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From Minerals to Materials: A Facile Synthetic Route to
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by

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FROM MINERALS TO MATERIALS: A FACILE SYNTHETIC ROUTE TO PRECERAMIC POLYMERS FOR ALUMINUM OXIDE

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ABSTRACT

Reaction of boehmite, $[Al(O)(OH)]_n$, with an excess of carboxylic acid (HO_2CR) results in the formation of the carboxy substituted alumoxanes, $[Al(O)_x(OH)_y(O_2CR)_z]_n$ where $2x + y + z = 3$ and R = alkyl substituents. The alumoxanes have been fully characterized by SEM, elemental analysis, IR and multinuclear NMR spectroscopy. The physical properties of the alumoxanes are highly dependent on the identity of R, and range from insoluble crystalline powders, e.g. R = CH_3 , to powders which readily form solutions or gels in hydrocarbon solvents, e.g. R = C_5H_{11} . All of the alumoxanes decompose under mild thermolysis to yield γ -alumina.

INTRODUCTION

The facile formation of ceramic materials from molecules, either by the pyrolysis of well characterized single-source precursors or via the sol-gel method, has undoubtedly been one of the significant contributions made by chemistry to materials science.¹ However, it is desirable not only to produce the ceramic *per se* but also to do so in a specific form: for example, a fiber, thin film or three-dimensional body. For this reason, there has been continued research effort aimed at the design of precursors with physical properties suitable for processing prior to pyrolysis. In the case of alumina (Al_2O_3) several groups have employed polymeric alumoxanes as precursors.^{2,3} The term alumoxane is used to describe any oligomeric material containing an aluminum-oxygen backbone with pendant organic ligands. Perhaps the most extensive study in this regard is that by Kimura and co-workers² in which they demonstrated that carboxy-substituted alumoxanes could be extruded to form preceramic fibers. However, in this and other work,⁴ the alumoxanes were prepared via a multi-step synthesis involving the hydrolysis of highly pyrophoric aluminum alkyls.

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Since this route yields products with variable stoichiometries, it would be desirable to prepare alumoxane preceramic polymers in a one-pot bench-top synthesis.

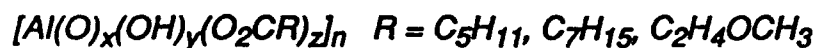
Our recent work has shown that the core structure of alumoxanes is not a linear chain, as often supposed, but similar to that of the mineral boehmite, $[Al(O)(OH)]_n$.⁵ From this, the following question may be posed: *Can alumoxanes be prepared directly from this mineral?* Herein we report the reaction of boehmite with carboxylic acids, and the formation of carboxy-substituted alumoxanes.

EXPERIMENTAL

Research grade pseudo-boehmite (100%) was kindly provided by American Cyanamid. All carboxylic acids were obtained commercially and were distilled prior to use. ¹³C CPMAS and ²⁷Al MAS NMR spectra were obtained on a Chemagnetics CMC-200A spectrometer operating at 50.177 and 51.992 MHz, respectively (see Text). Chemical shifts (δ) are reported relative to external samples of C_6Me_6 (132.0 ppm) and $Al(NO_3)_3 \cdot (H_2O)_x$ (0.0 ppm). Thermogravimetric analyses were obtained on a Seiko 200 TG/DTA instrument using a carrier gas of either air, nitrogen or argon. IR spectra were obtained as KBr pellets on a Nicolet DX-5 FTIR spectrometer. SEM studies were performed on a JEOL JSM-6400 scanning microscope. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, N.Y.



Boehmite (1.00 g, 16.7 mmol) was placed in a 150 mL flask with an excess of the appropriate acid (ca. 40 mL). The resulting slurry was heated to reflux for four days, after which time the excess acid was removed by distillation (760 mmHg). The white powdery product was washed successively with THF (25 mL) and pentane (25 mL), then dried under vacuum.



Boehmite (1.00 g, 16.7 mmol) and the appropriate acid (67.4 mmol) were refluxed in 60 mL xylenes for four days to yield a clear viscous solution which solidified to an immobile gel upon cooling to room temperature. Removal of the volatiles in vacuo yielded a white solid which was triturated with diethyl ether (50 mL) and washed with additional diethyl ether (50 mL). Drying in vacuo yielded a white powder.

RESULTS AND DISCUSSION

Refluxing powdered boehmite with an excess of a carboxylic acid, HO_2CR , either neat (e.g. $\text{R} = \text{CH}_3$, acetic acid) or as a xylene solution (e.g. $\text{R} = \text{C}_5\text{H}_{11}$, hexanoic acid), results in the formation of the corresponding carboxy-substituted alumoxane. The physical appearance and solubilities of the resulting materials are highly dependent on the identity of the carboxylate substituent. For $\text{R} = \text{C}_n\text{H}_{2n+1}$ ($n = 1-3$) and CH_2Cl the alumoxanes are white microcrystalline powders, insoluble in common organic solvents, whereas for $\text{R} = \text{C}_5\text{H}_{11}$, C_7H_{15} and $\text{C}_2\text{H}_4\text{OCH}_3$, the products are white solids, which readily form homogeneous solutions in CH_2Cl_2 and THF, from which thin films may be produced by spin coating (see below).

The elemental composition of the alumoxanes has been determined and indicates the presence of greater than one equivalent of carboxylic acid to aluminum. The carboxy-alumoxanes prepared by Kimura and co-workers^{2,4} were proposed to be of the general formula of $[\text{Al}(\text{O})(\text{O}_2\text{CR})(\text{HO}_2\text{CR})]_n$ in which one of the acid groups exists as the deprotonated form, while the remainder is protonated. In the present case, ^{13}C CP-MAS NMR spectroscopy indicates only a single carboxylate environment, while the observation of bands at 1586 ± 5 and $1470 \pm 8 \text{ cm}^{-1}$ in the IR spectra are consistent with a bridging mode of coordination. In addition, the IR spectra of the alumoxanes show broad absorption bands between 3700 and 3400 cm^{-1} , consistent with our previous assignment for an aluminum bound hydroxide group.⁵ Thus, based on charge and mass balance consideration and confirmed by NMR and IR spectral data we have determined that the alumoxanes prepared from boehmite have the general formula $[\text{Al}(\text{O})_x(\text{OH})_y(\text{O}_2\text{CR})_z]_n$.

If, as we have previously proposed,⁵ the core structure of alumoxanes is analogous to that of boehmite then one would expect the aluminum to retain predominantly six-fold coordination. This is clearly demonstrated to be the case by the ^{27}Al MAS NMR spectra of the alumoxanes, in which only a signal attributable to six-coordinate aluminum is detected ($\delta - 6$ to 0 ppm , $W_{1/2} = 1800 - 2000 \text{ Hz}$).

A sample of the boehmite examined by SEM prior to reaction with the carboxylic acid was found to consist of spherical featureless particles (see Figure 1) varying in size from $20 - 100 \mu\text{m}$ in diameter. The crystallite size in these particles was determined by XRD to be ca. 64 \AA (020 plane).⁶ In contrast, the alumoxanes exist as large "fluffy" conglomerates, $50 - 200 \mu\text{m}$ in size (see Figure 2), with a particle size estimated from SEM to be less than $0.1 \mu\text{m}$ in diameter. Thus, we propose that the carboxylic acids have cleaved the $\text{O}-\text{H}\cdots\text{O}$

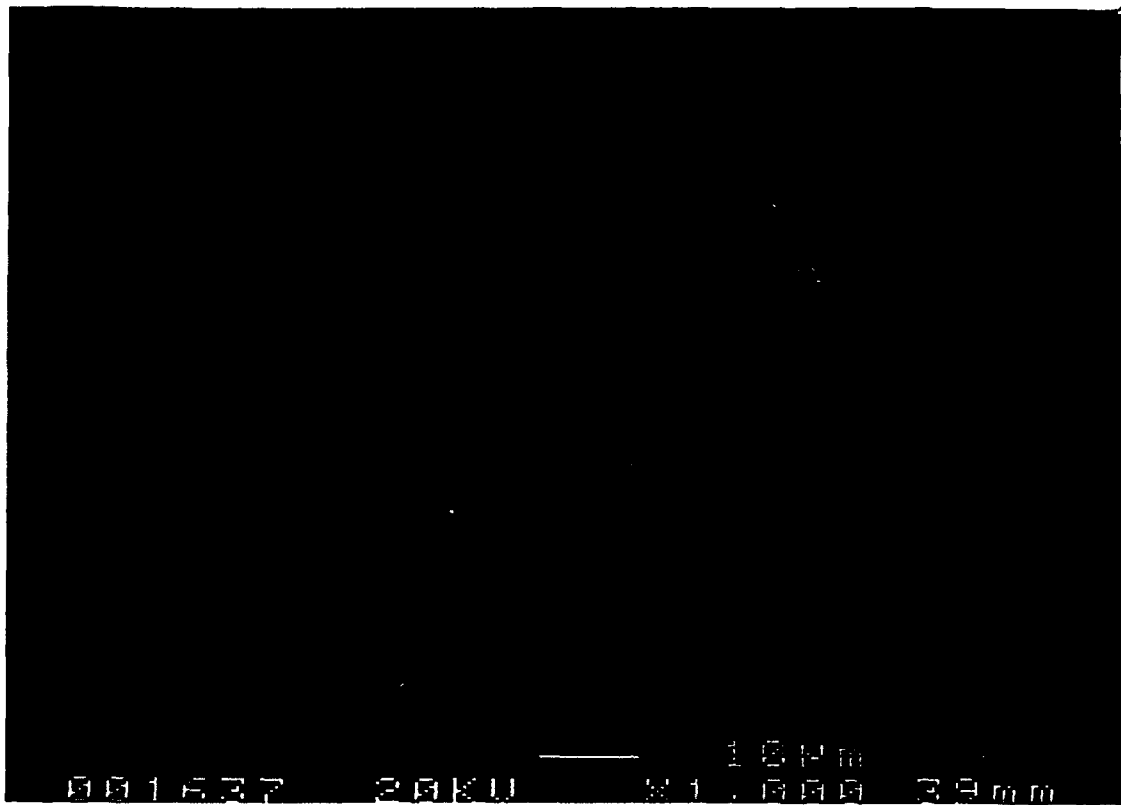


Figure 1. SEI micrograph of unreacted boehmite particle (American Cyanamid).

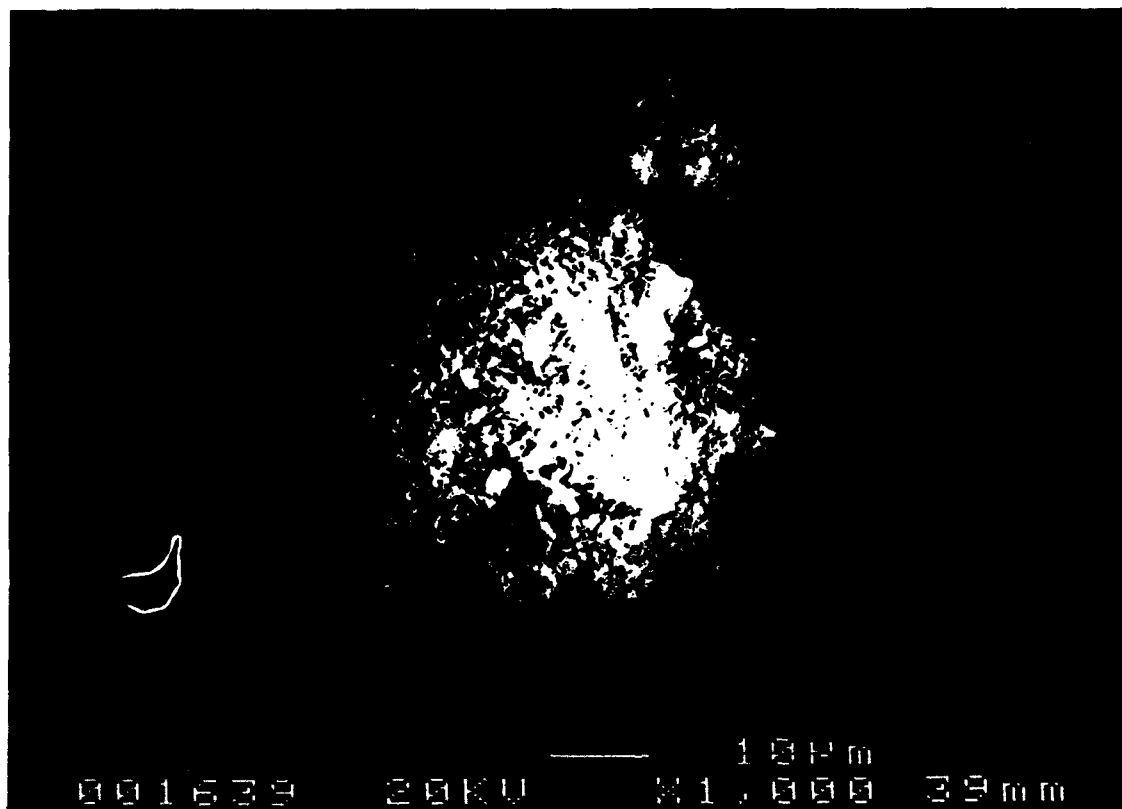


Figure 2. SEI micrograph of $[Al(O)_x(OH)_y(O_2CC_5H_{11})_z]_n$ particle.

hydrogen bonds linking the crystallite planes by replacement of hydroxy with carboxy groups. Despite the particulate nature of the alumoxanes homogenous, continuous films may readily be prepared by dissolution in either CH_2Cl_2 or THF followed by spin coating. For example, evaporation of a CH_2Cl_2 solution of the hexanoate-alumoxane on a glass slide yields a thin film the SEM of which is shown in Figure 3. The homogenous nature of these films implies that they consist of an interpenetrating organic/inorganic matrix.

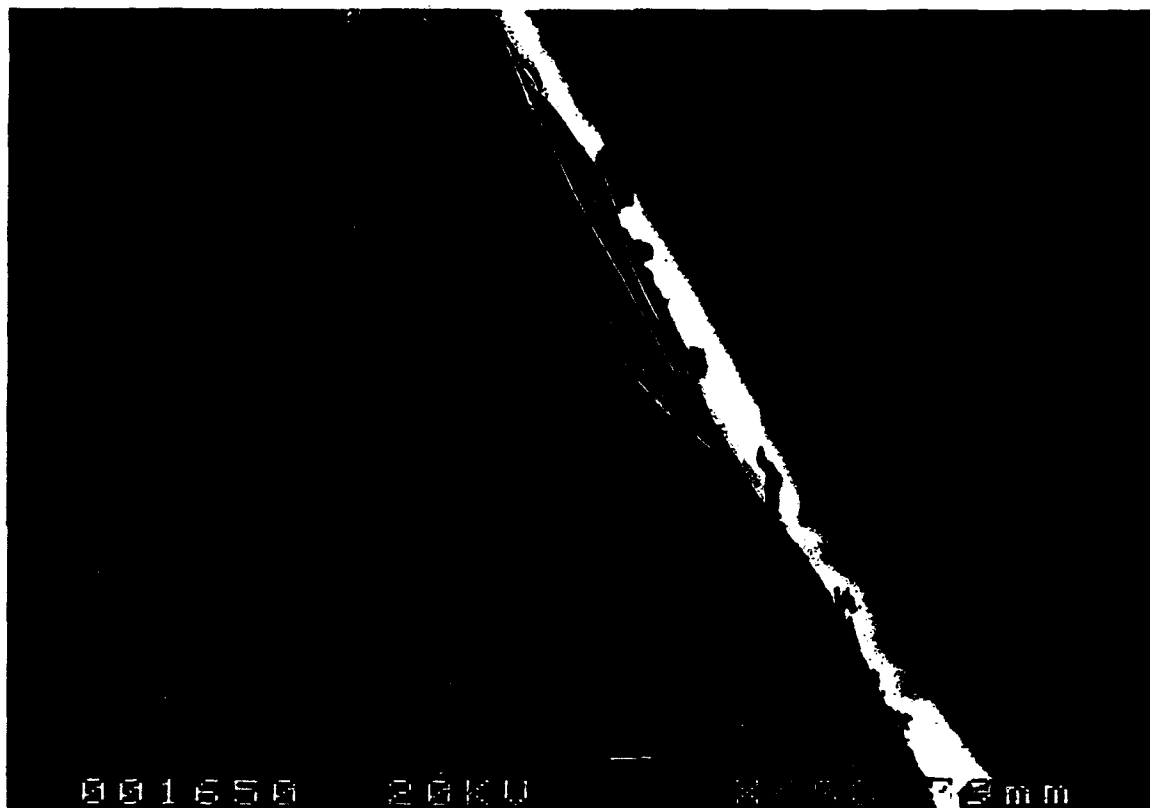


Figure 3. SEI micrograph of $[\text{Al}(\text{O})_x(\text{OH})_y(\text{O}_2\text{CC}_5\text{H}_{11})_z]_n$ film spin coated on glass from CH_2Cl_2 solution.

All of the alumoxanes prepared from boehmite decompose between 180 and 385 °C to give alumina in essentially quantitative yield. XPS and XRD spectra of the residues are consistent with their identity as γ -alumina. Carbon incorporation is found to be very low if the pyrolysis is carried out under an oxidizing atmosphere.

CONCLUSION

Alumoxanes of the general formula $[Al(O)_x(OH)_y(O_2CR)_z]_n$ have been prepared by refluxing boehmite with carboxylic acids under appropriate conditions. These products have been shown by scanning electron microscopy to consist of conglomerates of tiny particles (less than 0.1 μm in diameter). In addition, several alumoxanes form sols or gels in various solvents, which may be readily spin coated. Pyrolysis of the products under oxidizing conditions leads to the formation of γ -alumina with low carbon contamination.

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