

A New Route to Alumoxane Gel: A Versatile Precursor to γ -Alumina and Alumina-Based Ceramic Oxides

Kurikka V. P. M. Shafi,^{†,‡} Abraham Ulman,^{*,†,‡} Jriuan Lai,^{†,‡} Nan-Loh Yang,^{‡,§} and Min-Hui Cui^{†,§}

Department of Chemical Engineering, Chemistry & Material Science, Polytechnic University, 6 Metrotech Center, Brooklyn, New York 11201, Department of Chemistry, CUNY at Staten Island, 2800 Victory Boulevard, Staten Island, and The NSF Garcia MRSEC for Polymers at Engineered Interfaces

Received November 18, 2002; E-mail: aulman@duke.poly.edu

γ -Al₂O₃, a low-temperature metastable polymorph of alumina with wide range of surface hydroxyls, is a catalyst support. Alumina-based ceramics are important in many technologies. For example, yttrium aluminum garnet (Y₃Al₅O₁₂, YAG), a high-temperature stable material with the highest creep resistance of any known oxide material, is good for ceramic–matrix composites¹ and neodymium-doped YAG is a solid state laser material.²

Traditional synthesis of ceramic materials involves physical mixing of the individual oxides (or oxide precursors, such as carbonates and oxalates), sintering at high temperature for extended durations, grinding, and finally resintering. The long reaction time and high temperatures required for such a process do not give control of nanostructure, grain size, or size distribution, as this method is limited to micrometer-size mixing. Therefore, Sol-Gel synthesis has been used frequently.^{3–5} However, the inherent disadvantages of this method are the formation of multiphase materials and the lengthy processing time. A sonochemical process⁶ has been used to prepare various kinds of nanostructured amorphous magnetic materials, such as metal alloys⁷ and ferrites.⁸ It offers a reliable and facile route for the control of both the synthetic process and nanostructure in advanced materials. A major advantage of this process is that it provides chemical homogeneity and reactivity through atomic level mixing within the precursor system, and phase-pure crystalline materials can be prepared by annealing at reduced temperatures. Thus, materials with unusual and unique compositions, which might have novel properties, can be prepared. Here, we report a new sonochemical preparation of carboxyl-substituted alumoxane nanoparticles and show that it is a versatile precursor for preparation of γ -alumina. We have used the same route to form alumoxane gels doped with yttrium and successfully produced YAG nanoparticles. While this project is still actively pursued, and syntheses of other compositions of alumina-based ceramic materials are under investigation, we report here our preliminary observations.

Ultrasonication of aluminum hydroxy di(2-ethyl hexanoate) Al(HEHx) (2 g, Strem Chemicals) in *n*-decane (50 mL, Aldrich) results in a transparent gel. Concentration by vacuum evaporation followed by drying gives a semitransparent solid. Once the dried nanoparticles are exposed to a hydrocarbon solvent (e.g., hexane), the gel is formed again.

When metal carboxylates are heated to 200–300 °C, thermal decomposition occurs via a cyclic elimination mechanism to yield metal hydroxyl group and an olefin (Scheme 1).⁹ The cavitation events occurring during ultrasonication provide high temperatures, thus resulting in the facile decomposition reaction. The Al-OH moieties formed can react with each other to give an alumoxane bond (Al–O–Al) and a water molecule. Continuous decomposition

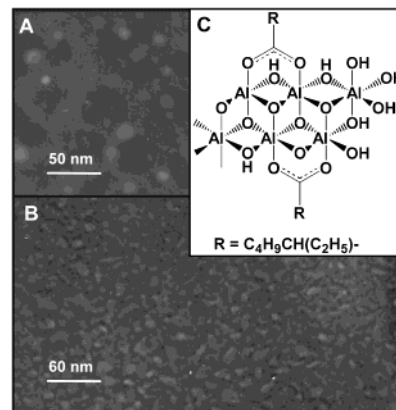
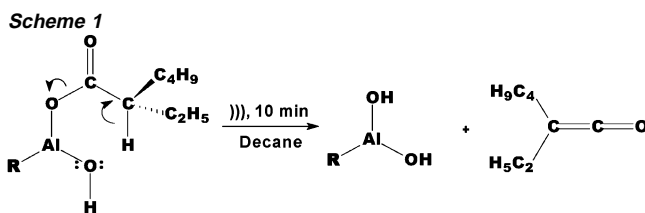


Figure 1. Transmission electron micrographs of as-prepared (A) and calcined alumoxane nanoparticles (B). (C) Suggested boehmite structure of the particles in (A).



and reaction will lead to the formation of polyalumoxane network, which might contain three-, four-, five-, and six-coordinated aluminum ions. An ²⁷Al NMR study (Figure 2) of the dried gel shows an isotropic chemical shift of 1.0 ppm, which indicates the six-coordinated Al³⁺ ions in a polyalumoxane network, similar to that in a boehmite structure (Figure 1C).

The FTIR spectrum (Supporting Information) of the dried gel nanoparticles reveals a hydroxyl-stretching band at 3794 cm⁻¹ and a bridging hydroxyl band at 1066 cm⁻¹, with both showing broadening, resulting from extensive hydrogen bonding in the network. In addition, the split of the carboxyl band (1575 and 1619 cm⁻¹) suggests bridging carboxylate bidentate ligands (Figure 1C). This structure was proposed before for a product obtained from a reaction of boehmite with carboxylic acids,¹⁰ involving heating the reaction mixture for extended hours. *The facile, one-pot sonochemical preparation of the boehmite structure described here is the first report of a non-hydrolytic gel route that results in an alumoxane network.*

A ¹³C NMR spectrum (Supporting Information) for the alumoxane gel after drying shows a carbonyl carbon at 183.30 ppm. Two new peaks appear in the polyalumoxane spectrum as compared to that of the Al(HEHx) sample. The first, at 18.99 ppm, is assigned to methyl groups of the ethyl substituents, and the other at 56.83 ppm is assigned to a carbon adjacent to a carbonyl. These might be assigned to 2-ethyl hexanoate groups adjacent to network junctions.

[†] Polytechnic University.

[‡] The NSF Garcia MRSEC for Polymers at Engineered Interfaces.

[§] CUNY at Staten Island.

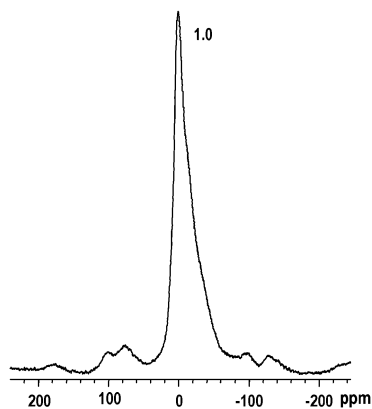


Figure 2. ^{27}Al MAS NMR spectrum of the dried gel nanoparticles.

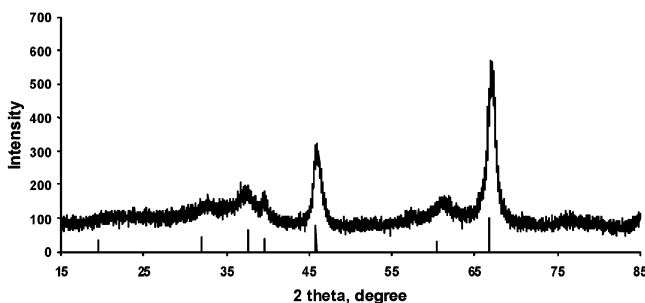


Figure 3. XRD pattern of the carboxy-substituted alumoxane nanoparticles heated at 700 °C for 5 h.

Thermogravimetric analysis (Supporting Information) of the dried gel nanoparticle reveals complete decomposition at ~ 500 °C. Therefore, the alumoxane nanoparticles were heated at 200 °C (RAMP is 2°/min) for 30 min and finally calcined at temperatures 700 to 900 °C for 5 h, yielding pure $\gamma\text{-Al}_2\text{O}_3$ nanoparticles. The transmission electron microscopy images (TEM, Phillips CM-12 transmission Electron Microscope, 100 keV) of the calcined nanoparticles (B) along with particles before heating (A) are shown in Figure 1. The nanoparticle size, even after heating at 900 °C, is less than 10 nm. Because of the small particle nature of the sample formed, and the homogeneous mixing at the atomic level provided by the ultrasonication, the transformation of the carboxy-substituted alumoxane to $\gamma\text{-Al}_2\text{O}_3$ occurs at 700–900 °C. The X-ray diffraction (XRD) pattern (Philips X-ray diffractometer, Cu K α radiation, $\lambda = 1.5418$ Å) of the calcined product (Figure 3) shows distinct diffraction peaks of γ -alumina with peak position and intensity matching with the standard diffraction pattern for face-centered cubic γ -alumina (JSPDS-29-0063). Solid-state ^{27}Al one-pulse MAS spectrum of $\gamma\text{-Al}_2\text{O}_3$ (Supporting Information) shows two resonances, at 5.6 and 64.6 ppm, corresponding to six- and four-coordinated aluminum species, respectively.^{11–13}

The formation of a gel was also observed when Al(HEHx) (2 g) was sonicated with other metal precursors, for example, yttrium 2-ethylhexanoate (1.85 g, Strem Chemicals), in *n*-decane (50 mL). As for the case of alumoxane gel, the mixed oxide gel (YAG gel) was also formed after 10 min of ultrasonication. After the gel was calcined at 900 °C for 5 h, the XRD (Figure 4) showed phase pure yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$ particles with no $\gamma\text{-Al}_2\text{O}_3$ phase. *It should be emphasized that only by sonication one can achieve this level of mixing that allows the formation of YAG hundreds of degrees below the commonly used temperature of 1400 °C to get phase pure garnet material.* The ^{27}Al solid-state NMR (Supporting Information) shows that three resonances were observed, with shifts at 1, 28, and 63 ppm, in line with literature values for six-, five-, and four-coordinated aluminum species, respectively.^{11–13} Fluorescence image (Supporting Information, and Figure 4 inset) of YAG nanoparticles taken using 480 nm excitation shows emission at 510 nm.

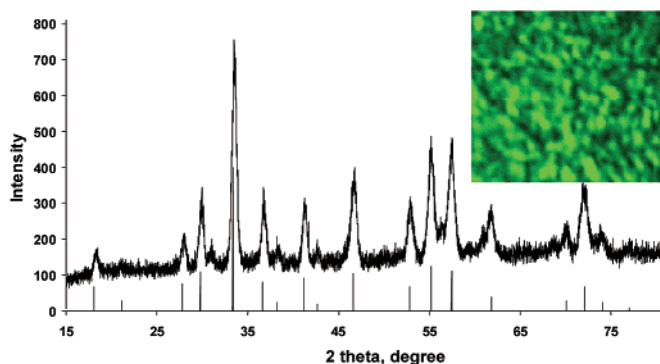


Figure 4. XRD pattern of the YAG nanoparticles. The inset is part of a fluorescence image of the nanoparticles using 480 nm excitation. The emission is at 510 nm. Grain size is ~ 800 nm.

We have presented a new, facile, and effective route for the preparation of $\gamma\text{-Al}_2\text{O}_3$ and alumina-based materials. By using ultrasonication of precursors that are soluble in hydrocarbon solvents (e.g., *n*-decane) complete mixing at the atomic level is achieved. The sonochemical reaction yields gel nanoparticles, which can reversibly collapse and reform, depending on the solvent used. Due to their large surface area-to-volume ratio, and the formation of complete mixed phases, calcination becomes possible at temperatures hundreds of degrees lower than required by traditional preparation routes using the oxides of the corresponding constituent ions. Ample experimental evidence was provided to support the proposed structures of the initial gel and the final alumina and YAG nanoparticles. While still in early stages of investigation, we have also prepared LaAlO_3 nanoparticles, and research is underway to develop a variety of alumina-based ceramic materials as well as functional coatings for these nanoparticles.

Acknowledgment. This work was funded by the NSF through the MRSEC for Polymers at Engineered Interfaces.

Supporting Information Available: FTIR and solid-state ^{13}C NMR spectra for Al(HEH) and the dried alumoxane gel, TG analysis curve of dried alumina gel. ^{27}Al NMR spectra of a $\gamma\text{-Al}_2\text{O}_3$ and YAG nanoparticles. Fluorescence image of YAG sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) King, H.; Hallooran, J. W. *J. Am. Ceram. Soc.* **1995**, *78*, 2141. (b) Morscher, G. N.; Chen, K. C.; Masdiyasin, K. S. *Ceram. Eng. Sci. Proc.* **1994**, *15*, 181.
- (2) Sekita, M.; Haneda, H.; Yamagitami, T.; Shirarasaki, S. *J. Appl. Phys.* **1990**, *67*, 453.
- (3) Tadanaga, K.; Morinaga, J.; Matsuda, A.; Minami, T. *Chem. Mater.* **2000**, *12*, 590.
- (4) Cheetham, A. K.; Mellot, C. F. *Chem. Mater.* **1997**, *9*, 2269.
- (5) Vioux, A. *Chem. Mater.* **1997**, *9*, 2292.
- (6) (a) Suslick, K. S. *Science* **1990**, *247*, 1439. (b) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397.
- (7) Shafi, K. V. P. M.; Gedanken, A.; Goldfarb, R. B.; Felner, I. *J. Appl. Phys.* **1997**, *81*, 6901.
- (8) Shafi, K. V. P. M.; Gedanken, A.; Prozorov, R.; Balogh, J. *Chem. Mater.* **1998**, *10*, 3445.
- (9) Shulman, G. P.; Trusty, M.; Vickers, J. H. *J. Org. Chem.* **1963**, *28*, 907.
- (10) Kareiva, A.; Harian, C. J.; MacQueen, D. B.; Cook, R. L.; Barron, A. R. *Chem. Mater.* **1996**, *8*, 2331.
- (11) Fyfe, C. A.; Bretherton, J. L.; Lam, L. Y. *J. Am. Chem. Soc.* **2001**, *123*, 5285.
- (12) Florian, P.; Gervais, M.; Douy, A.; Massiot, D.; Coutures, J.-P. *J. Phys. Chem. B* **2001**, *105*, 379.
- (13) Luan, Z.; Hartmann, M.; Zhao, D.; Zhou, W.; Kevan, L. *Chem. Mater.* **1999**, *11*, 1621.

JA0213625