$0.5[(OAl(OH)OAl(NO_3)]n$[a]		165	44.0		
$Al + 2NO_3 + OH$		168	44.8	16.67	0.60
$Al + NO_3 + 2OH$	”	123	32.8	11.38	1.63
$Al + 0.5\ NO_3 + 2.5\ OH$	”	100.5	26.8	6.97	2.49
$Al(OH)_3$	Boehmite	78	20.8	–	3.85
$0.5\ Al_2O_3$	Alumina	51	13.6	–	–

[a] Polymer species suggested by [5] (Fig. 1): unlikely because of III-coordinated Al units.

chains. The existence of such structural units is unlikely from our knowledge of solid state and aqueous aluminate chemistry, in which the aluminate species generally adopt IV-, V- or VI-fold co-ordination, and clusters rather than linear polymer chain species are formed [7–13]. In addition, the condensation model presumes that molecular N_2 species are evolved during the thermal decomposition reaction along with H_2O [5]. This disagrees with previous results and interpretations of the thermal decomposition of ANN [6], and also with our mass spectrometry results discussed below.

Calorimetric (DTA, DSC) and thermogravimetric (TGA) studies are currently thought to indicate that ANN first releases its water of crystallization (i.e., $3H_2O$) at 70–73 °C [6] (Fig. 1). The remaining nitrate compound then dissolves in this liquor until the evolved H_2O evaporates and recrystallization of the hexahydrate ($Al(NO_3)_3\cdot 6H_2O$: ANH) can occur. The resulting ANH then decomposes above 135 °C to form a mixture of basic hydroxylated aluminate salts that are not well characterized [6]. It has been proposed that HNO_3 vapor is evolved above 137 °C to produce a non-crystalline compound with approximate composition $4Al_2O_3\cdot 3N_2O_5\cdot 14H_2O$ [6]. Further heating to >200 °C results in the formation of various partly hydrated aluminas and eventually to anhydrous Al_2O_3. DTA/DSC studies show a first deep endotherm with three steps at 70–110 °C, 110–120 °C and 160–180 °C, that are thought to correspond to (a) dehydration of ANN to ANH, (b) removal of excess H_2O from the sample, and (c) further decomposition with presumed evolution of HNO_3 component to produce basic hydroxylated aluminate salts, respectively [5,6]. The endothermic processes lead to the water-soluble ceramic precursors studied here. Further heating is thought to lead to continued loss of hydrous and NO_3^- components up to ~390 °C, followed by an exotherm indicating crystallization of $\gamma - Al_2O_3$ or $\theta - Al_2O_3$ at ~800 °C and conversion to $\alpha - Al_2O_3$ above 1000 °C [5,6]. A similar model has been suggested to explain the sequence of decomposition events following γ-irradiation [14]. The initial steps in this suggested process, considering the release of H_2O and HNO_3 to be the most likely volatile components released in sequence [6], are summarized in Fig. 1(b) where they are viewed from the point of view of changes in the local Al^{3+} co-ordination environment that is considered to be completely surrounded by molecular H_2O or OH^- species. This schematic diagram does not consider any polymerization reactions that are likely to occur between aluminate species, or the possible role of NO_3^- as mono- or bidentate ligands within the primary co-ordination sphere perhaps even bridging between oligomer species.

In the present study, we used a combination of solid state ^{27}Al NMR, Raman and FTIR spectroscopy to determine the nature of the water-soluble ceramic precursors produced by partial thermal decomposition of ANN. The results show that the Al species in the amorphous solids are primarily in octahedral co-ordination, and that both molecular H_2O and NO_3^- groups are present. We also used ^{27}Al NMR spectroscopy to study the species present in the aqueous alumosols derived from the pre-ceramic precursors. Finally, we investigated the species evolved during thermal decomposition of ANN using mass spectrometry.

2. Experimental methods

Samples of aluminum nitrate nonahydrate, $Al(NO_3)_3\cdot 9H_2O$ (ANN) (Aldrich, 99.99% purity) were partially decomposed by heating at 125°C for periods of up to 72 h in air in a ventilated oven. The resulting amorphous samples had retained mass values of 27.3, 31.1, 34.2 and 37.2 wt% expressed as a weight percentage relative to the initial mass of ANN. Samples prepared with higher retained mass values suffered additional thermal decomposition and excessive shrinkage upon further processing, whereas continuing the decomposition process to <27% retained mass yielded materials that were no longer water-soluble, as has been observed previously [5]. The solid amorphous samples were examined by ^{27}Al magic angle spinning (MAS) NMR spectroscopy, as well as Raman and FTIR spectroscopy.

Usually, complete dissolution of the ceramic precursor samples occurred by stirring in deionised water at ambient T. However, for certain samples with 27–32% retained mass value, complete dissolution could only achieved by warming to 60–65 °C. Clear solutions were usually produced containing up to ~60% by weight of the solid amorphous material. However, alumosols prepared for the lowest retained mass samples were often turbid. The concentrated solutions were supersaturated in the solid phase, and spontaneous coatings occasionally occurred on glass surfaces and metal utensils (e.g., Ni or steel spatulae) dipped into the liquids. For most of the ^{27}Al NMR studies reported here, alumosols containing 10% by weight of the amorphous solid precursors were investigated. In addition, a batch of precursor was prepared with 31.2% retained mass value to investigate solutions as a function of alumosol concentration ranging from 10 to 35 wt%.

^{27}Al NMR spectroscopy experiments were carried out using a Varian-Unity spectrometer operating at 9.4 Tesla, corresponding to a Larmor frequency of 104.227 MHz for ^{27}Al. Solid state MAS NMR spectra were obtained using a Jakobsen 4 mm probe, utilizing sintered Si_3N_4 rotors spinning at 13 kHz. Solution phase NMR spectra of the alumosols were obtained by loading samples into sintered silica glass tubes. Because of the high viscosity of the alumosols, these were spun at high speeds to obtain the NMR