METAL-EXCHANGED CARBOXYLATO-ALUMOXANES AND PROCESS OF MAKING METAL-DOPED ALUMINA

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ABSTRACT

A method has been developed for the solution-based metal exchange of carboxylato-alumoxanes [AlO1(OR)(O2CR)]2 with a wide range of metal cations. Metal-exchanged carboxylato-alumoxanes are new, particularly those in which about 10% to about 50% or more of the Al ions are exchanged for other metal ions. Additionally, the carboxylic acid ligands can be stripped from the boehmite core of metal-exchanged carboxylato-alumoxanes at low temperature leading to the formation of metal-exchanged boehmite particles. These new material phases can be used as intermediates for preparation of mixed metal aluminum oxide materials. Thermolysis of the metal-exchanged carboxylato-alumoxanes or metal-exchanged boehmite particles results in doped aluminas (MA1Ox), binary (MAO), ternary (MMAMOx) and even more complex metal aluminum oxide compounds, where M and M' are metal ions other than those of aluminum and are preferably those of Lanthanide metals or transition metals. The method allows preparation of pure phase materials as well as the preparation of metastable metal aluminum oxide phases. The carboxylato-alumoxanes are prepared by the reaction of boehmite (or pseudoboehmite) with carboxylic acids in a suitable solvent. Up to at least half of the aluminum cations in the boehmite lattice of the carboxylato-alumoxanes can be replaced by the reaction of metal acylacetonates with the carboxylato-alumoxane in a suitable solvent. The metal exchange reaction can also be carried out by reaction with soluble metal salts. Reactions of boehmite with the metal acylacetonates (or soluble metal salts) do not lead to the metal exchange reaction observed for the carboxylato-alumoxanes.

29 Claims, 1 Drawing Sheet
METAL-EXCHANGED CARBOXYLATO-
ALUMOXANES AND PROCESS OF MAKING
METAL-DOPED ALUMINA

CROSS-REFERENCE TO RELATED
APPLICATIONS

This application claims priority to U.S. provisional appli-
cation Ser. No. 60/043,800, filed Apr. 11, 1997, pending
which is incorporated in its entirety herein.

FIELD OF THE INVENTION

This invention relates generally to a method for making
metal-doped metal oxide materials by a metal exchange
process that can be carried out in aqueous or organic
solutions.

The method allows synthesis of metal-exchanged carboxy-
lato-alumoxanes and metal-exchanged boehmite particles
which can be converted to binary, ternary and more
complex metal aluminium oxides upon thermal processing.
Metal aluminium oxide structural classes that can be pre-
pared by this method include, without limitation, spinels,
garnets, perovskites, β-alumina, and hexa-aluminates.
The oxide structure that is obtained from the carboxy-
lato-alumoxane depends on the metal used in the metal exchange
reaction and the ratio of the metal to aluminium in the final
product. For example exchanging yttrium into the alumox-
ane lattice to give a ratio of 3Y:5Al gives yttrium aluminium
garnet, or exchanging magnesium into the alumoxane lattice
to give a ratio of 1 Mg:2 Al gives magnesium aluminate
spinel.

BACKGROUND OF THE INVENTION

Binary and ternary metal aluminium oxides are technolo-
ergically important classes of materials with applications in
ceramics, optics, electronics, lasers and catalysis. MgAl2O4
(spinel) can be hot pressed into transparent windows with an
exceptional infrared transmission range. MgAl2O4 is also used
as refractory material for metal forming operations.
Y2Al4O12 (YAG) is widely used as a solid state laser material
(Nd:YAG), and as a high energy phosphor (blue). YAG also
has high temperature chemical stability and the highest
creep resistance of any known oxide, leading to its evalua-
tion as a promising fiber material for the preparation of
ceramic composites. La2O3 is used as a substrate material
for growth of thin film oxide superconductors. Mullite, an
aluminosilicate, and cordierite (magnesium aluminosilicate)
have exceptional high temperature shock resistance and chemical stability and the latter material is
widely used in automotive catalytic converters.

The first requirement of a successful ceramic process is
the availability of a good powder. Most of the advances in
ceramic processing can be traced directly to the develop-
ment of powders with controlled size and purity. Early
ceramic processing used mineral based precursors that had
a wide range of grain sizes and impurities. Ceramics formed
from the mineral precursors often had glassy phases that
reduced the performance of the ceramic. The development
of solution based precipitation techniques that produced fine
powders with well-defined particle size distributions and
high purity significantly improved the fabrication of ceramic
materials.

The traditional ceramic methods that are used to prepare
binary (or more complex) aluminium oxides involves the
physical mixing of the powders of the oxides (or oxide
precursors), sintering at high temperatures for extended
reaction times, grinding and re-sintering. High temperatures
and long reaction times are necessary to overcome the slow
 solid state diffusion since physical mixing is limited to the
micron scale. The traditional ceramic approach provides a
simple route to the preparation of powders, however the
powders must then be formed into the desired shape by
traditional processing methods (slip casting, extrusion, dry
pressing etc.) and sintered to fabricate the shaped ceramic
item.

In order to overcome the limitations of the traditional
ceramic powder processing methods, chemical routes to the
synthesis of complex aluminium oxide powders and ceramics
are increasingly being adopted. The most widely employed
methods are the sol-gel based techniques whose versatility,
and potentially atomic level homogeneity, make them desir-
able approaches for the preparation of arrangement of materials
and forms. Sol-gel synthesis of alumina has traditionally
been performed by the neutralization of a concentrated
aluminium salt solution. 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. To avoid this complication alumina gels are
often prepared from the hydrolysis of aluminium alkoxides,
[Al(OR)3]n, i.e.,

Although there can be significant advantages to the syn-
thesis of metal aluminium oxides via the sol-gel route (such
as preparation of small particles-size and good homogeneity)
there are a number of significant difficulties, including: long
reaction times required (often greater than 24 hours), the
addition of complexation agents that are necessary for
inhibition of premature precipitation, careful pH control of
the sol, low yields of gels from the alkoxide precursors, and
the relative instability of the sols. The instability of the sols
means that the sols must be prepared freshly, since storage
results in precipitation. Furthermore, the fabrication of
mixed metal aluminium oxides from alkoxides can be
problematic, since the alkoxides can have different hydroly-
sis rates leading to phase segregation in the gels. Also the
significant shrinkage of sol-gel based precursors leads to
extensive cracking. For this reason fabrication of large
ceramic objects via sol-gel routes is not generally feasible.
In combination, these issues make sol-gel routes to mono-
structural aluminium oxides inconvenient for many applica-
tions.

It is desirable, therefore to identify materials and pro-
cesses that can be used to prepare complex metal aluminium
oxides starting with stable low cost precursors. The synthetic
process should lend itself to the fabrication of a wide range
of metal aluminium oxides with fine control over composi-
tion and particle size. The present invention provides a
method of making metal aluminium oxides that provides
these benefits and avoids many of the problems of prior art
processes.

SUMMARY OF THE INVENTION

The present invention provides a solution-based metal-
exchange process for synthesis of metal aluminium oxides,
binary, ternary and more complex metal aluminium oxides.
The synthetic method is based on a metal-exchange reaction
between metal acetylacetones (or soluble metal
salts) and carboxylato-alumoxanes that can be described by
general formula:

\[ [\text{Al(OH)}3\text{(O2CR)}_2]_n \]
where $\chi$, y, and n can be variable depending on the preparation method of the boehmite and the amount of the carboxylic acid used, and where $R$ CO$_2$ is a mono-carboxylate, where R is an organic group containing carbon with optional hetero-atom functional groups, and is preferably an alkyl, alkenyl, aromatic, haloalkyl, or halolkenyl, haloaromatic group or an alkyl, alkenyl or aromatic ether group. These components are prepared by methods described in Landry et al. (1995), Apblett et al. (1992) and Kareiva et al. (1996). The composition of the carboxylato-alumoxanes varies dependent upon the starting materials employed and the details of the synthetic method employed as discussed in particular in Landry et al. (1995). The carboxylato-alumoxanes react to form metal-exchanged carboxylato-alumoxanes which can then be transformed to metal-exchanged boehmite particles and can be used as intermediates for preparation of mixed metal aluminum oxide materials. Al ions are exchanged for other metal ions by exchanging carboxylato-alumoxanes or metal-exchanged boehmite particles results in doped aluminas (M$_2$Al$_2$O$_4$, binary MAIO$_2$), ternary (MMAlO$_2$) and even more complex metal aluminate compounds with carboxylic acids in a suitable solvent, the use of aqueous solvent media being preferred. Up to about half of the aluminum cations in the boehmite lattice of the carboxylato-alumoxanes can be replaced by reaction of metal acetylacetonates with the carboxylato-alumoxane in a suitable solvent. The metal exchange reaction can also be carried out by reaction with soluble metal salts in a suitable solvent. The solvent can be dichloromethane or THF for example for alumoxanes soluble in organic solvents and water for alumoxanes soluble in water. Reactions of boehmite with the metal acetylacetonates (or soluble metal salts) do not lead to the metal exchange reaction observed for the carboxylato-alumoxanes.

**DESCRIPTION OF THE INVENTION**

This invention discloses a solution-based metal exchange process wherein metal cations can be exchanged for aluminum cations in the boehmite lattice of materials known as carboxylato-alumoxanes ([Al(x)O](OH))$_{2}$)Cl]$_{x}$ where $\chi$,y, and n are variable depending on the synthesis conditions used to prepare the boehmite and the synthesis conditions and concentrations of the carboxylic acid used in the preparation of the alumoxane. The metal-exchanged carboxylato-alumoxanes are readily converted to doped aluminas (M$_2$AIO$_2$, binary MAIO$_2$, ternary (MMAlO$_2$) where x is a number that renders the compound charge neutral) and even more complex metal aluminum oxide compounds upon thermal processing. These conversions are done by application of sufficient heat to decompose the carboxylic acid and preferably to allow diffusion of the metal cations. Temperatures in the range of 325° C. to 600° C. are sufficient to decompose the alumoxane to give metal-exchanged y-Al$_2$O$_3$. The temperatures required to cause diffusion of the cations to give the final oxide product depend on the cations exchanged and the structure to be formed. However, the temperature range for diffusion of the metal cations and formation of the end product is generally between 800° C and 1700° C.

The carboxylato-alumoxanes are prepared by the reaction of boehmite or pseudoboehmite with carboxylic acids in a solvent such as xylene for carboxylic acids that are highly hydrophobic (e.g. octanoic acid, lauric acid, steric acid, benzoic acid etc.) or water for carboxylic acids that are hydrophilic (hydroxyacetic acid, methoxyethoxyacetic acid, ethoxycarboxylic acid, 6-aminoacaproic acid, 4-hydroxybenzoic acid, lactic acid, etc.). In some cases, heating is required for exchange. The boehmite (or pseudoboehmite) source can be a commercial boehmite product such as CATAPAL (A, B, C, D, or E, Condea Vista Chemical Company) or boehmite.
prepared, for example, by the precipitation of aluminum nitrate with ammonium hydroxide followed by hydrothermal treatment at 200°C for 24 hours or by the hydrolysis of aluminum trialkoxides above 80°C. The carboxylic acid can be any monocarboxylic acid. Dicarboxylic acids cannot be used since they will cross-link the boehmite particles together leading to intractable products. The carboxylic acid can be aromatic or aliphatic, and can contain hetero-atom functional groups such as halogens, hydroxyls, amines, mercaptans, phosphines, etc. The metal exchange reaction does not appear to be sensitive to the type of monocarboxylic acid selected. However, the solution-based reaction does not occur in the absence of the carboxylic acids being bound to the surface of the boehmite particle.

The solution-based metal-exchange reaction is carried out by dispersing or solubilizing a carboxylato-alumoxane in a solvent along with either a metal salt or metal acetylacetonate. The solvent is chosen to solubilize the carboxylato-alumoxane and can be an organic solvent such as dichloromethane or THF (tetrahydrofuran) for carboxylato-alumoxanes that are prepared using hydrophobic carboxylic acids (e.g., octanoic acid, lauric acid, steric acid, etc.) or water for carboxylato-alumoxanes prepared using hydrophilic carboxylic acids (e.g., hydroxyacetic, hydroxybenzonic, aminobutyric, etc.) The metal salt or the metal acetylacetonate is dispersed in the solvent with the carboxylato-alumoxane and the metal exchange reaction is carried out between room temperature and the boiling point of the solvent. Solvents employed in this method include those that are mixtures of one or more components (e.g., aqueous alcohol). Successful metal exchange reactions of the carboxylato-alumoxanes have been carried out using boehmite to whose surface has chemically bound carboxylic acids as varied as hexanionic, dimethoxybenzonic, lauric acid, acetic acid, gluconic acid and methoxy (ethoxyethoxy)acetic acid have been bound. The carboxylic acid is believed to be attached through its oxygen atoms in a bridging mode to two aluminum cations. The metal exchange reaction depends primarily on the presence of a bound carboxylic acid and is independent of the nature of the carboxylic acid. Carboxylato-alumoxanes, where $\text{RCOO}^-$ is hexanionic, dimethoxybenzonic and lauric, are soluble in organic solvents. Alumoxanes where $\text{RCOO}^-$ is acetate, gluconate and methoxy (ethoxyethoxy)acetate, are soluble in water. Metal acetylacetonates, useful in this reaction, can be selected without limitation from the acetylacetonates of Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ti$^{4+}$, V$^{5+}$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Ga$^{3+}$, Y$^{3+}$, Zr$^{4+}$, Nb$^{5+}$, Ag$^{+}$, Cd$^{2+}$, In$^{3+}$, Sc$^{3+}$, Re$^{5+}$, Hf$^{4+}$, Pr$^{3+}$, La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Pr$^{3+}$, Th$^{4+}$, and U$^{6+}$ or mixtures thereof. In some cases, e.g., $\text{UO}_2$(acac)$_2$ and $\text{VO}_2$(acac)$_2$, metal oxide acetylacetonates can be used in the exchange reaction.

All metal acetylacetonate complexes are not equally reactive with the carboxylato-alumoxane materials. In general, the lanthanides can be readily metal exchanged into the boehmite lattice of the carboxylato-alumoxanes using lanthanide acetylacetonates by stirring the two reactants at room temperature in a few hours in THF or dichloromethane. Metal exchange with other metal acetylacetonates (such as cobalt (II) acetylacetonate or calcium acetylacetonate) requires heating (e.g., about 50°C—about 150°C, dependent at least in part on the solvent being used) and longer reaction times. For some metal acetylacetonates no metal-exchange reaction is observed. These metal acetylacetonates include chromium (III) acetylacetonate, molybdenum (VI) oxide acetylacetonate and bismuth (III) acetylacetonate. The former two metals are expected to be substitutionally inert based on their electron configuration.

At room temperature or temperatures near ambient (room temperature to about 100°C), stirring the metal acetylacetonate with the carboxylato-alumoxane in a solvent such as water (for hydrophilic alumoxanes) or THF, or dichloromethane (for hydrophobic alumoxanes) results in the formation of the metal exchanged alumoxane and the formation of $\text{Al}$(acac)$_3$.

For some metals, the metal exchange reaction can be carried out using metal salts that are not acetylacetonate complexes. For example, when water-soluble metal salts such as ammonium cerium nitrate ($\text{NH}_4$)[Ce(NO$_3$)$_6$] or ammonium ceric sulfate ($\text{NH}_4$)[Ce(SO$_4$)$_2$] or strontium nitrate or nickel nitrate or cadmium nitrate, are mixed in solution with the carboxylato-alumoxanes, the metal cations are exchanged for the aluminum cations in the boehmite lattice and $\text{Al}$(NO$_3$)$_3$ is formed. Metal-exchange reactions of this invention can be carried out with nitrate, sulfate, acetate salts (e.g., nickel or cobalt acetate) of the following metals: Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ti$^{4+}$, V$^{5+}$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Ga$^{3+}$, Y$^{3+}$, Zr$^{4+}$, Nb$^{5+}$, Ag$^+$, Cd$^{2+}$, In$^{3+}$, Sc$^{3+}$, Re$^{5+}$, Hf$^{4+}$, Pr$^{3+}$, La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Pr$^{3+}$, Th$^{4+}$, and U$^{6+}$ or mixtures thereof. In cases in which the exchange of multiple metal ions is desired, the metal exchange reaction of different metal ions can be carried out at the same time (using a mixture of appropriate starting metal-salts or acetylacetonate complexes) or by sequential metal-exchange reactions. The ratios of the exchanged metal concentrations in the final product are determined by the ratios of the metal complexes used in the metal exchange reaction. For example to prepare $\text{Zn}_2\text{Co}_2\text{Al}_2\text{O}_8$, one would use a 1:1 molar ratio of zinc to cobalt acetylacetonate (or a 1:1 molar ratio of the nitrates, sulfates or acetates). The ratio of Zn$^{2+}$ and Co$^{2+}$, to Al$^3+$ is chosen to be 0.5 to 1.0.

As noted in Kareva et al. 1996, the Ce(III)-doped alumoxane-formed aluminum oxide, unlike other alumoxane-formed mixed metal oxides examined in that reference (see Table 1, therein), had a color distinct from materials made by the ceramic method. The cerium-doped metal oxide made by the alumoxane route was yellow compared to the white oxide prepared by the ceramic route. Also compared to the white oxide prepared by the ceramic route, the yellow Ce-doped oxide of this invention exhibited an ESR signal (a broad intense resonance at g=2.21), which is consistent with the presence of Ce$^{3+}$. The alumoxane route, thus, in some cases, can prepare doped metal oxides that can not be prepared by the ceramic route. The ceramic route apparently gives Ce(IV)-doped oxide, while the alumoxane route gives a material that contains Ce$^{4+}$. Ce$^{3+}$/Ce$^{4+}$ has been proposed as the active species in supported combustion catalysts for diesel engines, thus stable-Ce(III)-doped alumina produced by the alumoxane route has potential for such catalyst applications. Mo-doped gamma alumina (~3 weight percent Mn) has been prepared by reaction of manganese acetylacetonate with carboxylato-alumoxanes to give a $\text{Mn}_2\text{Al}_2\text{O}_4$ support that is stable towards reaction with $\text{Co}_3\text{O}_4$. This allows preparation of high activity $\text{Co}/\text{Mn}$-Al$_2$O$_3$ oxidation catalysts. Thus a range of metal exchanged alumina catalysts and catalyst supports can be prepared by the use of metal exchanged carboxylato-alumoxane precursors.

Reaction of boehmite or pseudoboehmite with metal acetylacetonates or other insoluble metal salts does not lead to the formation of metal-exchanged boehmite or pseudoboehmite materials. The presence of the hydrophilic carboxylic acid is necessary for the metal-exchange reaction to occur. The carboxylic acid ligand can be stripped from the metal-exchanged carboxylato-alumoxane to give metal-
exchanged boehmite particles. The carboxylic acid can be stripped from the carboxylato-alumoxane, for example, by treatment with aqueous hydrogen peroxide solutions and heating to 25–100°C or by treatment with aqueous caustic solutions 3–6N KOH, 3–6NNaOH. These treatments result in a metal-exchanged boehmite particle that are free of the carboxylic acid attached to the surface of the carboxylic acid.

Using the metal acetylacetonate reagents and certain water-soluble nitrate, sulfate and acetate salts, a wide compositional range of mixed metal carboxylato-alumoxanes and mixed metal boehmite particles can be prepared. These mixed metal materials can then be thermally processed to provide a wide range of mixed metal aluminum oxide compositions that include but are not limited to M(M₂Al₃O₆)₃ (a=0–1, b=0–1, a+b=1), M₂M₃Al₃O₆ (a=0–1, b=0–1, a+b=1), M₃M₃Al₂O₆ (a=0–5, b=0–3, a+b=8), M₂M₃Al₁O₆ (a=0–3, b=0–1, a+b=4). Other compositions that include lattices possessing aluminum and oxygen with one or more non-aluminate cations can also be prepared by the metal-exchange reaction of this invention from carboxylato-alumoxane precursors.

Supporting evidence for the metal-exchange reaction of the carboxylato-alumoxanes from NMR and IR spectroscopy (Kareiva, et al. 1996) is presented below.

A detailed description of the metal exchange reaction (and characterization of the reaction) for the reaction of La(acac)₃ with hexanato-alumoxane follows. The doped carboxylato-alumoxane was prepared by mixing the carboxylato-alumoxane and La(acac)₃, (where acac is acetylacetonate) in deuterated dichloromethane. The reaction of La(acac)₃ was complete within 2 hours. The removal of the solvent under vacuum, followed by washing with Et₂O gave the La exchanged—carboxylato-alumoxane in almost stoichiometric yields. The dopants are taken up into the alumoxane’s lattice quantitatively. When the La/Al lanthanum acetylacetonate to alumoxane ratio is 1:11, the lanthanum hexaluminate is formed (La₂Al₁₁O₃₃) and when the ratio of La/Al is 1:1, the lanthanum aluminum perovskite is formed (LaAlO₃).

In order to probe the maximum level of dopant incorporation the synthesis of the La-doped alumoxane was carried out. It was found that at least 50% of the aluminum cations could be replaced and thermolysis of the resulting material gave LaAlO₃.

The physical appearance and solubilities of the La-doped carboxylato-alumoxanes are similar to those of the parent alumoxanes, except for having a color related to that of the La-dopant (light yellow for lanthanum, other colors are observed for other lanthanum group dopants, e.g. light purple for neodymium, white for yttrium). As with the parent alumoxanes, the doped-alumoxanes exist as large "fluffy" agglomerates, 50–200 μm in size, with a particle size estimated from SEM to be less than 0.1 microns in diameter. The X-ray diffraction of the doped-alumoxanes are essentially indistinguishable from those of the parent alumoxane. The La/Al atomic ratios for the La-doped alumoxanes were determined by microprobe analysis and are close to the values expected based upon the reaction ratios.

The IR spectra of the parent (methoxyethoxyethoxy) acetato-alumoxanes contain bands at 1596–1586 and 1473–1466 cm⁻¹, consistent with a bridging mode of coordination (Formula 1) of the carboxylic acid to the boehmite core. In addition, all of the IR spectra show a broad absorption band at 3700–3400 cm⁻¹ consistent with the presence of an aluminum-bound hydroxide group. Upon addition of the La(acac)₃ 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.

It has been previously demonstrated that the carboxylate alumoxanes (in common with all alumoxanes except those containing direct Al-C bonds) contain significant concentrations of acidic hydroxide groups (Landry et al. 1995). 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. In view of this we expected that the reaction of the carboxylate alumoxane with M(acac)₃ (where M depends on the valence of M) should proceed as shown in the following equation:

\[
\text{[Al(OH)₃(OH)₂][M(acac)₃]} \rightarrow \text{[Al(OH)₃(OH)₂]} \cdot \text{[M(acac)₃]} \cdot \text{H} \cdot \text{acac} \cdot \text{H}
\]

Although the hydroxide bands in the IR spectrum were altered upon reaction of the carboxylate alumoxane with M(acac)₃ there were no new bands assignable to the acac ligands, even when a large excess of the metal complex was employed.

To further study the reaction of the alumoxane precursors, solution NMR spectra were used to compare undoped and doped materials. The solution ¹H and ¹³C NMR of the parent carboxylato-alumoxanes indicated a single environment for the bridging carboxylates. The reaction sequence between La(acac)₃ and a hexanato-alumoxane was then followed by multi-nuclear NMR. The ¹³C and ¹⁷Al NMR spectra of the alumoxanes before doping consist of a broad resonance at ca. 6 ppm indicative of aluminum in an octahedral Al₂O₃ coordination environment. The reaction of La(acac)₃ with hexanato-alumoxane in CDC₁₃ was followed by ¹H NMR. Upon mixing, the resonances due to La(acac)₃ diminish in intensity, and two new resonances are observed: δ=5.46 (H, s) and 1.99 (H, s). These new signals are assigned to Al(acac)₃ by comparison with a commercial sample. Similarly, the ¹³C and ¹⁷Al NMR spectra of the reaction mixture confirm the presence of Al(acac)₃. If the reaction is carried out on a preparative scale, Al(acac)₃ can be isolated via crystallization.

Thus, the reaction of the La-acac complex with the alumoxane does not occur via reaction of the Al—OH groups but is believed to be the result of metal exchange and the leaching of aluminum from the boehmite core as shown by the reaction sequence below:

\[
\text{[Al(OH)₃(OH)₂][M(acac)₃]} \rightarrow \text{[M(acac)₃]} \cdot \text{[Al(OH)₃(OH)₂]} \cdot \text{H} \cdot \text{acac} \cdot \text{H}
\]

These results indicate that metal is incorporated into the boehmite-like lattice of the alumoxane. 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 is uncertain

It thus appears that the metal metathesis reaction results from the direct reaction of the metal-acac complex with the carboxylate alumoxane. This is supported by the following: (a) if free acac-H is observed during the reaction, and (b) no Al(acac)_3 is formed from the reaction of alumoxanes with acac-H alone. Furthermore, carboxylic acids, for example methoxy(ethoxy—ethoxy)acetic acid (MEEA-H), do not react with La(acac)_3 to give acac-H. Since other carboxylato-alumoxanes undergo metal exchange with the metal acylacetonates under the same conditions to give the same products, other carboxylic acids that have been used to prepare the alumoxanes should not react with La(acac)_3 to give acac-H. However, extension of the metal-exchange should proceed similarly in other metal acylacetoneates. Since the boehmite starting material does not react with either M(acac)_3, or acac-H, the carboxylate ligands on the alumoxane appear to assist metal metathesis. Evidence for this is observed from the 13C NMR spectrum of an alumoxane/La(acac)_3 reaction mixture. In addition to peaks due to the carboxylate a-carbons (O_2CR, d=185–174) and the carboxyl carbon of Al(acac)_3 (d=191-1), there is a peak at 191.4 ppm that can be assigned to L(acac)_3/MEEA-H, based upon a comparison with a genuine sample. The 13C NMR spectra of mixtures of La(acac)_3, with octanoic acid and tetraglyme also suggests that the interaction of L(acac)_3 with MEEA-H occurs via the carboxylate and not the polyether side chain. At the end of the reaction the free MEEA is seen in solution and is therefore still attached to the boehmite surface.

Metal exchange (transmetallation) reactions are well known for metal complexes and clusters. Transition metal complexes of monoanionic Schiff bases have been shown by Davies and coworkers (Cai et al. 1985, Davies et al. 1984, Davies et al. 1986, El-Toukhy et al. 1984) to be stoichiometric transmetalating agents for the replacement of copper in various tetrameric complex. However, the low temperature solution-based metal metathesis between a mononuclear metal complex and a mineral particle (albeit solubilized), as in this invention, is believed unique. In Schiff base transmetalations it is known that the driving force for the reaction is the formation of insoluble [CuL_2] or highly stable CuL co-products [where L=Schiff base]. In the present case, the driving force for transmetallation between the carboxylate alumoxanes and the metal acetylacetonate complexes is likely the formation of Al(acac)_3. However, in the case of soluble cerium salts, where the nitrate or sulfate salt are used, the driving force for reaction is either the formation of [Al(H_2O)]_3^+, which is observed by ^27Al NMR spectroscopy, or the binding of cerium into the alumoxane lattice.

Thermolysis of a carboxylato-alumoxane that has not been metal-exchanged gives γ-alumina, no matter what carboxylic acid is in the starting alumoxane. All of the metal-exchanged carboxylato-alumoxanes, up to a firing temperature of ~600–1100°C, give poorly crystalline metal doped γ-alumina structures. At higher temperatures (depending on the metal used and its concentration), the metal-exchanged carboxylato-alumoxanes transform to crystalline mixed metal oxides. For example, the use of yttrium in a 3:5 Y:Al ratio gives YAlO_3 at 1000°C and the use of La in a 1:11 ratio gives LaAlO_3 at 1400°C. In contrast at lower temperatures prepared by conventional ceramic methods under similar conditions result in formation of dopant oxide and Al_2O_3 instead of the metal exchanged γ-alumina phase. For example, the thermolysis product of a physical mixture of [NH_4]_2Co(NO_3)_4 and boehmite shows a diffraction pattern consistent with a mixture of γ-alumina and CeO_3, while the cerium obtained from the Ce-doped alumoxane is a Ceγ-alumina (i.e. the cerium is incorporated into the alumina lattice).

Table 1 provides a summary of typical metal cations that can be exchanged into carboxylato-alumoxanes and the types of products that can be formed.

Like traditional sol-gel methodology, the use of carboxylato-alumoxanes for the synthesis of aluminum-based oxide ceramics offers significant advantages over the ceramic method, including atomic scale mixing of metals and processability. However, unlike sol-gel synthesis the carboxylato-alumoxanes are stable both in solution and the solid state. In addition, whereas the choice of solvents in sol-gel synthesis is limited, the solubility of the carboxylato-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.

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. The alumoxane route is simple and can be halted and/or modified at any stage without significant detrimental effect on the products.

A careful control of pH, the use of additives to inhibit precipitation, and slow concentration steps are not required, making the alumoxane route easier and quicker. A final benefit with respect to large scale processing is the relatively low cost of the alumoxane precursors and the production of singles phases after only a single firing.

The metal exchange reaction of this invention has a number of advantages over sol-gel approaches. The physical properties and chemistry of the metal-exchanged carboxylato-alumoxanes can be readily controlled by the identity of the carboxylate group. For example use of a hydrophobic carboxylic acid such as octanoic acid gives an alumoxane soluble in dichloromethane and THF; use of hydroscopic acid gives alumoxanes that are soluble in water and the use carboxylic acids with bromo groups allows Grignard reagents to be used to modify the chemistry of the periphery
of the carboxylato-aluminoxane or the incorporation of amine functionalized carboxylic acids allows for amine chemistry to be carried out on the periphery of the carboxylato-

aluminoxane. Thus the presence of the carboxylic acids allows for metal ions to be incorporated into the surface lattice of the bochmite particles, allows the carboxylato-aluminoxanes to be soluble in aqueous or non-aqueous solvents and permits chemical reactions to be carried out using functional groups that are part of the carboxylic acid. The ability to readily exchange metal cations into the surface lattice of the bochmite particles covered with the carboxylic acids allows the metal cations to be atomically dispersed into the surface crystal lattice of the bochmite particle. This allows extremely fine control of the homogeneity of doping proce-
dure. In contrast to the sol-gel approaches, the carboxylato-
aluminoxanes are stable under a range of conditions thereby allowing processing under acidic and basic conditions. Furthermore, the bochmite and the carboxylic acids are both low in cost and low toxicity and can provide single phase products.

EXAMPLES

The following examples are presented to illustrate the ease and versatility of the approach and are not to be construed as in any way limiting the scope of the invention.

Example 1

Synthesis of Lanthanum-Exchanged Hexanoato-Aluminoxanes and the Subsequent Thermal Conversion to LaAlO3

A 1:1 ratio of hexanoato-aluminoxane and La(acac)3 was mixed in chloroform or THF at room temperature and stirred for one hour. The solution does not need to be dry and the weight amount of solvent generally used is in the range of 10 to 20 times that of the aluminoxane. Chloroform or THF solutions containing the hexanoato-aluminoxane in concentra-
tions greater than 10 wt % tend to gel. The solution was then removed under vacuum and the resulting powder was washed with ether. Calcination of the resulting powder at 1,000° C. resulted in the formation of LaAlO3. The XRD powder diffraction pattern of the resulting material showed it to be single phase LaAlO3.

Example 2

Synthesis of Lanthanum-Exchanged Glucoano-Aluminoxane and the Subsequent Thermal Conversion to LaAlO3

A 1:11 molar ratio of La(acac)3 and glucano-aluminoxane was mixed in water and stirred for two hours. The water was then removed under vacuum and the resulting powder was washed with methanol. Calcination of the resulting powder at 1,400° C. resulted in the formation of LaAl11O15. The XRD powder diffraction pattern of the resulting material showed it to be single phase LaAl11O15.

Example 3

Synthesis of Yttrium Exchanged Methoxy(EthoxyEthoxy) Acetat-Aluminoxane and the Subsequent Conversion to Y2Al12O31

A 3.5 molar ratio of Y(acac)3 and methoxy(ethoxyethoxy)acetatohexametallate were mixed in water and stirred for two hours. The water was then removed under vacuum and the powder was washed with methanol. Calcination of the resulting powder at 1,000° C. resulted in the formation of Y2Al12O31. The XRD powder diffraction pattern of the resulting material showed it to be single phase Y2Al12O31.

Example 4

Synthesis of Manganese Cobalt Exchanged Glucono-

ato-Aluminoxane and the Subsequent Thermal Conversion to MnCo2Gluc2Al2O4

A 0.5:0.5:2 molar ratio of Co(acac)3, Mn(acac)2 and gluconato-aluminoxane are mixed in water and stirred for two hours at 75° C. The water was then removed under vacuum and the powder washed with methanol. Calcination of the resulting powder at 1,000° C. resulted in the formation of MnCo2Gluc2Al2O4. The XRD powder diffraction pattern of the resulting material showed it to be single phase MnCo2Gluc2Al2O4.

Example 5

Synthesis of Manganese-Exchanged Methoxy (EthyloxyEthoxy)Acetato-Aluminoxane and the Subsequent Thermal Conversion to MnAl2O4

A 0.02:1 molar ratio of Mn(acac)3 and methoxy (ethyoxyethoxy)acetato-aluminoxane were mixed in water and stirred for two hours at 75° C. The water was then removed under vacuum and the powder washed with methanol. Calcination of the resulting powder at 1,000° C. resulted in the formation of MnAl2O4. The XRD powder diffraction pattern of the resulting material showed it to be single phase MnAl2O4 material.

Example 6

Synthesis of Calcium-Exchanged Octanoato-Aluminoxane and the Subsequent Thermal Conversion to CaAl5O10

A 1:12 molar ratio of Ca(acac)2 and octanoato-aluminoxane are mixed [Dissolved? in THF and stirred for two hours at 50° C. The THF was then removed under vacuum and the powders washed with methanol. Calcination of the resulting powders at 1,400° C. resulted in the formation of CaAl5O10. The XRD powder diffraction pattern of the resulting material showed it to be single phase CaAl5O10.

Those of ordinary skill in the art will appreciate that procedures, techniques, and materials particularly starting materials, reagents, solvents, quantities and reaction condi-
tions other than those specifically described herein can be readily used in the synthetic methods of these inventions without departing from the spirit and scope of this invention. All such alternative or functionally equivalent procedures, techniques, and materials are considered to be encompassed by this invention.

REFERENCES


Kareiva, A.; C. J. Harlan; D. B. MacQueen; R. L. Cook; A. R. Barron, Chemistry of Materials, 1996, 8(9), 2331.


All of the references cited herein are hereby incorporated by reference in their entirety herein.
Typical Metal Cations that can be exchanged into aluminates and typical products formed by thermal treatment of the metal-exchanged aluminates.

<table>
<thead>
<tr>
<th>Periodic Group</th>
<th>Exchanged</th>
<th>Examples of Types of Products Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group IA</td>
<td>Li, Na, K</td>
<td>Beta-Alumina</td>
</tr>
<tr>
<td>Group IIA</td>
<td>Mg, Ca, Sr, Ba</td>
<td>bhtite, spinel</td>
</tr>
<tr>
<td>Group IIIB</td>
<td>Sc, Y, La, Ce</td>
<td>hexa-aluminates, perovskites, garnets</td>
</tr>
<tr>
<td>Group IIIB</td>
<td>Ti, Zr, Hf</td>
<td>metal exchanged gamma-alumina</td>
</tr>
<tr>
<td>Group VIIIB</td>
<td>Mn, Re</td>
<td>metal exchanged gamma-alumina, spinel</td>
</tr>
<tr>
<td>Group VIIIB</td>
<td>Fe, Ru, Os, Pt, Ni, Pd, Rh, Ir</td>
<td>metal exchanged gamma-alumina, spinel</td>
</tr>
<tr>
<td>Group IB</td>
<td>Cu, Ag</td>
<td>metal exchanged gamma-alumina, spinel</td>
</tr>
<tr>
<td>Group VB</td>
<td>Zn, Cd, Hg, Ga, In</td>
<td>metal exchanged gamma-alumina, spinel</td>
</tr>
<tr>
<td>Lanthanides</td>
<td>Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Th</td>
<td>hexa-aluminates, perovskites, garnets</td>
</tr>
<tr>
<td>Actinides</td>
<td>Tb, U</td>
<td>metal exchanged gamma-alumina</td>
</tr>
</tbody>
</table>

What is claimed is:

1. A metal-exchanged carboxylato-aluminate.
2. The metal-exchanged carboxylato-aluminate of claim 1 wherein 10% or more of the aluminum ions of the aluminates are replaced with another metal ion or other metal ions.
3. The metal-exchanged carboxylato-aluminate of claim 1 wherein from about 10% to about 50% of the aluminum ions of the aluminates are replaced with another metal ion or other metal ions.
4. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is a metal ion selected from the group Ca²⁺, Sr²⁺, Co²⁺, Ni²⁺, Mg²⁺, Fe²⁺ or Cu²⁺ and mixtures thereof.
5. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is selected from the group of the lanthanide metals.
6. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is selected from the group of the lanthanide metals.
7. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is a metal ion selected from the group Ca²⁺, Sr²⁺, Co²⁺, Ni²⁺, Mg²⁺, Fe²⁺ or Cu²⁺ and mixtures thereof.
8. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is a metal ion selected from the group Ca²⁺, Sr²⁺, Co²⁺, Ni²⁺, Mg²⁺, Fe²⁺ or Cu²⁺ and mixtures thereof.
9. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is Na⁺, K⁺, or their mixtures with Li⁺ or Mg⁺.
10. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is Na⁺, K⁺, or their mixtures with Li⁺ or Mg⁺.
11. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is Na⁺, K⁺, or their mixtures with Li⁺ or Mg⁺.
12. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is Na⁺, K⁺, or their mixtures with Li⁺ or Mg⁺.
13. The metal-exchanged carboxylato-aluminate of claim 1 wherein the exchanged metal is selected from the group Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Ti³⁺, V³⁺, Mn²⁺, Fe²⁺, Fe³⁺(Co³⁺, Ni³⁺, Cu²⁺, Zn²⁺, Ga³⁺, Y³⁺, Zr⁴⁺, Nb⁵⁺, Nb⁶⁺, Mo⁷⁺, Re⁷⁺, Re⁸⁺, Pd²⁺, La³⁺, Ce³⁺, Nd³⁺, Pr³⁺, Th⁴⁺, U⁴⁺ and mixtures thereof.
14. The metal-exchanged carboxylato-aluminate of claim 1 that is formed by metal exchange of a carboxylato-aluminate with a metal acetylacetonate.
15. The metal-exchanged carboxylato-aluminate of claim 1 that is formed by metal exchange of a carboxylato-aluminate with a metal salt.
16. A method for making a metal-exchanged carboxylato-aluminate which comprises the steps of:
   (a) combining a carboxylato-aluminate wherein the carboxylic acid ligands are monocarboxylic acid ligands with a metal acetylacetonate or mixture of metal acetoacetates solubilized or dispersed in a solvent to effect a metal-exchange reaction and
   (b) isolating said metal-exchanged carboxylato-aluminate.
17. The method of claim 16 further comprising the step of preparing said carboxylato-aluminate by reaction of boehmite or pseudoboehmite with a monocarboxylic acid.
18. The method of claim 16 wherein said carboxylato-aluminate is water soluble and said combination is solubilized or dispersed in water.
19. The method of claim 16 wherein said carboxylato-aluminate is soluble in dichloromethane or tetrahydrofuran and said combination is solubilized or dispersed in dichloromethane or tetrahydrofuran.
20. The method of claim 16 wherein said carboxylato-aluminate comprises a ligand wherein said carboxylic acid ligand is acetic, glucono, methyl(ethylxoy)xyctetate, hexanoate, dimethyl, benzoate, or laurate.
21. A method for preparing a metal-doped binary or tertiary alumina which comprises the step of heating a metal-exchanged carboxylato-aluminate prepared by the method of claim 16 to strip the carboxylic acid ligands therefrom or form said alumina.
22. The method of claim 21 wherein the binary or tertiary alumina is a γ-alumina.
23. The method of claim 21 wherein the heating step is performed at temperatures ranging from 325⁰C to 600⁰C.
24. The method of claim 21 wherein the heating step is performed at temperatures ranging from 800⁰C to 1700⁰C.
25. The method of claim 21 wherein, in the metal-exchanged carboxylato-aluminate, the exchanged metal is a metal ion selected from the group Cs⁺, Sr⁺, Co⁺, Ni⁺, Mg²⁺, Fe²⁺, Cu²⁺ and mixtures thereof.
26. The method of claim 21 wherein, in the metal-exchanged carboxylato-aluminate, the exchanged metal is a lanthanide metal.
27. The method of claim 21 wherein, in the metal-exchanged carboxylato-aluminate, the exchanged metal is an alkaline metal ion, an alkaline earth metal ion, a transition metal ion, an anide metal ion, a Group III B metal ion, a Group IVB metal ion or mixtures thereof.
28. The method of claim 21 wherein the metal-doped alumina is selected from those having the compositions: M₂M₁₂Al₆O₁₆, where a=0−1, b=0−1, and a+b=1; M₃M₂Al₆O₁₆, where a=0−1, b=0−1, and a+b=1; (M₁₂)₂Al₆O₁₆, where a=0−3, b=0−3, and a+b=3; and (M₁₂)₃Al₆O₁₆, where a=0−1, b=0−1, and a+b=1 and wherein M₁ and M₂ represent different metals, and are not aluminum.
29. The method of claim 16 further comprising the step of heating the combination of step (a) at or below the boiling point of the solvent.

* * * * *
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

At the 9th line of the Abstract, please replace “boebmite” with -- boehmite -- .

Column 1,
Line 31, please insert a period after “spinel”.
Line 41, please replace “Y₃Al₂O₉” with -- Y₃Al₅O₁₂ -- .

Column 2,
Line 16, please replace “of arrange” with -- arrange -- .

Column 3,
Line 1, please delete “are”.
Line 30, please insert a period after “hydroxyls”.
Line 67, please replace “M₂Al₇O₃₉” with -- M₆Al₉O₁₆ -- .

Column 5,
Line 18, please replace “solvent” with -- solvent -- .
Line 35, please delete “have been bound”.
Line 65, please replace a “acetylacetonate” with -- acetylacetonate -- .

Column 9,
Line 2, please insert a period after “uncertain”
Line 31, please replace “n free” with -- no free -- .
Line 52, please replace “suggests” with -- suggest -- .
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 11.
Line 12, please replace “can” with -- to --.
Line 54, please replace “Acetat-Alumoxane” with -- Acetato-Alumoxane --.
Line 62, please replace “Y₂Al₅O₁₂” as -- Y₃Al₅O₁₂ --.

Column 12.
Line 4, please insert a period after “methanol”.
Line 29, please delete “[DISSOLVED?]”.

Signed and Sealed this
Eleventh Day of September, 2001

Attest: 

Nicholas P. Gendic

Attesting Officer

NICHOLAS P. GODIC
Acting Director of the United States Patent and Trademark Office
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,207,130 B1
DATED : March 27, 2001
INVENTOR(S) : Kareiva et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1,
Line 4, please insert:

-- STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT
This work was supported by the Office of Naval Research, Contract No. N00014-95-C-0266. The United States government has certain rights in this invention. --

Signed and Sealed this
Sixth Day of November, 2001

Attest:

Nicholas P. Godici
Attaching Officer
Acting Director of the United States Patent and Trademark Office

NICHOLAS P. GODICI
Abstract.
Line 9, please replace “boehmite” with -- boehmite --.

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Line 65, please replace a “acetylacetonac” with -- acetylacetonate --.

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Column 12,
Line 4, please insert a period after “methanol”.
Line 29, please delete “[DISSOLVED?]”.

Signed and Sealed this
Twenty-seventh Day of November, 2001

Atest:

Nicholas P. Lodici

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