Carboxylate-Substituted Alumoxanes as Processable Precursors to Transition Metal−Aluminum and Lanthanide−Aluminum Mixed-Metal Oxides: Atomic Scale Mixing via a New Transmetalation Reaction

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Carboxylate−alumoxanes, $[Al(O)_x(OH)_y(O_2CR)_z]_n$, have been uniformly doped with a transition metal or lanthanide. Thermolysis of the doped alumoxanes yields homogeneous mixed-metal oxides. The carboxylate−alumoxanes were synthesized by the reaction of boehmite, $[Al(O)(OH)]_n$, with either hexanoic, octanoic, methacrylic, or [(methoxyethoxy)-ethoxy]acetic acids. Reaction of the carboxylate alumoxane with either a metal acetylacetonate complex, $M(acac)_3$ (M = Mn, La, Er), $V(O)(acac)_2$, or a salt, $[NH_4]_2[Ce(NO_3)_6]$ and $[NH_4]_4[Ce(SO_4)_4]$, results in transmetalation and the formation of a doped-alumoxane. Upon thermolysis these doped-alumoxanes result in homogeneous mixed-metal oxides. The formation of single-phase materials is similar to that of traditional sol−gel methodologies; however, the alumoxane precursors are indefinitely stable, in solid and solution. In addition, these precursors show no propensity to segregation or polymerization and are readily processed in aqueous or hydrocarbon medium. The stability of the doped alumoxanes and uniformity of the subsequent oxide is a consequence of the atomic level mixing produced by a unique substitution reaction. A transition-metal or lanthanide ion is exchanged for an aluminum ion within the alumoxane nanoclusters and the elimination of Al^{3+} as $Al(acac)_3$ or $[Al(H_2O)_6]^{3+}$. Evidence for this reaction is obtained from NMR and IR spectroscopy. The doped-alumoxane precursors have been characterized by IR and NMR spectroscopy and TG/DTA. The resulting mixed-metal oxide ceramics have been characterized by scanning electron and scanning electron microscopy (SEM), ESR, microprobe analysis, and X-ray diffraction.

Introduction

Aluminum oxides are an ubiquitous part of modern technology with a combined annual production of over 30 million tons.[2] Applications include precursors for the production of aluminum metal, catalysts and porous catalyst supports, structural ceramic materials, oxidation/corrosion resistant coatings, reinforcing agents for plastics and rubbers, and dielectrics in the electronics industry. It is as a consequence of their wide application that there is continued interest in the development of new synthetic methods for their production. Of particular interest in recent years is the development of economically viable and environmentally benign methods with a wide range of synthetic flexibility.

Although the applications for aluminum oxides themselves are extensive, ternary systems, such as mullite ($Al_6Si_2O_{13}$), YAG ($Y_3Al_5O_{12}$), hibonite ($CaAl_{12}O_{19}$), and β-alumina ($NaAl_{11}O_{17}$) can offer advantages over those of the binary aluminum oxides. For example, YAG has high-temperature chemical stability and the highest creep resistance of any known oxide, leading to its evaluation as a promising fiber material for the preparation of ceramic composites.[3] Mullite has exceptional high-temperature shock resistance and is widely used in high-temperature structural applications.[4] Aluminates possessing β-alumina or magnetoplumbite structures are being evaluated as interfacial coatings for ceramic matrix composites.[5] In addition to improved physical properties, aluminum oxides doped with an alkali, alkaline-earth, transition-metal, or lanthanide oxides are of interest for catalysts, catalyst precursors, and catalyst supports (corderite, barium hexaluminate), solid-state laser materials (Nd:YAG, $Cr:Al_2O_3$), and ionic conducting solids (β-,β''-alumina).

The traditional ceramic method for the synthesis of binary aluminum oxides involves the physical mixing of the separate oxides (or oxide precursors such as

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carbonates and oxalates),[6] sintering at high temperatures for extended reaction times, grinding, and resintering. The high temperatures and long reaction times are necessary to overcome slow solid-state diffusion since physical mixing is limited to the micron scale. In addition, while the traditional mixing/sintering approach may provide a simple route to the desired ternary or doped material, it is possible to produce only powders, which must be subsequently processed to form items with the desired shape. It is for this reason that chemical routes to complex aluminum oxide ceramics have become more extensively investigated. The most widely employed method is sol−gel synthesis whose versatility and potentially atomic level homogeneity make it advantageous for the preparation of a range of materials and forms.[7] Sol−gel synthesis of alumina has traditionally been performed by the neutralization of a concentrated aluminum salt solution;[8] however, the strong interactions between the freshly precipitated alumina gels and ions from the precursors solutions make it difficult to prepare the gels in pure form.[9] To avoid this complication, alumina gels are often prepared from the hydrolysis of aluminum alkoxides, $[Al(OR)_3]_n$ (eq 1).[10]

$$Al(OR)_3 \xrightarrow{H_2O} Al\ gel \xrightarrow{\Delta} Al_2O_3 \qquad (1)$$

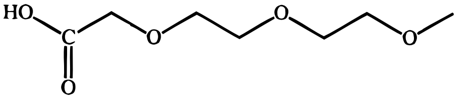
Despite the advantages of this sol−gel synthesis over the traditional ceramic approach, there are a number of significant difficulties, including long reaction times required (often greater than 24 h), the addition of complexing agents being necessary for inhibition of premature precipitation, and careful pH control of the sol, the cost of the raw materials [e.g., $Al(O^iPr)_3$ = \$20−40 kg^{-1}], the use of mineral acids (e.g., nitric acid), and finally the sols being necessarily prepared freshly since storage results in precipitation. In combination, these issues make sol−gel routes to monolithic aluminum oxides inconvenient for many applications.

It is desirable, therefore, to develop new synthetic methodologies to overcome the drawbacks in both the sol−gel and traditional ceramic processing methods. In this regard we have reported an alternative to the "bottom-up" approach of hydrolyzing small molecules to form alumina-based ceramic precursors; as is used in sol−gel synthesis. We have developed a "top-down" approach based upon the reaction of boehmite, $[Al(O)(OH)]_n$, with carboxylic acids.[11] The physical properties of the resulting alumoxanes[12] may be readily controlled by the identity of the carboxylate group[11] and can be easily converted to γ-Al_2O_3 upon mild thermolysis.[13] Furthermore, the alumoxanes are indefinitely stable under ambient conditions and are adaptable to a wide range of processing techniques. Given the advantages observed for the application of carboxylate alumoxanes, e.g., the low price of boehmite (\$0.5 kg^{-1}) and the availability of an almost infinite range of carboxylic acids, make these species ideal as precursors for ternary and doped aluminum oxides.

We have investigated the application of our carboxylate alumoxanes as suitable precursors for transition-metal- and lanthanide-doped aluminum oxide ceramics. The results of this study are presented herein.

Results and Discussion

Synthesis and Characterization of Transition-Metal and Lanthanide Doped-Alumoxanes. The carboxylate-substituted alumoxanes were prepared as previously discussed.[11] Pseudo-boehmite was refluxed in a xylene solution of the appropriate carboxylic acid, HO_2CR. The alumoxanes were isolated by either filtration of the cooled reaction mixture or removal of all volatiles under vacuum, followed by washing with Et_2O to remove traces of free acid. For the present study four different carboxylate alumoxanes were prepared: from hexanoic acid $[HO_2C(CH_2)_4CH_3]$, octanoic acid $[HO_2C(CH_2)_6CH_3]$, methacrylic acid $[HO_2CC(CH_3){=}CH_2]$, and [(methoxyethoxy)ethoxy]acetic acid $[HO_2CCH_2(OCH_2CH_2)_2OCH_3$, MEEA, **I**]; see Experimental Section. The MEEA−alumoxane is soluble in water and $CHCl_3$, while the hexanoate, ocatanoate, and methacrylate alumoxanes are soluble in $CHCl_3$. For each of the metal systems studied two samples were prepared, one from the MEEA−alumoxane and the other from another of the chloroform-soluble alumoxanes.



(**I**)

To demonstrate the suitability and versatility of our alumoxane approach to the synthesis of mixed-metal oxide ceramics, we have chosen two transition metal (manganese and vanadium) and three lanthanide (lanthanum, cerium and erbium) dopants. Lanthanide doping of alumina has been demonstrated to provide enhanced thermal stability;[14] for example, $LaAlO_3$ shows enhanced properties as a high-temperature catalyst support.[15] In addition, in a highly dispersed form, lanthanides and transition metals both offer selective emissions for thin-film electroluminescent (TFEL) displays.[16] For example, manganese is currently used as the dopant in the most efficient yellow-orange TFEL phosphor.[17] The choice of acetylacetenoate complexes

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[12] The term alumoxane is given to aluminum oxide macromolecules traditionally formed by the hydrolysis of aluminum compounds or salts, AlX_3 where X = R, OR, $OSiR_3$, or O_2CR.

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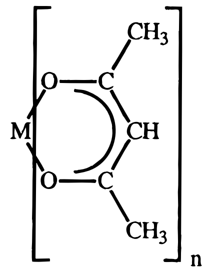
Table 1. Summary of Physical Data for the Carboxylate–Alumoxanes and the Ceramic Products of Their Pyrolysis

	precursor				ceramic			
metal	aluminum source	metal source	solvent	color	T_{dec} (°C)	ceramic yield (%)	color	M:Al ratio
V	methacrylato–alumoxane	$VO(acac)_2$	$CHCl_3$	pale green	500	42.1	pale yellow	1:15.5
	MEEA–alumoxane	$VO(acac)_2$	H_2O	pale green	500	40.0	pale yellow	
	boehmite	$VO(acac)_2$	none[a]	*b*	500	65.5	green	1:15
Mn	octanato–alumnoxane	$Mn(acac)_3$	$CHCl_3$	light brown	500	33.7	light brown	1:16
	MEEA–alumoxane	$Mn(acac)_3$	H_2O	light brown	500	23.1	light brown	
	$Al(NO_3)_3{\cdot}(H_2O)$	$Mn(acac)_3$	H_2O	light brown	500	43.4	light brown	
	boehmite	$Mn(acac)_3$	none[a]	*b*	500	62.3	light brown	1:15
La	octanato–alumoxane	$La(acac)_3$	$CHCl_3$	colorless	400	59.0	white	1:1.5
	MEEA–alumoxane	$La(acac)_3$	$CHCl_3$	colorless	400	42.2	white	1:1
	MEEA–alumoxane	$La(acac)_3$	H_2O	colorless	400	42.2	white	1:1
	boehmite	$La(acac)_3$	none[a]	*b*	400	40.1	white	1:1
Ce	hexanato–alumoxane	$[NH_4]_2[Ce(NO_3)_6]$	$CHCl_3$	yellow	500	37.3	yellow[c]	1:14.7
	MEEA–alu moxane	$[NH_4]_2[Ce(NO_3)_6]$	H_2O	yellow	500	24.3	yellow[c]	
	boehmite	$[NH_4]_2[Ce(NO_3)_6]$	none[a]	*b*	500	59.8	white[d]	1:15
Er	hexanato–alumoxane	$Er(acac)_3$	$CHCl_3$	pink	600	35.1	pink	1:14
	MEEA–alumoxane	$Er(acac)_3$	H_2O	pink	600	33.4	pink	
	boehmite	$Er(acac)_3$	none[a]	*b*	600	63.6	pink	1:15

[a] Physical mixture. [b] Color of the respective metal complex. [c] Ce^{4+}/Ce^{3+}. [d] Ce^{4+}.

(**II**) and nitrate precursor compounds was based upon minimum cost and maximum availability.



M = Mn, La, Er; n = 3

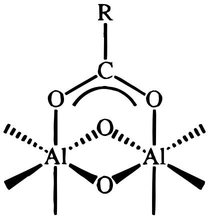
M = V(O); n = 2

(II)

The doped alumoxanes were prepared by mixing solutions of a carboxylate alumoxane and the appropriate metal precursor compound. The times required for complete reaction of the transition metal or lanthanide with the alumoxane varied (see below); however, all reactions were complete within 2 h. The removal of the solvent under vacuum, followed by washing with Et_2O, gave the doped alumoxane in almost stoichiometric yield. The dopants are taken up into the alumoxane's lattice quantitatively. To probe the maximum level of dopant incorporation, the synthesis of the La-doped alumoxane was carried out with an excess of lanthanum resulting in a 1:1.5 ratio in the doped alumoxane. A summary of the various metal–alumoxane combinations is given in Table 1.

The physical appearance and solubilities of the doped carboxylate–alumoxanes are similar to those of the parent alumoxanes, except for having a color related to that of the dopant metal; see Table 1. As with the parent alumoxanes the doped-alumoxanes exist as large "fluffy" agglomerates, 50–200 μm in size, with a particle size estimated from TEM to be less than 0.1 μm in diameter. The X-ray diffraction of the doped alumoxanes are essentially indistinguishable from those of the parent alumoxane.[11] The M:Al atomic ratios for the doped alumoxanes were determined by microprobe analysis are close to the values expected based upon the reaction ratio.

The IR spectra of all the parent carboxylate–alumoxanes contain bands at 1596–1586 and 1473–1466 cm^{-1}, consistent with a bridging mode of coordination (**III**) of



(III)

the carboxylate to the boehmite core.[18] In addition, all of the IR spectra show a broad absorption bands at 3700–3400 cm^{-1}, consistent with our previous assignment for an aluminum-bound hydroxide group. Upon addition of the metal complex, there is a reduction in the intensity of the hydroxide resonances and a broadening of the carboxylate bands; however, there are no resonances assignable to the metal precursor complex. We have previously demonstrated that the carboxylate alumoxanes (in common with all alumoxanes except those containing direct Al–C bonds[19]) contain significant concentrations of acidic hydroxide groups.[11] Metal acetylacetonate complexes are known to be hydrolyzed to the appropriate oxide or hydroxide and consequently have been widely used in sol–gel type synthesis.[20] In view of this, we expected that the reaction of the carboxylate alumoxane with $M(acac)_n$ should proceed as shown in eq 2. While the hydroxide bands in the IR

$$[Al(O)_x(OH)_y(O_2CR)_z] + yM(acac)_3 \rightarrow [Al(O)_x\{OM(acac)_n\}_y(O_2CR)_z] + y\text{acac-H} \quad (2)$$

spectrum were altered upon reaction of the carboxylate alumoxane with $M(acac)_n$, there were no new bands assignable to the acac ligands, even when a large excess of the metal complex is employed.

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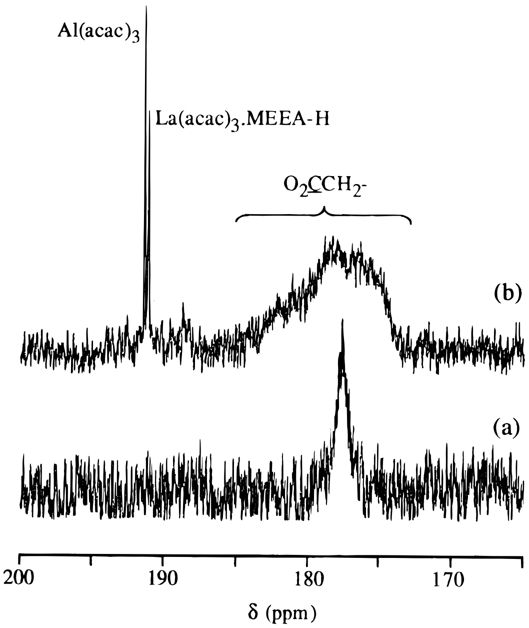

Figure 1. Selected region of the ^{13}C NMR spectra ($CDCl_3$) of MEEA−alumoxane (a) and the reaction mixture of MEEA−alumoxane and $La(acac)_3$ (b). Peak assignments are shown for clarity.

NMR Study of the Reaction of Carboxylate Alumoxanes with Metal Acetylacetenoate Complexes. To further study the reaction of the alumoxane precursors, solution NMR spectra were used to compare undoped and doped materials. The solution ^1H and ^{13}C NMR of the parent carboxylate−alumoxanes indicate a single environment for the bridging carboxylates;[11] see Figure 1a. The ^{27}Al NMR spectra of the alumoxanes before doping consist of a broad resonance at ca. 6 ppm indicative of aluminum in an octahedral AlO_6 coordination environment (Figure 2a).[21]

Reaction of $La(acac)_3$ with hexanoate alumoxane in $CDCl_3$ was followed by ^1H NMR. Upon mixing, the resonances due to $La(acac)_3$ diminish in intensity, and two new resonances are observed: $\delta = 5.48$ (1H, s) and 1.99 (6H, s). These new signals are assigned to $Al(acac)_3$ by comparison with a commercial sample.[22] Similarly, the ^{13}C and ^{27}Al NMR spectra of the reaction mixture confirm $Al(acac)_3$ formation (Figures 1b and 2b, respectively). If the reaction is carried out on a preparative scale, $Al(acac)_3$ may be isolated via crystallization from a toluene/hexane solution or washed out with Et_2O.

Thus, the reaction of the metal−acac complex with the alumoxane does not occur via the expected reaction of the Al−OH groups (eq 2) but is a result of metal exchange and the leaching of aluminum from the boehmite core (i.e., eq 3). We propose that the incorporation of the metal occurs into the boehmite-like lattice of the alumoxane (Scheme 1); however, the exact ligand environment of the doping metal is uncertain, i.e., the extent to which the carboxylate ligands are involved in the coordination to the dopant metal. However, the ^{13}C NMR spectrum (Figure 1b) indicates the presence of at least one new carboxylate environment (possibly due to a lanthanum−carboxylate).

$$[Al(O)_x(OH)_y(O_2CR)_z] + nM(acac)_3 \rightarrow [Al_{1-n}M_n(O)_x(OH)_y(O_2CR)_z] + Al(acac)_3 \quad (3)$$

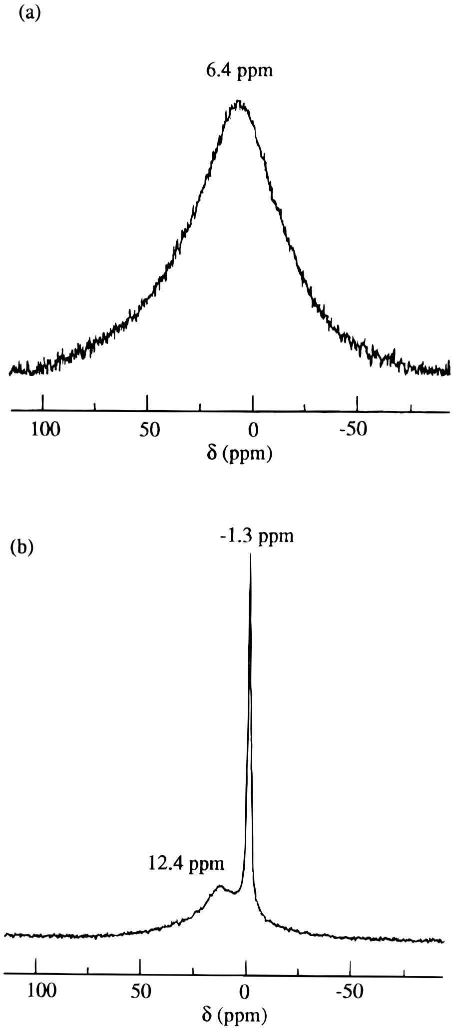

Figure 2. ^{27}Al NMR spectra ($CDCl_3$) of MEEA−alumoxane (a) and the reaction mixture of MEEA−alumoxane and $La(acac)_3$ (b).

It appears that the metal metathesis reaction must result from the direct reaction of the metal−acac complex with the carboxylate alumoxane. Evidence supporting this idea includes (a) no free acac-H is observed during the reaction, (b) no $Al(acac)_3$ is formed from the reaction of alumoxanes with acac-H alone, and (c) MEEA-H does not react with $La(acac)_3$ to give acac-H. Since the boehmite starting material does not react with either $M(acac)_n$ or acac-H,[23] we presume that the carboxylate ligands on the alumoxane assist metal metathesis. Evidence for this is obtained from the ^{13}C NMR spectrum of an alumoxane/$La(acac)_3$ reaction mixture (Figure 1b). In addition to peaks due to the carboxylate α-carbons (O_2CR, $\delta = 185-174$) and the

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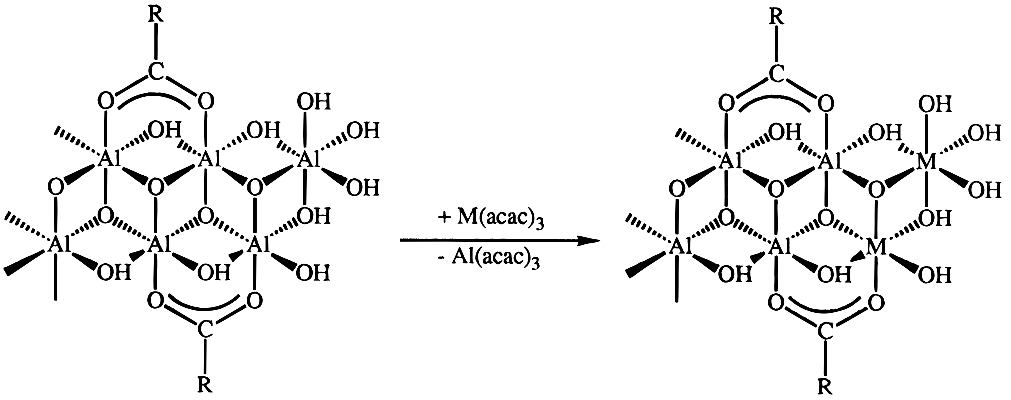
[21] The ^{27}Al NMR resonances observed for six-coordinate aluminum centers are usually sharp ($W_{1/2} = 3-70$ Hz) as is observed for $Al(acac)_3$. However, as a consequence of the multiple aluminum sites expected in carboxylate alumoxanes, broader resonances are expected. Furthermore, this effect is exacerbated by the large size of the carboxylate alumoxanes causing slow tumbling on the NMR time scale. For a discussion of the characterization of ^{27}Al NMR spectral shifts, see: Barron, A. R. *Polyhedron,* **1995**, *14*, 3197.

[22] ^1H NMR ($CDCl_3$): 5.48 (1H, s, CH), 1.99 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$): 191.4 (O=*C*), 101.9 (*C*H), 27.7 (*C*H_3).

[23] At high temperatures (>350 °C) a reaction is observed between $Y(acac)_3$ and boehmite, although the uniformity of the subsequent ceramic is low: Kareiva, A.; Barron, A. R., unpublished results.

Scheme 1. Schematic Representation of the Reaction of Carboxylate Alumoxane with M(acac)$_3$



carbonyl carbons of Al(acac)$_3$ ($\delta = 191.4$), there is a peak at 191.1 ppm (see Figure 1b) that is assigned as La(acac)$_3$·MEEA-H, based upon a comparison with a genuine sample. The ^{13}C NMR spectra of mixtures of La(acac)$_3$ with octanoic acid and tetraglyme[24] suggest that the interaction of La(acac)$_3$ with MEEA-H occurs via the carboxylate and not the polyether side chain. Since no free MEEA-H is detected at the completion of the metal exchange reaction, the presence of La(acac)$_3$·MEEA-H must be an intermediate in the insertion of lanthanum into the alumoxane structure.

Metal-exchange (transmetalation) reactions are well-known for metal complexes and clusters. For example, transition-metal complexes of monoanionic Shift bases have been shown to be stoichiometric transmetalating agents for the replacement of copper in various tetranuclear complexes.[25] However, the room-temperature metal metathesis between a mononuclear metal complex and what may be considered as a solubilized mineral particle is to our knowledge unique. In Shift base transmetalations it is known that the driving force for the reaction is the formation of insoluble [CuL]$_x$ or highly stable CuL$_2$ coproducts. In the present case, we presume that the driving force for transmetalation between the carboxylate alumoxanes and the metal acetylacetonate complexes is the formation of Al(acac)$_3$. However, in the case of cerium, when the nitrate or sulfate salts are used, the driving force is either the formation of [Al(H$_2$O)$_6$]$^{3+}$, which is observed by ^{27}Al NMR spectroscopy,[26] or the binding of cerium into the alumoxane lattice.

Thermal Decomposition of Doped Alumoxanes and Characterization of Mixed-Metal Oxides. The TG/DTA of the doped alumoxanes prepared are similar to their parent alumoxanes. In general two major decomposition regions are observed: the relative mass loss and temperatures at which these regions occur is dependent on the identity of the carboxylic acid and the dopant element. A representative example (the Er-doped hexanoate−alumoxane) is shown in Figure 3, along with the TG/DTA for the hexanoate-alumoxane, Er(acac)$_3$·H$_2$O, and boehmite. In all cases the TGA of the doped alumoxane is distinct from that of a physical mixture of the constituent parts consistent with the formation of a new species.

To ascertain whether the aluminum oxide formed from the thermolysis of the alumoxane retains the shape of the alumoxane precursor, filter paper was impregnated with Ce-doped MEEA−alumoxane from aqueous solution. The paper was pyrolyzed to give a free-standing ceramic. The filter paper (pretreatment and alumoxane coated) and the ceramic product were analyzed by SEM. The SEM of the untreated-uncoated sample (see Figure 4a) shows the paper to consist of interwoven fibers, 5−40 μm in diameter The Ce-doped MEEA−alumoxane treated paper is visually indistinguishable from their untreated equivalents. However, SEM images (Figure 4b) revealed that large deposits had formed between the fibers. As can be seen from Figure 4c, the Ce-doped aluminum oxide ceramic formed upon oxidative thermolysis at 600 °C retains the structure of the paper fibers with little evidence for particulate oxide residues. These studies suggest that the carboxylate alumoxanes can be used for the fabrication of ceramic coatings on nonplanar substrates.[27]

All of the carboxylate−alumoxanes previously prepared from boehmite decompose to give γ-alumina.[11] Up to a firing temperature of 600 °C all of the doped alumoxanes give poorly crystalline γ-Al$_2$O$_3$ with no evidence for the formation of the dopant's oxide.[28] This is in contrast to samples prepared by the ceramic method under similar conditions (see Table 1 and Experimental Section). For example, the X-ray diffraction of the ceramic obtained from the Ce-doped alumoxane (Figure 5a) is that of γ-Al$_2$O$_3$, while a sample prepared from the thermolysis of a physical mixture of [NH$_4$]$_2$[Ce(NO$_3$)$_6$] and boehmite shows diffraction pattern (Figure 5b) consistent with a mixture of γ-Al$_2$O$_3$ (JCPDS 10-0425) and CeO$_2$ (JCPDS 34-0394); see Figure 5c. The formation of a homogeneous mixed-metal oxide from the alumoxane as opposed to a mixture of oxides by the ceramic route is also suggested by the SEM images of the representative ceramic samples.

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(24) ^{13}C NMR (CDCl$_3$) for the acetylacetenoate carbonyl carbon in La(acac)$_3$ ($\delta = 189.9$), La(acac)$_3$·MEEA-H ($\delta = 191.1$), La(acac)$_3$.octanoic acid ($\delta = 191.1$), La(acac)$_3$·tetraglyme ($\delta = 189.7$).

(25) See, for example: (a) Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidus, M. *Inorg. Chim. Acta* **1984**, *84*, 41. (b) El-Toukhy, A.; Cai, G. -Z.; Davies, G.; Gilbert, T. R.; Onan, K. D.; Veidus, M. *J. Am. Chem. Soc.* **1984**, *106*, 4596. (c) Cai, G. -Z.; Davies, G.; El-Toukhy, A.; Gilbert, T. R.; Henary, M. *Inorg. Chem.* **1985**, *24*, 1701. (d) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 2269.

(26) The ^{27}Al NMR (D$_2$O) spectrum for a mixture of MEEA−alumoxane and [NH$_4$]$_4$[Ce(SO$_4$)$_4$] shows a sharp resonance at 0.5 ppm ($W_{1/2} = 22$ Hz) consitent with the formation of [Al(H$_2$O)$_6$]$^{3+}$, see: Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London 1978.

(27) Uniform, adherent 0.5 μm ceramic coatings may be produced on 5 μm diameter carbon fibers using MEEA−alumoxane.

(28) Seperate experiments indicate that in all cases the appropriate oxide of the dopant metal crystallizes under identical conditions.

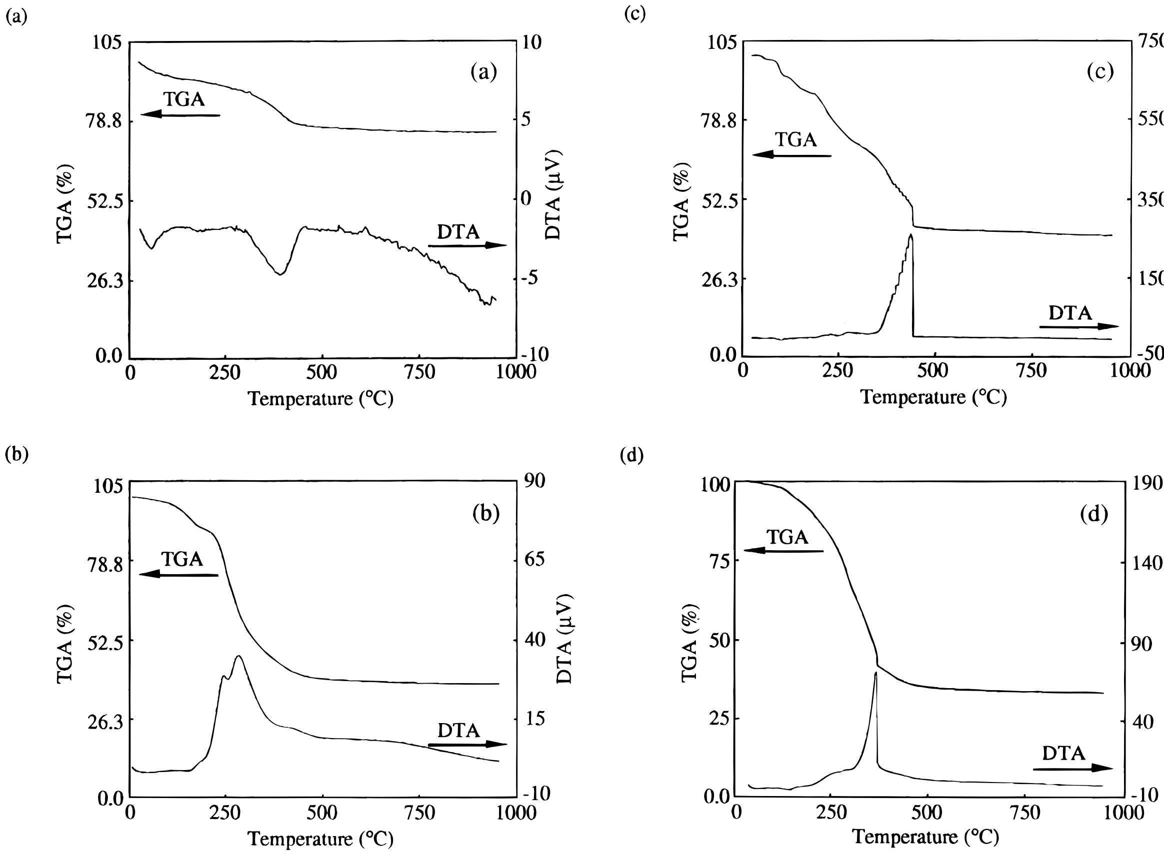

Figure 3. TG/DTA analysis of (a) boehmite, (b) hexanoate–alumoxane, (c) Er(acac)$_3$·H$_2$O, and (d) Er-doped hexanoate–alumoxane.

Figure 6a shows a SE image of Er-doped alumina formed from Er-doped hexanoate–alumoxane and consists of microcrystalline particles forming 100 μm sized agglomerates. Similar morphologies are found for materials prepared by traditional sol–gel processes; see below. In contrast the SEM micrograph (Figure 6b) of the material formed from the thermolysis of a physical mixture of boehmite and Er(acac)$_3$ shows spherical particles (nearly identical with the boehmite source[11]) covered with particulate matter (presumable Er$_2$O$_3$). EDX and microprobe analysis indicate that the M:Al ratio increases slightly upon calcination of the doped alumoxane, suggesting that a volatile aluminum compound is liberated. In fact, Al(acac)$_3$ sublimes intact at ca. 190 °C (760 mmHg, O$_2$), and a comparison of the TGA of Al(acac)$_3$ with the La-doped alumoxanes suggests that Al(acac)$_3$ is indeed liberated. This is in agreement with the NMR results discussed above.

With the exception of the Ce-doped aluminum oxide, each of the alumoxane-formed mixed-metal oxides have similar colors to the materials made by the ceramic method (see Table 1). In the case of the cerium, the doped alumina made by the alumoxane route is yellow, as compared to the white oxide (Al$_2$O$_3$/CeO$_2$) made by the ceramic route. Anhydrous CeO$_2$ is white, while the hydrate of CeO$_2$ is yellow, suggesting that the alumoxane-produced material is perhaps hydrated. However, the yellow color is retained upon heating above 600 °C for 4 h. In addition, whereas the white Ce-doped alumina and CeO$_2$ are ESR silent, the ESR of the Ce-doped alumina prepared from the alumoxane exhibits a broad intense resonance at $g = 2.21$ (see Figure 7) consistent with the presence of some Ce^{3+}. The isotropic nature of the signal would be expected for a centrosymmetric coordination environment, such as is present for the octahedral vacancies in γ-Al$_2$O$_3$. X-ray photoelectron (XPS) measurements are consistent with the presence of Ce^{4+} and Ce^{3+}.[29] We propose therefore that as the doped alumoxane is converted into oxide, the cerium is incorporated into the lattice as both Ce^{3+} and Ce^{4+}. The greater ionic radii of cerium (Ce^{4+} = 0.92 Å, Ce^{3+} = 1.034 Å) as compared to Al^{3+} (0.51 Å) suggests that the cerium does not substitute aluminum as Cr^{3+} (0.63 Å) does in ruby. Instead the cerium is possibly situated at grain boundaries. However, the oxidative stability of the Ce(III) is clearly related in some manner to its incorporation into the alumina lattice. The formation of a stable Ce(III)-doped alumina offers potential application as a supported combustion catalyst for diesel engines, where Ce^{4+}/Ce^{3+} has already been proposed to be the active species.

Thermolysis of the high-lanthanum-doped alumoxane at 1000 °C yields crystalline LaAlO$_3$ (JCPDS 31-0022); see Figure 8. Samples containing a slight excess of aluminum also show a small amount of γ-Al$_2$O$_3$ by XRD, while incomplete reaction of La(acac)$_3$ with the alumoxane, in water, results in the formation of La$_2$O$_3$ in addition to LaAlO$_3$. However, if the exact stoichiometry is employed and reaction of La(acac)$_3$ with the alumoxane is allowed to reach completion, a pure phase of LaAlO$_3$ is produced.[30]

Comparison of the Alumoxane Precursor Route with Other Synthetic Techniques. Like traditional sol–gel methodologies, the use of carboxylate alumoxanes for the synthesis of aluminum-based oxide ceram-

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(29) MacInnes, A. N., personal communication.

(30) YAG (Y$_3$Al$_5$O$_{12}$) and hibonite (CaAl$_{12}$O$_{19}$) have been formed from the yttrium- and calcium-doped alumoxanes, see: Harlan, C. J.; Kareiva, A.; MacQueen, D. B.; Cook, R.; Barron, A. R. *Adv. Mater.*, in press.

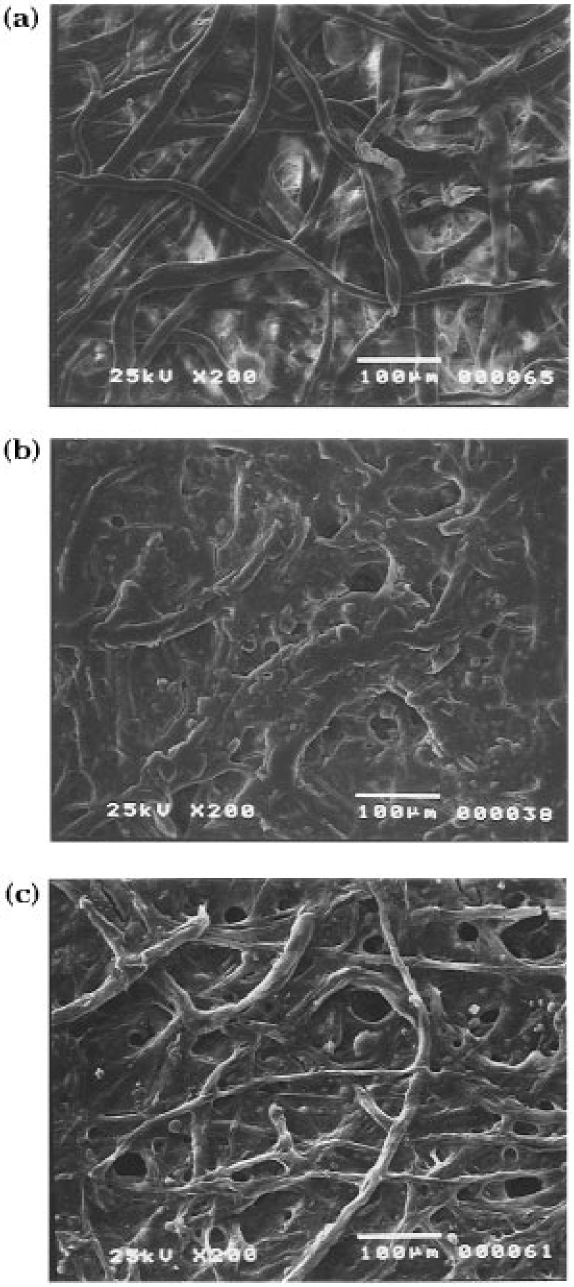

Figure 4. SEM images of Whatman #1 filter paper: untreated (a), coated with Ce-doped MEEA−alumoxane (b), and fired in O_2 at 600 °C (c).

ics offers significant advantages over the ceramic method, e.g., atomic scale mixing of metals and processability. Furthermore, the incorporation of metals into the alumoxane core structure allow for the formation of metastable phases.[31] However, unlike sol−gel synthesis the carboxylate alumoxanes are infinitely stable in both solution and the solid state. In addition, whereas the choice of solvents in sol−gel synthesis is limited, the solubility of the carboxylate alumoxanes is dependent on the identity of the carboxylic acid residue, which is almost unrestricted. The solubility of the alumoxanes may therefore be readily controlled so as to make them compatible with any co-reactants. Table 2 shows a comparison of the ceramic and sol−gel methods with

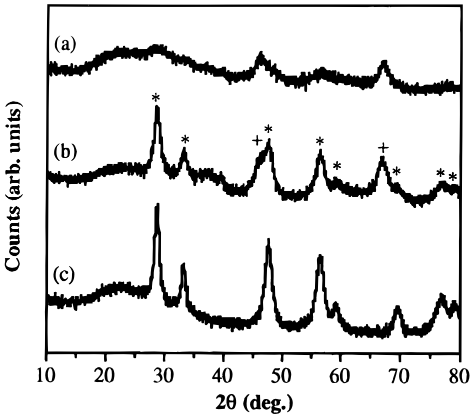

Figure 5. XRD of Ce-doped alumina prepared from Ce-doped octanoate−alumoxane at 600 °C (a) and a physical mixture of boehmite and $[NH_4]_2[Ce(NO_3)_6]$ heated to 600 °C (b). The XRD of CeO_2 prepared from the thermolysis of $[NH_4]_2[Ce(NO_3)_6]$ is given for reference (c). The alumina (+) and CeO_2 (*) are marked for clarity in (b).

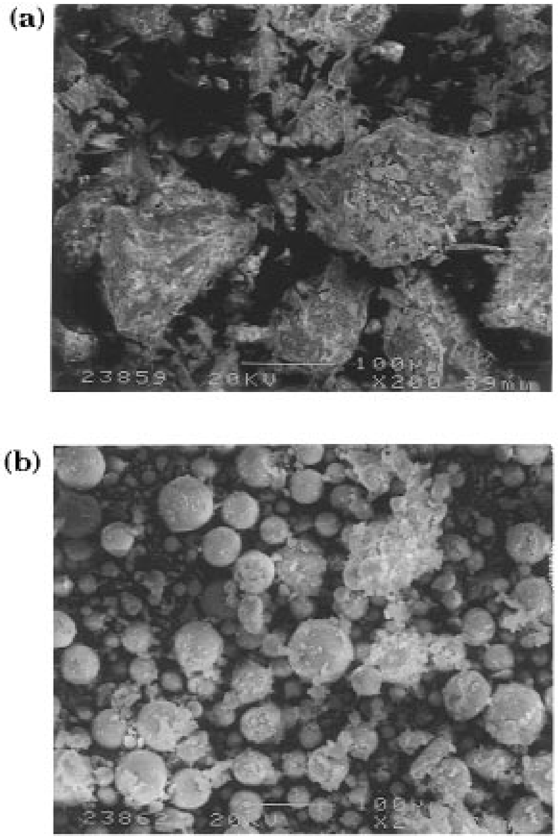

Figure 6. SEM images of Er-doped alumina: prepared from Er-doped hexanoate−alumoxane (a) and a physical mixture of boehmite/$Er(acac)_3$ (b).

that of the carboxylate alumoxanes for the synthesis of ternary aluminum oxides.

While these advantages are significant, the alumoxanes have further benefits with respect to large scale production of ternary and quaternary ceramics. The most dramatic is the simplicity of the alumoxane methodology. A comparison of the synthesis of Mn-doped alumina by the alumoxane and sol−gel routes may be ascertained from Schemes 2 and 3,[32] respectively. The alumoxane route is simple and can be halted and/or modified at any stage without significant effect on the products. A careful control of pH, the use of additives to inhibit precipitation, and slow concentration

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(31) The formation of $Y_4Al_2O_9$ is observed during the synthesis of $Y_3Al_5O_{12}$ (YAG) from Y-doped MEEA−alumoxane, see ref 3.

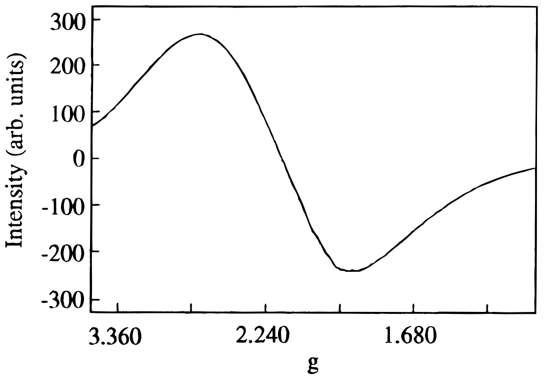


Figure 7. Solid-state ESR spectrum (298 K) of Ce^{4+}/Ce^{3+}-doped alumina formed by the thermolysis of Ce-doped hexanoate–alumoxane.

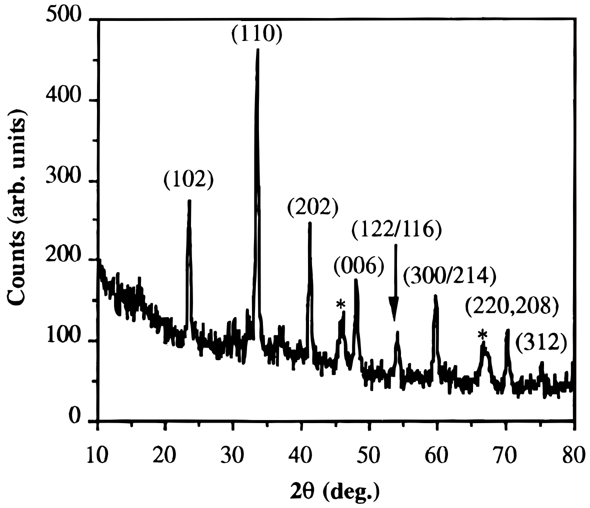


Figure 8. XRD of $LaAlO_3$ prepared from La-doped octanoate–alumoxane at 1000 °C. $LaAlO_3$ peaks are indexed, asterisks refer to γ-Al_2O_3 impurities.

Table 2. Comparison of the Alumoxane Method with the Ceramic Method and Sol–Gel Synthesis for the Synthesis of Ternary Aluminum Oxides

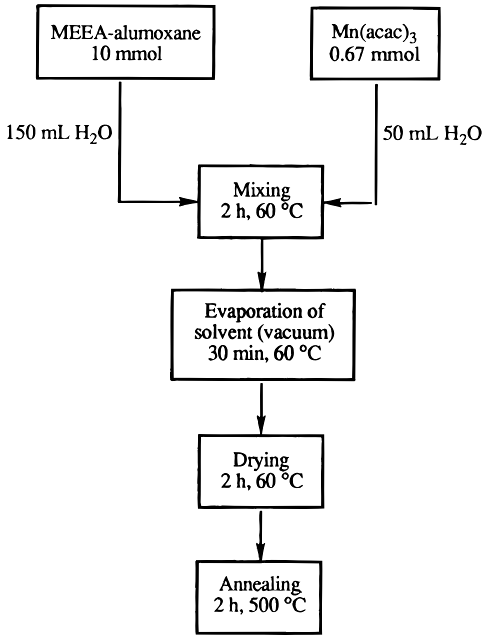
	alumoxane	sol–gel	ceramic method
methodology	simple	complex	simple
atomic mixing	yes	yes	no
metastable phases	yes	yes	no
stability	excellent	poor	infinite
solubility	readily controlled	difficult to control	none
proccesability	good	good	poor
time	<8 h	>20 h	days
cost	low	medium–high	low

steps are not required, making the alumoxane route easier and quicker; see Table 2. A final benefit with respect to large-scale processing is the relatively low cost of the alumoxane precursors.

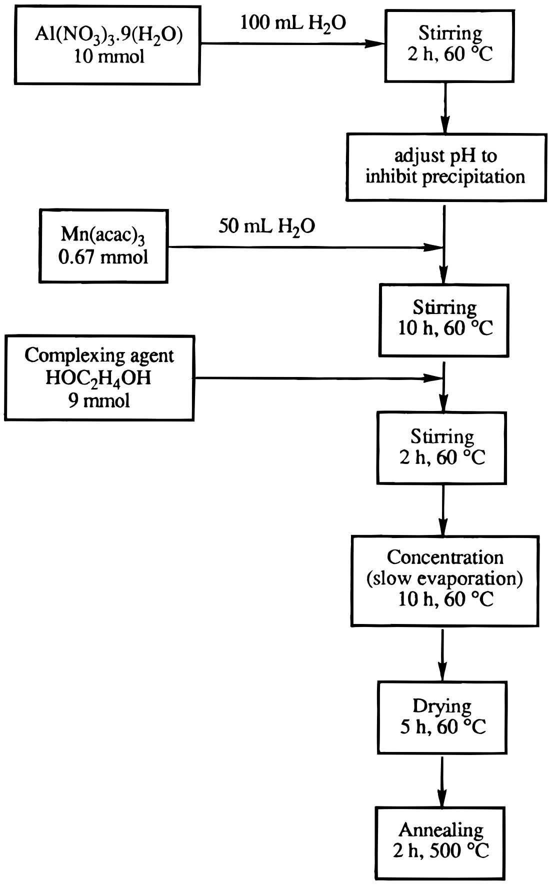
Conclusion

It is increasingly recognized that progress in the preparation of novel oxide-based materials requires the development of new synthetic techniques that lead to solids possessing unique structures and properties. The ceramic method (cycles of grinding one or more oxides and heating) for preparation of oxides is a relatively brute-force method compared to the sophistication of methodologies available for the synthesis of organic compounds. The synthesis of organic compounds relies primarily on kinetic control of synthetic pathways via

Scheme 2. Schematic Representation of the Preparation of Mn-Doped Aluminum Oxides by the Alumoxane Route



Scheme 3. Schematic Representation of the Preparation of Mn-Doped Aluminum Oxides by Sol–Gel Synthesis



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(32) The protocol used in Scheme 3 was based upon the method reported previously for alumina, see: (a) Teichner, S. J.; Nicolaon, G. A.; Vicarini, M. A.; Gardes, G. E. E. *Adv. Colloid Interface Sci.* 1976, **5**, 245. (b) Yoldas, B. E. *J. Mat. Sci.* 1975, **10**, 1856.

group-by-group assembly of the whole molecule. The formation of ceramic materials on the other hand is controlled by the diffusion of ionic and atomic species through reactants and products to give the final product. An awareness of the limitations of the ceramic method as a technique for the production of advanced materials has increased efforts directed toward the development of mild chemistry-based approaches that occur at low temperatures. These methods, loosely grouped under the name *chimie douce* (soft chemistry),[33] pay close attention to structure, stability, and the mechanisms of product formation.

We have demonstrated that carboxylate alumoxanes may be readily doped with transition metals and lanthanides. The metal becomes incorporated into the boehmite-like core of the alumoxane, with the concomitant elimination of $Al(acac)_3$. As a consequence of atomic scale mixing, ternary aluminum oxides are readily formed with modest reaction times. In this regard the alumoxane methodology represents a direct competitor to traditional sol−gel synthesis. However, unlike sol−gels where solubility must be carefully controlled, the solubility of the carboxylate alumoxanes is determined by the identity of the carboxylate substituents. Furthermore, while the instability of sol−gels precludes their long-term storage, the alumoxanes may be stored indefinitely without decomposition in solid or solution. The water solubility of the MEEA−alumoxane offers the possibility of the production of aluminum-containing ceramics from aqueous solution at normal pH without the use of additives. The only obvious limitation to the range of ceramics possible from the alumoxane methodology is the requirement that aluminum must be a constituent.

Experimental Section

Melting points and thermogravimetric/differential thermal analyses were obtained on a Seiko 200 TG/DTA instrument using a carrier gas of either dry nitrogen, air, or oxygen. The ramp rate was 5 °C min^{-1} for all samples, with a data collection of 1 s^{-1}. Infrared spectra (4000−400 cm^{-1}) were obtained using Nicolet 5ZDX-FTIR and Perkin-Elmer Series 1600 spectrometers, as Nujol mulls on KBr plates. Solution ^1H, ^{13}C, and ^{27}Al NMR spectra were obtained on either Bruker AM-400, Bruker AM-300, or Bruker AM-250 spectrometers. Chemical shifts are reported relative to external $SiMe_4$ (external), $[Al(H_2O)_6]^{3+}$ (external), or $CDCl_3$ (solvent) unless otherwise stated. ESR spectra were collected on a Varian E-109 spectrometer interfaced via a SRS 245 interface module and a Capital Equipment Co. GPIB driver to an IBM PC. To enable XRD analysis, samples powders were mounted on glass slides prior to analysis. Data were collected on Scintag and Siemens diffractometers, with a scan rate of 1° min^{-1}. SEM studies were performed on JEOL JSM-35 scanning microscope. A small amount of the as-synthesized material was attached to an aluminum stub with graphite paint. Due to the insulating nature of the materials, focusing and visual examination was problematical. Therefore, in some cases a thin layer of gold was sputtered onto the sample to provide a conducting surface.

Research grade pseudo-boehmite (100%) was kindly provided by American Cyanamid. All carboxylic acids, $Mn(acac)_3$, $La(acac)_3$, $Er(acac)_3$, $V(O)(acac)_2$, $[NH_4]_2[Ce(NO_3)_6]$, and $[NH_4]_4[Ce(SO_4)_4]$ were obtained commercially (Strem and Aldrich) and were used as received. For ^1H NMR studies $Mn(acac)_3$ was recrystallized prior to use. A summary of reaction conditions is given in Table 1.

Synthesis of Hexanato−Alumoxane. Boehmite (5.0 g, 83 mmol) and hexanoic acid (38.0 mL, 303 mmol) were combined in a 500 mL round-bottom flask with xylenes (275 mL) and refluxed for 4 days. The xylenes were distilled under vacuum, and the residual solid was triturated with ethanol (3 × 150 mL) and filtered. The remaining solid was dried under vacuum (10^{-2} Torr) for 3−12 h, leaving a white powder.

Synthesis of Octanato-Alumoxane. Boehmite (5.0 g, 83 mmol) and octanoic acid (53.0 mL, 334 mmol) were reacted and worked up in a similar manner as for hexanato-alumoxane yielding a white powder.

Synthesis of Methacrylato−Alumoxane. Boehmite (3.0 g, 50 mmol) and methacrylic acid (17.0 mL, 200 mmol) were reacted and worked up in a similar manner as for hexanato−alumoxane, yielding a white powder.

Synthesis of MEEA−Alumoxane. *Method 1.* Boehmite (3.0 g, 50 mmol) and [(methoxyethoxy)ethoxy]acetic acid (30.0 mL, 200 mmol) were reacted and worked up in a similar manner as for hexanato−alumoxane, yielding a clear sticky solid which contained a small amount of unreacted [(methoxyethoxy)ethoxy]acetic acid as determined by ^{13}C NMR.

Method 2. Boehmite (14.0 g, 233 mmol) and [(methoxyethoxy)ethoxy]acetic acid (126 g, 707 mmol) were refluxed in xylenes for 24 h, resulting in a viscous gel with some brown pyrolized material attached to the side of the flask. The brown material was removed manually, and the gel was poured into hexanes (300 mL) and stirred briefly, and the solvent decanted off. Et_2O (300 mL) was added, stirred for 20 min, and filtered off. This was repeated, and then the remaining solid was pumped dry (10^{-2} Torr, 2 h). CH_2Cl_2 (250 mL) was added to the remaining solid and allowed to form a homogeneous gel. Hexanes (100 mL) were added, and about 150 mL of solvent was removed in vacuo. Hexanes (150 mL) were added, and an additional 100 mL of solvent was removed in vacuo. Additional hexanes (100 mL) were added, and the solvent was removed via filtration. The white solid thus obtained was air-dried for several hours and then left under vacuum (10^{-2} Torr) overnight, resulting in a hard white dense material.

Method 3. Boehmite (20 g) and [(methoxyethoxy)ethoxy]-acetic acid (240 mL) are refluxed in xylenes (1 L) for 3 days in a 3 L round-bottom flask equipped with a mechanical stirrer and reflux condenser. Hexanes (700 mL) are added to the stirring solution, resulting in the separation of a white solid. The solvent is filtered off through a large medium-porosity glass frit attached into a sidearm flask connected to an aspirator. The solid is then washed with ether (500 mL) by stirring for several hours and filtered off. This washing process is repeated three times with one washing done overnight. The remaining solid is subjected to vacuum (10^{-2} Torr) for at least 5 h, then added to water (300 mL), and stirred overnight. The water solution is centrifuged at 6000 rpm for 1 h and decanted. The water is removed in vacuo at 50 °C until a clear viscous solution is obtained. The MEEA−alumoxane solution is poured into a crystallizing dish and dried for 2−3 days at 50 °C, resulting in about 50 g of MEEA−alumoxane which readily redissolves in water, methylene chloride, and chloroform.

Synthesis of Vanadium-Doped Methacrylato−Alumoxane. A solution of methacrylato−alumoxane (0.8 g) in $CHCl_3$ (200 mL) was added to $V(O)(acac)_2$ (0.098 g) in $CHCl_3$ (50 mL). The reaction was stirred overnight at room temperature. Volatiles were removed under vacuum resulting in a gray/green material which was washed with Et_2O and dried in air.

Synthesis of Vanadium-Doped MEEA−Alumoxane. To a solution of MEEA−alumoxane (0.5 g) in H_2O (150 mL) was added $V(O)(acac)_2$ in H_2O (50 mL). The reaction was stirred 20 h at room temperature. Volatiles were removed under vacuum, resulting in a gray/green material.

Synthesis of Manganese-Doped Octanato−Alumoxane. To a solution of octanoate alumoxane (1.436 g) in $CHCl_3$ (250 mL) in a 500 mL round-bottom flask was added $Mn(acac)_3$ (166 mg) in $CHCl_3$ (50 mL). After stirring overnight with a magnetic stirrer, the solvent was removed under vacuum, and the resulting solid washed with EtOH and dried in air.

Synthesis of Manganese-Doped MEEA−Alumoxane. To a solution of MEEA−alumoxane (0.5 g) in H_2O (150 mL)

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(33) Gopalakrishnan, J. *Chem. Mater.* **1995**, *7*, 1265.

was added $Mn(acac)_3$ (0.5 g) in H_2O. The reaction was stirred 20 h at room temperature. Volatiles were removed under vacuum, and the resulting brown solid was washed with EtOH and dried in air.

Synthesis of Lanthanum-Doped Octanato−Alumoxane. Octanato−alumoxane (0.5 g) and $Ln(acac)_3\cdot 8\%\ H_2O$ (0.63 g) were added to $CHCl_3$ (40 mL) and refluxed 48 h. Volatiles were removed under vacuum. The solid was extracted with toluene (30 mL) and filtered, leaving 0.48 g white solid which was dried under vacuum.

Synthesis of Lanthanum-Doped MEEA−Alumoxane. *Method 1.* To a solution of MEEA−alumoxane (2.0 g) in $CHCl_3$ (50 mL) was added $Ln(acac)_3\cdot 8\%\ H_2O$ (1.2 g) in $CHCl_3$ (50 mL). The reaction was refluxed overnight and filtered away from a small amount of precipitate. Volatiles were removed under vacuum and the solid was extracted with Et_2O (120 mL). The Et_2O was filtered off, and the solid dried under vacuum. The Et_2O extract was evacuated to dryness and the ^1H NMR spectrum of the resulting off-white solid showed it to be almost exclusively $Al(acac)_3$.

Method 2. MEEA−alumoxane (1.0 g) and $Ln(acac)_3\cdot 8\%\ H_2O$ (1.8 g) were added to H_2O (30 mL) and stirred overnight at room temperature. EtOH (ca. 10 mL) was added and the volatiles were removed under vacuum. Separation of $Al(acac)_3$ and La-loaded alumoxane was achieved by dissolving the crude product in toluene (ca. 20 mL) followed by precipitation via addition of hexanes (30 mL). The resulting precipitate, isolated by filtration and dried under vacuum, contained only a trace of $Al(acac)_3$ as shown by ^1H NMR. The filtrate was evacuated to dryness and was shown, via ^1H NMR, to contain $Al(acac)_3$ and a small amount of La-loaded MEEA−alumoxane.

Synthesis of Cerium-Doped Hexanato−Alumoxane. To a solution of hexanato−alumoxane (1.75 g) in $CHCl_3$ (250 mL) was added $(NH_4)_2Ce(NO_3)_6$ (0.37 g) in H_2O (50 mL). The mixture was stirred for 18 h, and then volatiles were removed under vacuum, resulting in a yellow solid which was washed with EtOH and dried in air.

Synthesis of Cerium-Doped MEEA−Alumoxane. To a solution of MEEA−alumoxane (0.5 g) in H2O (150 mL) was added $(NH_4)_2Ce(NO_3)_6$ (0.08 g) in H_2O (50 mL). The reaction was stirred for 20 h, and then volatiles were removed under vacuum. The resulting yellow solid was washed with EtOH and dried in air.

Synthesis of Erbium-Doped Hexanato−Alumoxane. To a solution of hexanato−alumoxane (1.75 g) in $CHCl_3$ (200 mL) was added $Er(acac)_3\cdot H_2O$ in $CHCl_3$ (50 mL). The reaction was stirred overnight followed by removal of volatiles under vacuum, resulting in a pink material. The solid was washed with EtOH and dried in air.

Synthesis of Erbium-Doped MEEA−Alumoxane. To a solution of MEEA−alumoxane (0.5 g) in H_2O (150 mL) was added $Er(acac)_3\cdot H_2O$ in H_2O (50 mL). The reaction was stirred 20 h then volatiles were removed under vacuum. The resulting pink solid was washed with EtOH and dried in air.

Synthesis of Doped Aluminum Oxides. The synthesis of manganese doped alumina is given below. A summary of reaction conditions is given in Table 1.

Method 1. The manganese doped octanoate−alumoxane (5.0 g) was heated to 500 °C, under a flow of dry air, for 2 h.

Method 2. A mixture of boehmite (5.0 g) and $Mn(acac)_3$ (2.5 g) was ground in an agate pestle. The mixture was then heated to 500 °C, under air, for 2 h, reground, and heated for a further 2 h.

Method 3. $Al(NO_3)_3\cdot 9(H_2O)$ (3.75 g) was dissolved in H_2O (100 mL), and the pH carefully adjusted to 5−6 by the addition of NaOH solution. To this solution was first added $Mn(acac)_3$ (0.235 g) and then ethylene glycol (0.25 mL). The solvent was removed by slow evaporation, and the resulting solid heated to 500 °C for 2 h; see Scheme 3.

Acknowledgment. Financial support for this work was provided by the Office of Naval Research (N00014-91-J-1934 and N00014-95-C-0266). The Fulbright Foundation is acknowledged for a Fellowship (A.K.). We are indebted to Dr. J. D. Carruthers at American Cyanamid for the generous gift of boehmite. Prof. D. L. Callahan, Dr. S. L. Stoll, and Dr. E. G. Gillan (Rice University) and Dr. Mark Mullins (Harvard University) are acknowledged for assistance with SEM, XRD, ESR, and microprobe measurements.

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