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SYNTHESIS AND CHARACTERIZATION OF ALUMINUM PROPIONATE SOL-GEL DERIVED A 203

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### ABSTRACT

 $Al_{20}$  has been synthesized from aluminum propionate  $[Al(CO_2CH_2CH_3)_3]$  by Sol-Gel techniques. Methods of characterization include: x-ray powder diffraction, scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR). Solution and solid state <sup>13</sup>C and <sup>27</sup>Al NMR data is coupled with both x-ray diffraction powder data and SEM in order to understand the transition from sol + gel + amorphous powder + crystalline powder in the sonicated and unsonicated aluminum propionate precursor, and  $Al_{20}$  powders. Results indicate that the sonicated dried powder is crystalline, having the  $\gamma Al_{20}$  structure while the unsonicated dried powder is amorphous and crystallizes at 800°C with the  $\alpha Al_{20}$  3 structure. These differences in crystallinity are further substantiated by solid state <sup>27</sup>Al NMR chemical shifts and line widths at half height.

MATERIALS INDEX: Sol-gel, aluminum propionate, aluminum oxide, A&27 NMR, C-13 NMR, x-ray diffraction, scanning electron microscopy.

#### Introduction

Sol-gel technology has been extensively utilized for processing nuclear fuel pellets and powders. Currently, the direct firing of gels is being explored to produce ceramics without the use of any intervening powder steps as an extension of Yoldas work on glasses and polycrystalline oxides [1-3].

This is motivated by (1) the high purity and homogenity available in solids; (2) the potential ability in a viscous liquid to minimize the sources of defects; (3) the ability to visually examine many gel products for defects after drying; and (4) the shaping potential offered by a "plastic" gel. Furthermore, much lower temperatures can be used to fire gels to a fully dense ceramic (e.g., ThO<sub>2</sub>, [4]) than are required for conventional powder processed bodies.

Key problems in the direct firing of gels are the determination of (1) how to control the large shrinkages involved in the gellation of sols, (2) the size and shape limitations necessary to avoid cracking or distortion, and (3) the range of compositions and materials to which direct gel processing can be applied. J. COVINO, et al.

The sol-gel process is now a well-accepted technique for preparing monolithic glass articles without melting. This technique has been applied not only to the preparation of single component oxide glasses, for example,  $SiO_2$ [5-7], but also more recently to the preparation of multicomponent oxide [8] and oxynitride [9] glasses. For processes that use metal alkoxides or metal organics as glass precursors, monolithic glass formation consists of (1) growth and linkage of polymer units to form a gel, (2) desiccation of the gel under ambient or hypercritical conditions to form, respectively, a porous xerogel or aerogel, and (3) heat treatment of the porous gel at a temperature sufficiently high to convert it to a dense, glass-like solid.

The purpose of this paper is to describe a technique for producing  $Al_{203}$  powders via a sol-gel process starting from the aluminum propionate. The mechanistic aspects of the sol + gel + amorphous powder + crystalline powder transitions will allow for the systematic synthesis of particular crystalline forms under reduced temperatures and pressures. Our approach has been to prepare gels of aluminum propionate under acidic conditions and to dehydrate these materials at temperatures of 600°C and 800°C. The effect of pretreatment of the sol phase with sonication was also investigated.

Our methods of characterization included x-ray powder diffraction scanning electron microscopy and nuclear magnetic resonance (NMR). While it was expected that NMR data alone would not be sensitive to long range order (crystallinity) it was hoped that observation of the entire transition from sol + gel + amorphous powder + crystalline powder for the aluminum propionate system by  $^{13}$ C and  $^{27}$ Al would lead to some understanding of the basic process. This data would be coupled with both x-ray diffraction powder patterns and scanning electron microscopy in order to understand the sol-gel process of Al<sub>2</sub>O<sub>3</sub> from aluminum propionate.

### Experimental

### Sample Preparation

One gram of  $A^{\ell}(CO_2CH_2CH_3)_3$  was mixed with 26 ml of distilled water. To this mixture 200 drops of concentrated HCl was added. To this solution 10 ml of methanol was also added and a pH of 0.7 was measured. This solution was heated in a H<sub>2</sub>O bath to 40-50°C for 6 hours and left to gel over the weekend.

Sonication of a second solution prepared identical to the above described method, was performed at 4.4 amp D.C. for 10 minutes. The temperature of this solution ranged from 34-60°C during the sonication process. This solution was also left to gel over the weekend.

The sonicated sample never gelled even after numerous repeated attempts to prepare the solution. Crystallization took place and the product was characterized. On the other hand, the non-sonicated sample did gel after approximately 3 days. This sol + gel transition was also characterized. Following the gel formation, the aluminum gel was dehydrated to a powder at temperatures of 600°C and 800°C. These two powders were also characterized.

## Sample Characterization

X-ray analysis. Samples prepared by the above procedures have been analyzed by x-ray powder diffraction. Diffractometer scans were taken on a Phillips

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diffractometer with a  $\theta$ -compensating slit, diffracted beam monocromator, scintillator with pulse-height discrimination, and a copper source (CuKa = 1.5418Å, Ka<sub>1</sub> = 1.5405Å, Ka<sub>2</sub> = 1.5444Å).

Scanning Electron Microscopy (SEM). Scanning electron microscopy was employed in order to measure particle size distribution on the powder samples. Scanning electron micrographs were taken on an Amray 1400 with 40Å lateral resolution electron microscope.

<u>Nuclear Magnetic Resonance (NMR)</u>. All NMR spectra were recorded with the use of an NT-200-WB spectrometer operating at 50 MHz for  $^{13}$ C. NMR spectra of solutions and gels under acidic aqueous conditions were acquired with inverse gated broad band 'H decoupling (to reduce sample heating). 3-(trimethylsily1)-1-propane sulfonic acid (DSS) in D<sub>2</sub>0 was used as an external solution reference. Solution state  $^{27}$ Al spectra were recorded with a one pulse sequence and referenced to Al (H<sub>2</sub>0)<sub>6</sub><sup>3+</sup>. Solid samples were combined with 5% by weight KBr (to allow for spinning speed calibration) and ground with a mortar and pestal prior to loading in the sample rotors. Samples were spun at the magic angle 54.7° with respect to the field at 3-3.5 KHz. Free induction decays were acquired with a one pulse sequence and referenced to the solution state sample of Al (H<sub>2</sub>0)<sub>6</sub><sup>3</sup>+.

## Results and Discussion

A series of  ${}^{1}$ H decoupled  ${}^{13}$ C spectra were recorded for solutions and gels of acidic aluminum propionate. These are displayed in Figure 1. In all cases, <sup>13</sup>C resonances are apparent corresponding to the three carbons of the three propionate group, with the resonances centered at 12 ppm (broad, methyl carbons), 31 ppm (methylene carbons), 183 ppm (carboxyl carbons). Spectrum A is representative of a solution of  $A\ell(CO_2CH_2CH_3)_3$  with acid and methanol. The broad nature of the methyl resonance is perhaps a consequence of a hindered. rotation or possibly due to its being the free end of a "leash" and assuming a number of unequivalent conformations with respect to the growing Al-O-Al matrix. Presonication of this solution leads to the <sup>13</sup>C spectrum shown in Figure 1b. We note that the carboxyl resonance at ≈183 ppm remains sharp with no apparent change in its chemical shift or line shape. The resonance assigned to the methylene carbons centered at  $\alpha$  32 ppm appears to have sharp and broad components in contrast to the unsonicated sample. The methyl resonance centered at 12 ppm displays a similar broadening though, in this case, it is not quite so obvious given the nature of the methyl resonance for the unsonicated sample. There is also other evidence for the breakdown of the  $A^{\ell}(CO_{2CH_{2}CH_{3}})_{3}$  skeleton, as demonstrated by other broad resonances observed in the aliphatic and carboxyl-ate regions of the  $^{13}$ C NMR spectrum. Our rationalization for these differences requires an apriori knowledge of the effect of sonification on the resultant aluminum oxides formed upon dehydration.

It was found by x-ray powder diffraction that presonication of the  $Al(CO_2CH_2CH_3)_3$  solutions leads upon dehydration to a crystalline  $Al_2O_3$  structure. This result indicated to us that presonication of the  $Al(CO_2CH_2CH_3)_3$  solution had the effect of breaking up  $Al - CO_2CH_2CH_3$  groups and inducing the polymerization of Al-O units prior to the dehydration step. In light of this result, we can understand the  $^{13}C$  NMR spectrum of sonicated  $Al(CO_2CH_2CH_3)_3$  solution as indicating some degree of aluminum oxide polymerization, and thus many environments for the propionate groups (broad  $^{13}C$  resonances) depending on the extent of polymerization.

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The <sup>13</sup>C NMR spectrum of the A<sup> $\ell$ </sup> (C0<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> gel very clearly displays the three resonances expected for the propionate group. All <sup>13</sup>C resonances are broad (\*120 Hz at half height), however, this can be rationalized from the nature of the sample, a viscous gel which did not flow very readily. Thus the motions of the propionate groups are hindered and a line shape approaching the solid state line shape is observed.

Attempts to observe solid state <sup>13</sup>C spectra of dehydrated powders and calcined powders were unsuccessful due to dilution of the carbon containing species.

The results of some solution state  ${}^{27}$ Al NMR [10,11] studies on Al(CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> solutions and gels are shown in Figure 2. All of the solutions gave very similar spectra with one sharp resonance (18 Hz wide at half height) centered at 0 ppm as expected for an octahedral Al environment like Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> the reference sample. The solution state  ${}^{27}$ Al NMR spectrum of an Al(CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> gel indicates a mixture of two types of tetrahedral Al sites[11] with components centered at 0 ppm and -25 ppm. The line width for these resonances is estimated at 1500 Hz at half height.

In Figure 3 the x-ray powder spectra for the sonicated and unsonicated dried powders and the calcined samples (600°C and 800°C) are showed. As can be seen, the dried alumina sample and the dried sonicated alumina sample have significantly different x-ray powder patterns. The sonicated sample forms a crystalline powder which can be indexed as the  $\gamma-A\ell_20_3$  form while the unsonicated sample remains poorly crystalline to temperatures as high as 600°C. The energy



FIG. 1. <sup>13</sup>C Solution Spectra of Aluminum Propionates. A. Nonsonicated solution, B. Sonicated solution, C. Gelled nonsonicated solution.

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absorbed by the solution during sonication causes the organic species to dissociate and form a stable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase faster than the unsonicated sample.



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Scanning electron micrographs of the dried powder, sonicated powder, and annealed powder are shown in Figure 4.

(a)

(b)

(c)





FIG. 4. SEM Photographs of Aluminum Oxide Powders Prepared Under Different Conditions. (a) Dried powder derived from Aluminum gel, (b) Sonicated powder, (c)  $\alpha A l_2 O_3$  powder annealed @ 800°C derived from Aluminum gel.

Solid state <sup>27</sup>Al NMR [12,13] of various dehydrated powders derived from sonicated and unsonicated sol-gel mixtures were studied. A representative series of spectra are displayed in Figure 5. Powder samples derived from

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$$A1_2O_3$$

sonicated and from unsonicated solutions were examined by solid state  ${}^{27}$ Al NMR. In addition, two unsonicated samples calcined at 600 and 800°C were studied. First and second order spinning side bands are observed in each  ${}^{27}$ Al spectrum at the spinning speed of ~3500 Hz. The  ${}^{27}$ Al chemical shifts and line widths are listed in the Table below along with a summary of the x-ray powder diffraction results.

Sample	<sup>27</sup> Al Chemical Shift <sup>1</sup> (PPM)	Line Width at Half Height <sup>2</sup> (HZ)	Powder Diffraction
Sonicated Powder Unsonicated-800° Calcined	2.0 0.6	1300 1200	Crystalline YAL <sub>2</sub> O <sub>3</sub> Crystalline aAL <sub>2</sub> O <sub>3</sub> (Curundum Structure)
Unsonicated-600° Calcined Unsonicated Powder	-3.5 0.1	2100 2000	Amorphous Amorphous

<sup>1</sup>Chemical shifts were obtained from a line fitting program provided by GE/NMR and are referenced to external  $A \chi(H_2 0)_6^{3+}$  at 0 ppm





FIG. 5. Solid State <sup>27</sup>Al NMR of Various Dehydrated Powders Derived From Sonicated and Unsonicated Sol-Gel Mixtures. (a) Sonicated powder, (b) Unsonicated 800°C, (c) Unsonicated 600°C, (d) Unsonicated powder.

The  $^{27}$ Al chemical shifts are relatively constant, however, linewidths appear to yield a test of crystallinity. Amorphous samples, have linewidths of 2000-2100 Hz while crystalline samples have linewidths of 1200-1300 Hz. It would be helpful to run these samples at higher field strengths to ascertain whether it might be possible to observe separate  $^{27}$ Al resonances for different Al environments [12].

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# Conclusions

The sol-gel derived synthesis of a variety of Al<sub>2</sub>O<sub>3</sub> from aluminum propionate has been discussed. Solution and solid state <sup>13</sup>C and <sup>27</sup>Al NMR data was coupled with both x-ray powder diffraction data and SEM photographs in order to understand the transition from sol + gel + amorphous powder + crystalline powder in the sonicated and unsonicated aluminum propionate precursor, and Al<sub>2</sub>O<sub>3</sub> powders. Results from these experiments indicate that the sonicated dried powder is crystalline, having the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure while the unsonicated dried powder is amorphous and crystallizes at 800°C with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure.

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