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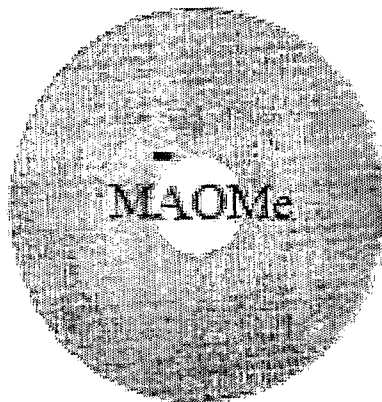
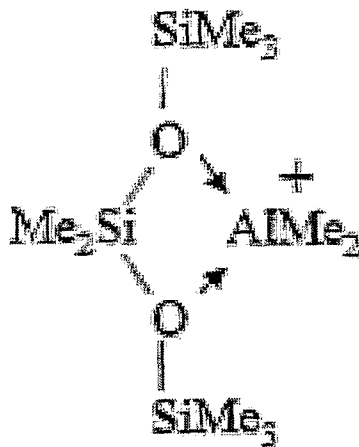
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(54) Title: ALUMINOXANATE SALT COMPOSITIONS HAVING IMPROVED STABILITY IN AROMATIC AND ALIPHATIC SOLVENTS



(57) Abstract: The present invention provides soluble aluminoxanate salt compositions, methods for preparing soluble aluminoxanate salt compositions, catalyst compositions comprising soluble aluminoxanate salt compositions, and methods for polymerizing olefins using catalyst compositions comprising soluble aluminoxanate salt compositions. Aluminoxanate salt compositions of the present invention are soluble in aromatic and aliphatic solvents and have improved solution stability and superior activator efficiency as compared to conventional aluminoxanes or modified aluminoxanes.

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ALUMINOXANATE SALT COMPOSITIONS HAVING IMPROVED STABILITY IN AROMATIC AND ALIPHATIC SOLVENTS

FIELD OF THE INVENTION

[0001] The present invention relates to aluminoxate salt compositions. More particularly, the present invention relates to soluble aluminoxanate salt compositions that are of particular utility in the formation of new catalyst systems. This invention is also directed to methods for the preparation of such soluble aluminoxanate salt compositions and catalyst systems, and to the use of such catalyst systems in the polymerization of olefinic monomers.

BACKGROUND OF THE INVENTION

[0002] Aluminoxane compositions are widely used in combination with various types of metallocenes and transition metal compounds to prepare catalyst systems for polymerizing olefinic monomers. However, certain limitations are associated with standard aluminoxane solutions, such as instability to gel formation and poor solubility, especially in aliphatic solvents. In addition, methylaluminoxane (MAO), the most commonly used aluminoxane, has lower solubility in organic solvents than higher alkylaluminoxanes and tends to be cloudy or gelatinous due to oligomerization and agglomeration. Attempts to improve the solubility of methylaluminoxane include hydrolyzing a mixture of trimethylaluminum with a C₂-C₂₀ alkylaluminum compound such as, for example, triethylaluminum, tri-n-propylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum or a triarylaluminum to produce a modified MAO. Such modified MAOs are described, for example, in U.S. Patent. No. 5,157,008. While modified MAOs have improved solubility in commercial solvents, these compounds often have poor solution stability.

[0003] U.S. Patent Nos. 5,565,395; 5,670,682; and 5,922,631 and WO 03/082879 describe various aluminoxanate salts and liquid clathrate compositions. However, while these aluminoxanate salts and liquid clathrate compositions are soluble in certain solvents, they are practically insoluble in standard industrial solvents, for example, aliphatic and aromatic solvents.

[0004] Therefore, there is a need for aluminoxane compositions that are soluble in aliphatic and aromatic solvents. Further, there is a need for catalyst systems for polymerizing olefinic monomers employing such aluminoxane compositions. It is to these and other needs that the present invention is directed.

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention is directed to soluble aluminoxanate salt compositions, methods for preparing soluble aluminoxanate salt compositions, supported and unsupported

catalyst compositions comprising soluble aluminoxanate salt compositions, methods for preparing these catalyst compositions, and methods for polymerizing olefinic monomers using these catalyst compositions. In the course of examining aluminoxanate compositions, it was discovered that ionic aluminoxanate salts and liquid clathrate compositions can be modified such that they are soluble in aliphatic and aromatic solvents.

[0006] In one aspect, the present invention encompasses a soluble aluminoxanate salt composition comprising the contact product of:

(a) at least one ionic aluminoxanate composition having the general formula



wherein:

L is a stabilizing ligand;

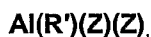
R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms;

AO is an aluminoxane moiety;

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive;

(b) at least one organometallic compound such as an alkylaluminum compound having the general formula



wherein:

R' is an alkyl group having from about four to about twenty carbon atoms; and

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms; and

(c) at least one inert organic solvent.

The present invention also encompasses a soluble aluminoxanate salt composition having the general formula



wherein:

L is a stabilizing ligand;

R is a hydrocarbyl group having from one to about twenty carbon atoms;

R' is an alkyl group having from about four to about twenty carbon atoms;

AO is an aluminoxane moiety;

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive.

[0007] Another aspect of this invention encompasses a soluble methylaluminoxanate salt composition having the general formula



wherein:

L is a stabilizing ligand;

Me is a methyl group;

R' is an alkyl group having from about four to about twenty carbon atoms;

MAO is a methylaluminoxane moiety; and

m is 1, 2, or 3, inclusive.

[0008] Yet another aspect of this invention encompasses a mixed aluminoxanate composition comprising:

(a) a soluble aluminoxanate salt composition having the general formula



(b) a soluble aluminoxanate salt composition having the general formula



(c) a soluble aluminoxanate salt composition having the general formula:



(d) any combination thereof;

wherein:

L is a stabilizing ligand;

R is a hydrocarbyl group having from one to about twenty carbon atoms;

R' is an alkyl group having from about four to about twenty carbon atoms;

AO is an aluminoxane moiety or a mixture of aluminoxane moieties; and

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive.

[0009] The present invention further comprises a catalyst composition comprising a soluble aluminoxanate salt composition and at least one complex of a transition metal of Group 3, 4, 5, 6, 7, 8, 9, 10, or 11 of the Periodic Table of Elements, including the lanthanide and actinide series. The catalyst composition can be unsupported or supported on an organic or inorganic carrier material.

[00010] This invention also encompasses a method for polymerizing olefinic monomers comprising contacting under polymerization conditions at least one olefinic monomer and a catalyst system comprising a soluble aluminoxanate salt composition of the present invention and at least one transition metal complex.

BRIEF DESCRIPTION OF THE DRAWINGS

- [00011] Figure 1 is a visual representation of an octamethyltrisiloxane-complexed dimethylaluminum methylaluminoxane (DMAM-OMTS).
- [00012] Figure 2 illustrates the proton NMR spectra of the ionic aluminoxanate of Figure 1, and its methylaluminoxane and octamethyltrisiloxane precursors.
- [00013] Figure 3 illustrates the ^{29}Si NMR spectra of the ionic aluminoxanate of Figure 1, and its octamethyltrisiloxane precursor.
- [00014] Figure 4 illustrates the ^{27}Al NMR spectra of the ionic aluminoxanate of Figure 1, and its methylaluminoxane precursor.
- [00015] Figure 5 illustrates the proton NMR spectra of conventional methylaluminoxane and a crown-ether-complexed dimethylaluminum methylaluminoxanate.
- [00016] Figure 6 illustrates the ^{29}Si NMR spectra of the ionic aluminoxanate of Figure 1 treated with tri-n-octylaluminum and conventional methylaluminoxane treated with tri-n-octylaluminum.
- [00017] Figure 7 illustrates the ^{29}Si NMR spectra of the ionic aluminoxanate of Figure 1 treated with triisobutylaluminum and conventional methylaluminoxane treated with triisobutylaluminum.
- [00018] Figure 8 illustrates the proton NMR spectra of the ionic aluminoxanate of Figure 1 treated with tri-n-octylaluminum and conventional methylaluminoxane treated with tri-n-octylaluminum.
- [00019] Figure 9 illustrates the ^{27}Al NMR spectra of the ionic aluminoxanate of Figure 1 treated with tri-n-octylaluminum and conventional methylaluminoxane treated with tri-n-octylaluminum.

DETAILED DESCRIPTION OF THE INVENTION

[00020] The present invention provides soluble aluminoxanate salt compositions, methods for preparing soluble aluminoxanate salt compositions, supported and unsupported catalyst compositions comprising soluble aluminoxanate salt compositions, and methods for polymerizing olefins using catalyst compositions comprising soluble aluminoxanate salt compositions.

Soluble Aluminoxanate Salt Compositions and Components

[00021] Soluble aluminoxanate salt compositions in accordance with the present invention comprise the contact product of:

- (a) at least one ionic aluminoxanate composition having the general formula



wherein:

L is a stabilizing ligand;

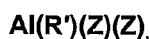
R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms;

AO is an aluminoxane moiety;

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3 inclusive;

(b) at least one organometallic compound such as an alkylaluminum compound having the general formula



wherein:

R' is an alkyl group having from about four to about twenty carbon atoms; and

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms; and

(c) at least one inert organic solvent.

[00022] Soluble aluminoxanate salt compositions in accordance with another aspect of the present invention have the general formula



wherein:

L is a stabilizing ligand;

R is a hydrocarbyl group having from one to about twenty carbon atoms;

R' is an alkyl group having from about four to about twenty carbon atoms;

AO is an aluminoxane moiety;

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive.

[00023] A further aspect of the present invention encompasses a soluble methylaluminoxanate composition having the general formula



wherein:

L is a stabilizing ligand;

Me is a methyl group;

R' is an alkyl group having from about four to about twenty carbon atoms;

MAO is a methylaluminoxane moiety; and

m is 1, 2, or 3, inclusive.

[00024] Yet another aspect of this invention encompasses a mixed aluminoxanate composition comprising

- (a) a soluble aluminoxanate salt composition having the general formula



- (b) a soluble aluminoxanate salt composition having the general formula



- (c) a soluble aluminoxanate salt composition having the general formula



- (d) any combination thereof;

wherein:

L is a stabilizing ligand;

R is a hydrocarbyl group having from one to about twenty carbon atoms;

R' is an alkyl group having from about four to about twenty carbon atoms;

AO is an aluminoxane moiety or a mixture of aluminoxane moieties; and

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive.

The Ionic Aluminoxanate Composition

[00025] Ionic aluminoxanate compositions employed in the present invention include aluminoxanate salts having a chelated dihydrocarbylaluminum group as the cation and an aluminoxanate moiety as the anion. Dihydrocarbylaluminum aluminoxanate salts have the following general formula:



wherein

L is a stabilizing ligand;

R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms;

AO is an aluminoxane moiety;

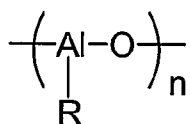
X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive.

[00026] Examples of stabilizing ligands include, but are not limited to, monosiloxanes, polysiloxanes, monoethers, polyethers, monothioethers, polythioethers, a multidentate ligand comprising oxygen coordinating atoms, nitrogen coordinating atoms, phosphorous coordinating atoms, sulfur coordinating atoms, oxygen crown ether ligands, nitrogen crown ether ligands, nitrogen and oxygen crown ether ligands, or any combination thereof.

Examples of crown ether structures include, but are not limited to, 12-crown-4, 15-crown-5, or 18-crown-6. Stabilizing ligands can be either bidentate or monodentate ligands. When L is a bidentate ligand, m is 1. When L is a monodentate ligand, m is 2. In one aspect of the present invention, R is an alkyl, cycloalkyl, aryl, or aralkyl group. In another aspect R is a C₁₋₈ alkyl group. In yet another aspect of the present invention, R is a methyl group. In a further aspect of the present invention, X is an alkyl group which can be the same as or different from the R group. Examples of X groups which can be employed in the present invention include, but are not limited to, alkyl, cycloalkyl, aryl, or aralkyl groups, halides, or pseudohalides. Pseudohalides include, but are not limited to, oxyhalide groups, hydrocarbyloxy groups, amido groups (e.g., —NR₂), hydrocarbylthio groups (e.g., —SR groups), and the like. Hydrocarbyloxy groups comprise, without limitation, —OR groups such as alkoxy, aryloxy, cycloalkoxy, arylalkoxy, and the like. In one aspect of the present invention, X is a methyl group or fluoride.

[00027] Aluminoxane moieties (AO) can include any suitable hydrocarbylaluminoxanes having at least one hydrocarbyl moiety having from one to about twenty carbon atoms, for example, alkylaluminoxanes, cycloalkylaluminoxanes, arylaluminoxanes, aralkylaluminoxanes, or any combination thereof. Hydrocarbylaluminoxanes can exist in the form of linear or cyclic polymers with the simplest monomeric compound being a tetraalkylaluminoxane such as tetramethylaluminoxane, (CH₃)₂Al—O—Al(CH₃)₂, or tetraethylaluminoxane, (C₂H₅)₂Al—O—Al(C₂H₅)₂. In one aspect of the invention, the aluminoxanes can be oligomeric materials, sometimes referred to as polyalkylaluminoxanes, containing the repeating unit



where R is a C₁-C₁₀ alkyl group and n is a number from about 4 to about 20. Aluminoxanes employed in the present invention can contain linear, cyclic, cross-linked species, or any combination thereof. Examples of hydrocarbylaluminoxanes which can be employed in the present invention include, but are not limited to, methylaluminoxanes (MAO), modified MAOs, ethylaluminoxanes (EAO), isobutylaluminoxanes (IBAO), n-propylaluminoxanes, n-octylaluminoxanes, phenylaluminoxanes, or any combination thereof. WO 03/082466 describes a crystal structure of a discrete hydrocarbyl haloaluminoxane, having the general formula Me₉Al₁₈O₁₃Cl₁₃, which can also be used as a suitable aluminoxane moiety in the present invention. The hydrocarbylaluminoxanes can contain up to about 20 mole percent (based on aluminum atoms) of moieties derived from amines, alcohols, ethers, esters, phosphoric and carboxylic acids, thiols, aryl disiloxanes, alkyl disiloxanes and the like to further improve activity, solubility and/or stability.

[00028] Aluminoxanes can be prepared as known in the art by the partial hydrolysis of hydrocarbylaluminum compounds. Hydrocarbylaluminum compounds or mixture of compounds capable of reacting with water to form an aluminoxane can be employed in the present invention. For example, hydrocarbylaluminum compounds include, but are not limited to, trialkylaluminum, triarylaluminum, mixed alkyl-aryl aluminum, or any combination thereof. The hydrocarbylaluminum compounds can be hydrolyzed by adding either free water or water-containing solids, which can be either hydrates or porous materials which have absorbed water. Because it is difficult to control the reaction by adding water, even with vigorous agitation of the mixture, the free water can be added in the form of a solution or a dispersion in an organic solvent. Suitable hydrates include, but are not limited to, salt hydrates such as, for example, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{LiBr} \cdot 2\text{H}_2\text{O}$, $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{LiI} \cdot 2\text{H}_2\text{O}$, $\text{LiI} \cdot 3\text{H}_2\text{O}$, $\text{KF} \cdot 2\text{H}_2\text{O}$, $\text{NaBr} \cdot 2\text{H}_2\text{O}$, or any combination thereof. Alkali or alkaline earth metal hydroxide hydrates are also suitable hydrates and include, but are not limited to, $\text{NaOH} \cdot \text{H}_2\text{O}$, $\text{NaOH} \cdot 2\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{KOH} \cdot 2\text{H}_2\text{O}$, $\text{CsOH} \cdot \text{H}_2\text{O}$, $\text{LiOH} \cdot \text{H}_2\text{O}$, or any combination thereof. Mixtures of salt hydrates and alkali or alkaline earth metal hydroxide hydrates can also be used. The molar ratios of free water or water in the hydrate or in porous materials such as alumina or silica to total alkylaluminum compounds in the mixture can vary widely, such as for example, from about 2:1 to about 1:4. In another aspect, molar ratios can range from about 4:3 to about 2:7.

[00029] Suitable hydrocarbylaluminoxanes and processes for preparing hydrocarbylaluminoxanes are described in U.S. Patent Nos. 4,908,463; 4,924,018; 5,003,095; 5,041,583; 5,066,631; 5,099,050; 5,157,008; 5,157,137; 5,235,081; 5,248,801, and 5,371,260. Methylaluminoxanes can contain varying amounts, for example, from about 5 to about 35 mole percent, of the aluminum value as unreacted trimethylaluminum (TMA).

[00030] Ionic aluminoxanates are substantially free of occluded non-ionic organoaluminum compounds such as alkylaluminums and non-ionic alkylaluminoxane species. The ionic aluminoxanate contains, if any, less than about 5 mole percent of aluminum in the form of trialkylaluminum as determined by proton NMR. In one aspect, the ionic aluminoxanate contains, if any, less than about 1 mole percent of aluminum in the form of trialkylaluminum.

[00031] In one aspect of the present invention, ionic aluminoxanate compositions include those in which the composition has a siloxane or polysiloxane ligand and in which the composition is characterized by a downfield shift in ^1H NMR as compared to the NMR of the aluminoxane from which the ionic aluminoxanate was prepared ("parent aluminoxane"). Ionic aluminoxanate compositions of the present invention can further be characterized by (i) a ^{27}Al NMR with at least one large and broad peak shifted upfield from the parent

aluminoxane peak, and (ii) at least one smaller peak shifted downfield from the parent aluminoxane peak. The large and broad peak corresponds to the anion of the ionic aluminoxanate and the smaller peak corresponds to the cation of the ionic aluminoxanate composition. In a further aspect of the present invention, aluminoxanate compositions are characterized by an increase in conductivity of at least 10 micro-mhos as compared to the parent aluminoxane.

[00032] In one aspect of the present invention, ionic aluminoxanate compositions can be prepared by contacting, in any order, (i) at least one suitable aromatic solvent; (ii) at least one aluminoxane; and (iii) at least one hydrocarbylpolsiloxane. Suitable aluminoxanes include, but are not limited to, hydrocarbylaluminoxanes, such as one or more alkylaluminoxanes, one or more cycloalkylaluminoxanes, one or more arylaluminoxanes, one or more aralkylaluminoxanes, or any combination thereof. Typically, aluminoxanes having alkyl groups having from one to about eight carbon atoms are used, such as methylaluminoxane. The hydrocarbylpolsiloxane can have from about 3 to about 18 silicon atoms in the molecule which are separated from each other by an oxygen atom such that there is a linear, branched, or cyclic backbone of alternating silicon and oxygen atoms, with the remainder of the four valence bonds of each silicon atom individually satisfied by hydrocarbyl groups or hydrogen atoms. In another aspect of the present invention, the univalent hydrocarbyl groups of the polysiloxane each contain, independently, up to about 18 carbon atoms, for example, alkyl, cycloalkyl, aryl, or aralkyl groups. Examples of polysiloxanes include, but are not limited to, octamethyltrisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, and tetradecamethylhexasiloxane. Suitable aromatic solvents include, but are not limited to, benzene, toluene, xylene, ethylbenzene, cumene, tetrahydronaphthalene, or any mixtures of aromatic solvents, such as BTX.

[00033] In another aspect of this invention, ionic aluminoxanate compositions can be prepared by contacting, in any order, (i) at least one suitable aromatic solvent; (ii) at least one aluminoxane; and (iii) at least one aliphatic or crown polyether, to form a clathrate. Suitable aluminoxanes include, but are not limited to, hydrocarbylaluminoxanes, such as one or more alkylaluminoxanes, one or more cycloalkylaluminoxanes, one or more arylaluminoxanes, one or more aralkylaluminoxanes, or any combination thereof. Typically, aluminoxanes having alkyl groups having from one to about eight carbon atoms are used, such as methylaluminoxane. Examples of suitable aliphatic or crown polyethers which can be employed in the present invention include, but are not limited to, dimethoxyethane, diethoxyethane, 1-ethoxy-2-methoxyethane, dipropoxyethane, 1,2-dimethoxypropane, 1,3-dimethoxypropane, 1,2-dimethoxybutane, 2,3-dimethoxybutane, 1,3,5-trimethoxypropane,

18-crown-6 polyether, or analogs and homologs thereof. Suitable aromatic solvents include, but are not limited to, benzene, toluene, xylene, ethylbenzene, cumene, tetrahydronaphthalene, or any mixtures of aromatic solvents, such as BTX.

[00034] Preparation of ionic aluminoxanate clathrates generally results in a two-phase liquid system, wherein the denser lower liquid is typically the clathrate, and is readily separated from the supernatant liquid upper layer by conventional separation techniques. Exemplary processes for preparing the ionic aluminoxanate compositions include, for example, the following steps:

(1a) forming a stable liquid clathrate, such as, for example, as described in U.S. Patent Nos. 5,670,682 and 5,922,631, by contacting

- (i) at least one aluminoxane compound,
- (ii) an effective amount of at least one organic, inorganic, organometallic compound, or any combination thereof, and
- (iii) an aromatic organic solvent; and

(1b) washing the liquid clathrate one or more times with an aromatic solvent, each time forming a two-phase system composed of a lower layer of a viscous liquid composed of the aluminoxanate composition and included aromatic solvent, and an upper layer of a less dense liquid which is removed and discarded.

[00035] An effective amount of organic, inorganic, or organometallic compound as used herein is an amount which is sufficient to form a stable clathrate, but insufficient to cause the aluminoxanate to be incapable of activating a transition metal complex catalyst system. The volume of aromatic organic solvent used relative to the initial liquid clathrate is variable, and is not critical as long as it is sufficient to form a stirrable solution.

[00036] In another aspect of the present invention, solid ionic aluminoxanate compositions are optionally prepared by:

(2a) recovering the aluminoxanate solids from the viscous liquid in step (1b) above by:

- (i) precipitating the solids by mixing a liquid non-solvent such as a liquid paraffin or cycloparaffin hydrocarbon with the viscous liquid, isolating the solids by any suitable physical liquid/solids separation, such as filtration, centrifugation, or decantation, and preferably drying the solids, for example, under vacuum at ambient room temperature;
- (ii) optionally diluting the viscous liquid with a suitable aromatic solvent, followed by spray drying the viscous liquid, typically at a temperature of up to about 50°C;
- (iii) removing the included aromatic solvent from the viscous liquid by vacuum distillation; or
- (iv) removing the less dense liquid and the included aromatic solvent from the two-phase liquid formed in (b).

[00037] In yet another aspect of the present invention, solid ionic aluminoxanate compositions are prepared by:

(3a) thoroughly washing the liquid clathrate formed in step (1a) above to form a two-phase liquid system;

(3b) removing the upper layer of less dense liquid; and

(3c) removing the aromatic solvent from the lower viscous liquid by vacuum distillation to isolate particulate aluminoxanate solids.

In a further aspect of this invention, solid ionic aluminoxanate compositions are prepared by:

(4a) thoroughly washing the liquid clathrate formed in step (1a) above to form a two phase liquid system;

(4b) removing the upper layer of less dense liquid;

(4c) mixing an inert, liquid non-solvent with the viscous liquid to form a slurry comprised of precipitated aluminoxanate solids and a liquid phase; and

(4d) recovering the precipitated solids from the liquid phase.

[00038] Examples of liquid non-solvents which can be employed in the present invention include, but are not limited to, liquid paraffinic or cycloparaffinic hydrocarbons, such as liquid pentane, hexane, heptane, octane, nonane, decane, cyclopentane, alkylcyclopentanes, cyclohexane, alkylcyclohexanes, or any combination thereof. The addition of non-solvent should be in an amount sufficient to produce the desired yield of precipitated solids. This amount can be determined by adding the non-solvent in portions and observing whether addition of further non-solvent results in more precipitate formation.

[00039] In another aspect of the present invention, the solid ionic aluminoxanate composition can be prepared by:

(5a) mixing the solids precipitated in step (2a), (3c), or (4d) with fresh aromatic solvent to reform a clathrate;

(5b) washing the clathrate as in step (1b);

(5c) recovering precipitated solids as in step (2a), (3c), or (4d).

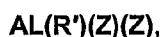
[00040] The preparation processes described in steps (1)-(5) can be conducted at ambient room temperatures (e.g., 25°C to 30°C) or at suitably reduced or elevated temperatures, for example, in the range of about 10°C to about 100°C. In one aspect of the present invention, the preparation is carried out at temperatures in a range of about 20°C to about 80°C.

[00041] The precipitated ionic aluminoxanate solids formed in steps (2a), (3c), and (4d) will typically have a higher electrical conductivity than an unprecipitated liquid clathrate, such as the liquid clathrate in step (1b). Accordingly, the solid ionic aluminoxanate compositions are more ionic than the liquid clathrate ionic aluminoxanate compositions. Similarly, the

recovered solids of step (5c) will have a higher electrical conductivity than the precipitated solids formed in steps (2a), (3c), and (4d). The precipitated solids can be rewashed with fresh aromatic solvent as many times as necessary to achieve the desired electrical conductivity, or until no additional increase in electrical conductivity is observed.

The Alkylaluminum Compound

[00042] Alkylaluminum compounds employed in the present invention include trialkylaluminum compounds and substituted trialkylaluminum compounds having the following general formula:



wherein:

R' is an alkyl group having from about four to about twenty carbon atoms; and

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms.

[00043] Suitable alkylaluminum compounds include, but are not limited to, tributylaluminum, triisobutylaluminum, tri-n-octylaluminum, or any combination thereof. Substituted alkylaluminum compounds include, but are not limited to, dialkylaluminum halides and alkylaluminum dihalides. The halide substituent can be selected from bromide, chloride, or fluoride. In one aspect, the halide substituent is fluoride. Examples of pseudohalide groups which can be employed in the present invention include, but are not limited to, are oxyhalide groups, hydrocarbyloxy groups (—OR groups such as alkoxy, aryloxy, cycloalkoxy, arylalkoxy, etc.), amido groups (—NR₂), hydrocarbylthio groups (—SR groups), azides, cyanide, cyanate, thiocyanate, isocyanate, isothiocyanate, and the like.

The Inert Organic Solvent

[00044] Inert organic solvents employed in the present invention include any suitable aromatic solvents, aliphatic solvents, halogenated solvents, or any combination thereof. In one aspect of the present invention, aliphatic solvents employed in the present invention have from 1 to 12 carbon atoms. Examples of aliphatic solvents include, but are not limited to, pentane, isopentane, cyclopentane, alkylcyclopentane, hexane, cyclohexane, alkylcyclohexane, heptane, octane, decane, dodecane, hexadecane, octadecane, or any combination thereof. Mixtures of aliphatic solvents can be employed in the present invention and include, but are not limited to, isopar C and isopar E. Examples of aromatic solvents include, but are not limited to, benzene, chlorobenzene, ethylbenzene, toluene, xylene, cumene, or any combination thereof.

Optional Support Materials

[00045] The soluble aluminoxanate salt composition can optionally be supported on any suitable organic or inorganic carrier. Support materials used in accordance with this invention can be any finely divided inorganic solid support such as talc, clay, silica, alumina, silica-alumina, or any combination thereof. Support materials can also include particulate, organic resinous support materials including, but not limited to, spheroidal, particulate, or finely-divided polyethylene, polyvinylchloride, polystyrene, or any combination or modification thereof. In another aspect of this invention, support materials are inorganic particulate supports or carrier materials such as magnesium halides, inorganic oxides and mixed inorganic oxides, aluminum silicates, inorganic compositions containing inorganic oxides, or any combination thereof. Non-limiting examples of inorganic compositions containing inorganic oxides include kaolinite, attapulgite, montmorillonite, illite, bentonite, halloysite, similar refractory clays, or any combination thereof. Examples of inorganic oxides include, but are not limited to, silica, alumina, silica-alumina, magnesia, titania, zirconia, or any combination thereof. In one aspect of the invention, the support is anhydrous or substantially anhydrous. Inorganic oxides can be dehydrated to remove water. The support can also be calcined or chemically treated with known conventional reagents to remove hydroxyl groups and/or water from the carrier. Suitable conventional reagents include, but are not limited to, aluminum alkyls, lithium alkyls, silylchloride, aluminoxanes, ionic aluminoxanates, or any combination thereof.

[00046] The specific particle size, surface area, and pore volume of the support material determine the amount of support material that is desirable to employ in preparing the catalyst compositions, as well as affect the properties of polymers formed with the aid of the catalyst compositions. These properties are frequently taken into consideration in choosing a support material for use in a particular aspect of the invention. A suitable support material such as silica typically will have a particle diameter in a range of about 0.1 to about 600 microns, or in a range of about 0.3 to about 100 microns; a surface area in a range of about 50 m²/g to about 1000 m²/g, or, in another aspect of the present invention, in a range of about 100 m²/g to about 500 m²/g; and a pore volume in a range of about 0.3 cc/g to about 5.0 cc/g, or, in another aspect of the present invention, in a range of about 0.5 cc/g to about 3.5 cc/g. It is also desirable to employ supports with pore diameters in a range of about 50 angstroms to about 500 angstroms. To ensure its use in dehydrated form the support material can be heat treated at about 100°C to about 1000°C for a period of about 1 hour to about 100 hours, or, in another aspect of the present invention, from about 3 to about 24 hours. The treatment can be carried out in a vacuum or while purging with a dry inert gas such as nitrogen.

[00047] As an alternative, the support material can be chemically dehydrated. Chemical dehydration is accomplished by slurrying the support in an inert low-boiling solvent, such as, for example, heptane, in the presence of a dehydrating agent, such as, for example, triethylaluminum, in a moisture and oxygen-free environment.

Preparation of the Soluble Aluminoxanate Salt Composition

[00048] This invention encompasses methods for preparing soluble aluminoxanate salts comprising contacting at least one ionic aluminoxanate, at least one inert organic solvent, and at least one alkylaluminum compound, in any order. In this aspect, the soluble aluminoxanate salt is obtained when the components are contacted in any sequence or order.

[00049] In another aspect of the present invention, a two-phase ionic aluminoxanate liquid clathrate system is prepared by contacting (i) at least one aluminoxane compound; (ii) an effective amount of at least one organic, inorganic, organometallic compound, or any combination thereof; and (iii) an aromatic organic solvent to form a liquid clathrate system. Subsequently, the liquid clathrate system is contacted with an alkylaluminum compound to form the soluble aluminoxanate salt composition. The less dense upper layer can optionally be removed before adding the alkylaluminum compound.

[00050] Alternatively, the ionic aluminoxanate solids can be removed from the liquid clathrate system by:

(i) decanting the less dense upper layer; precipitating the solids by mixing a liquid non-solvent such as a liquid paraffin or cycloparaffin hydrocarbon with the viscous liquid; isolating the solids by any suitable physical liquid/solid separation, such as filtration, centrifugation, or decantation; and preferably drying the solids, for example, under vacuum at ambient room temperature;

(ii) decanting the less dense upper layer; optionally diluting the viscous liquid with a suitable aromatic solvent; and spray drying the viscous liquid, typically at a temperature of up to about 50°C;

(iii) decanting the less dense upper layer and removing the included aromatic solvent from the viscous liquid by vacuum distillation; or

(iv) removing the less dense liquid and the included aromatic solvent from the two-phase liquid using any suitable method known in the art.

[00051] The ionic aluminoxanate solids can first be contacted with an alkylaluminum compound to form a mixture, after which the mixture is subsequently contacted with an organic solvent to form the soluble aluminoxanate salt composition. In another aspect of the invention, an ionic aluminoxanate solid is first contacted with an aromatic solvent to form a liquid clathrate, and the clathrate is subsequently contacted with an alkylaluminum

compound to form the soluble aluminoxanate salt composition. Alternatively, the ionic aluminoxanate solids and an aliphatic solvent are first contacted together to form a slurry, and the slurry is subsequently contacted with the alkylaluminum compound to form the soluble aluminoxanate salt composition. The soluble aluminoxanate salt compositions are typically prepared at temperatures in a range of about 20°C to about 80°C.

[00052] The present invention further encompasses methods to produce supported soluble aluminoxanate salt compositions comprising contacting at least one ionic aluminoxanate, at least one inert organic solvent, at least one alkylaluminum compound, and at least one organic or inorganic support material, in any order. In one aspect, the soluble aluminoxanate salt composition is prepared and subsequently contacted with a support material to form the supported composition. For example, the supported composition can be prepared by forming a slurry of (i) the soluble aluminoxanate salt composition dissolved in an aromatic or aliphatic solvent and (ii) a particulate support or carrier material. In another aspect, the supported composition can be prepared by forming a slurry of (i) an ionic aluminoxanate liquid clathrate system and (ii) an alkylaluminum supported on a particulate carrier material. In addition, any other sequential combination is suitable for forming the supported soluble aluminoxanate salt compositions of the present invention.

[00053] Preparation of the soluble aluminoxanate salt is generally conducted under a conventional inert atmosphere using substantially inert anhydrous materials. Typically, temperatures for preparation are in a range from about 20°C to about 80°C, although higher and lower temperatures are also suitable.

[00054] The molar ratio of the aluminum atoms derived from the ionic aluminoxanate compound to the aluminum atoms derived from the alkylaluminum compound is in a range of about 2:1 to about 1000:1. In another aspect, the molar ratio is in a range of about 10:1 to about 50:1.

Catalyst Compositions and Components

[00055] This invention encompasses supported and unsupported catalyst compositions prepared using soluble aluminoxanate salt compositions. Catalyst systems employed in one aspect of the present invention comprise the contact product of

- (I) a soluble aluminoxanate salt composition selected from:
 - (a) at least one soluble aluminoxanate salt composition having the general formula $[L_m((R)(R')Al)^+[(AO)X]^-]$,
 - (b) at least one soluble aluminoxanate salt composition comprising the contact product of:
 - (i) at least one ionic aluminoxanate composition having the general formula $[L_mR_2Al]^+[(AO)X]^-$,

- (ii) at least one organometallic compound such as an alkylaluminum compound having the general formula $\text{Al}(\text{R}')(\text{Z})(\text{Z})$, and
- (iii) at least one inert organic solvent;
- (c) at least one soluble methylaluminoxane salt composition having the general formula $[\text{L}_m(\text{Me})(\text{R}')\text{Al}]^+[(\text{MAO})\text{Me}]^-$, and
- (d) at least one mixed aluminoxanate composition comprising:
 - (i) a soluble aluminoxanate having the general formula $\text{L}_m(\text{R})(\text{R}')\text{Al}^+[(\text{AO})\text{X}]^-$,
 - (ii) a soluble aluminoxanate having the general formula $[\text{L}_m(\text{R})(\text{R}')\text{Al}]^+[(\text{AO})\text{X}]^-$,
 - (iii) a soluble aluminoxanate having the general formula $[\text{L}_m(\text{R}')(\text{R}')\text{Al}]^+[(\text{AO})\text{X}]^-$, or
 - (iv) any combination thereof; and
- (II) at least one complex of a transition metal of Group 3, 4, 5, 6, 7, 8, 9, 10, or 11 of the Periodic Table of Elements, including the lanthanide series and the actinide series;

wherein:

L is a stabilizing ligand,

R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms,

R' is, independently, an alkyl group having from about four to about twenty carbon atoms,

AO is an aluminoxane moiety,

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide,

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms,

MAO is a methylaluminoxane moiety,

Me is a methyl group, and

m is 1, 2, or 3, inclusive.

[00056] As employed in the present invention, where multiple R groups are present in a given component or in the various components of a composition, each R can be the same or different. Likewise, where multiple R' groups are present in a given component or in various components of a composition, each R' can be the same or different.

Transition Metal Complexes

[00057] Soluble aluminoxanate salt compositions of the present invention can be used with any known transition metal catalyst compound in which the transition metal is a Group 3

to 11 transition metal of the Periodic Table of Elements, including compounds of a metal of the lanthanide or actinide series. The Periodic Table of Elements referred to herein is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*. Suitable catalyst compounds can also be described as d- and f- block metal compounds. See, for example, the Periodic Table of Elements appearing on page 225 of Moeller, et al., *Chemistry*, Second Edition, Academic Press, copyright 1984. In one aspect of the present invention, the metal constituent is a compound of Fe, Co, Ni, Pd, or V. In another aspect the metal constituent is a compound of the metals of Groups 4-6 (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W). In yet another aspect, the metal constituent is a Group 4 metal, for example, titanium, zirconium, or hafnium.

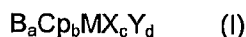
[00058] Thus, the transition metal catalyst compounds used in this invention can be one or more of any Ziegler-Natta catalyst compound, any metallocene, any compound of constrained geometry, any late transition metal complex, or any other transition metal compound or complex reported in the literature or otherwise generally known in the art to be an effective catalyst compound when suitably activated, including mixtures of at least two different types of such transition metal compounds or complexes, such as for example a mixture of a metallocene and a Ziegler-Natta olefin polymerization catalyst compound.

[00059] Among the transition metal compounds of the metals of Groups 3, 4, 5, and 6 which can be used as the transition metal component of the catalyst compositions of this invention are the compounds of such metals as scandium, titanium, zirconium, hafnium, cerium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, thorium and uranium, often referred to as Ziegler-Natta type olefin polymerization catalysts. Compounds of this type can be represented by the formula $MX_n(OR)_m$ in which M represents the transition metal atom or a transition metal atom cation containing one or two oxygen atoms such as vanadyl, zirconyl, or uranyl, X represents a halogen atom, OR represents a hydrocarboxy group having up to about 18 carbon atoms, or up to about 8 carbon atoms, or an alkyl of up to about 4 carbon atoms, such as an alkyl, cycloalkyl, cycloalkylalkyl, aryl, or aralkyl group, n and m are positive integers except that either one of them (but not both) can be zero, and $n + m$ is the valence state of the transition metal. Illustrative of some of the transition metal compounds which can be employed in the present invention include, but are not limited to, titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride, titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium triiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, vanadium dichloride, vanadium trichloride, vanadium

metal compounds include, but are not limited to, TiCl_4 , ZrCl_4 , HfCl_4 , or TiCl_3 . These compounds can also be used in chelated form in order to facilitate solubility. Suitable chelated catalysts of this type are known and reported in the literature.

[00061] Metallocenes are another broad class of olefin polymerization catalyst compounds with which the soluble aluminoxanate salt compositions can be used in forming the catalyst compositions of this invention. As used herein, the term "metallocene" includes metal derivatives which contain at least one cyclopentadienyl (Cp) moiety. Suitable metallocenes are well known in the art and include the metallocenes of Groups 3, 4, 5, 6, including lanthanide and actinide metals. For example and without limitation, the metallocenes which are described in U.S. Patent Nos. 2,864,843; 2,983,740; 4,665,046; 4,874,880; 4,892,851; 4,931,417; 4,952,713; 5,017,714; 5,026,798; 5,036,034; 5,064,802; 5,081,231; 5,145,819; 5,162,278; 5,245,019; 5,268,495; 5,276,208; 5,304,523; 5,324,800; 5,329,031; 5,329,033; 5,330,948; 5,347,025; 5,347,026; and 5,347,752 can be employed in the present invention.

[00062] Metallocene structures in this specification are to be interpreted broadly, and include structures containing 1, 2, 3, or 4 Cp or substituted Cp rings. Thus, metallocenes suitable for use in this invention can be represented by Formula (I):



where Cp, independently in each occurrence, is a cyclopentadienyl-moiety-containing group which typically has in the range of 5 to about 24 carbon atoms; B is a bridging group or *ansa* group that links two Cp groups together or alternatively carries an alternate coordinating group such as alkylaminosilylalkyl, silylamido, alkoxy, siloxy, aminosilylalkyl, or analogous monodentate hetero atom electron donating groups; M is a d- or f-block metal atom; each X and each Y is, independently, a group that is bonded to the d- or f-block metal atom; a is 0 or 1; b is an integer from 1 to 3; c is at least 2; and d is 0 or 1. The sum of b, c, and d is sufficient to form a stable compound, and often is the coordination number of the d- or f-block metal atom.

[00063] Cp is, independently, a cyclopentadienyl, indenyl, fluorenyl or related group that can π -bond to the metal, or a hydrocarbyl-, halo-, halohydrocarbyl-, hydrocarbylmetaloid-, and/or halohydrocarbylmetaloid-substituted derivative thereof. Cp typically contains up to 75 non-hydrogen atoms. B, if present, is typically a silylene ($-\text{SiR}_2-$), benzo ($\text{C}_6\text{H}_4<$), substituted benzo, methylene ($-\text{CH}_2-$), substituted methylene, ethylene ($-\text{CH}_2\text{CH}_2-$), or substituted ethylene bridge. In one aspect, M is a metal atom of Groups 4-6. In another aspect, M is a Group 4 metal atom, such as hafnium, zirconium, or titanium. X can be a divalent substituent such as an alkylidene group, a cyclometallated hydrocarbyl group, or any other divalent chelating ligand, two loci of which are singly bonded to M to form a cyclic moiety which includes M as a member. Each X, and if present, Y, can be, independently in

each occurrence, a halogen atom, a hydrocarbyl group (alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl, *etc.*), hydrocarbyloxy, (alkoxy, aryloxy, *etc.*) siloxy, amino or substituted amino, hydride, acyloxy, triflate, and similar univalent groups that form stable metallocenes. The sum of b, c, and d is a whole number, and is often from 3-5. When M is a Group 4 metal or an actinide metal, and b is 2, the sum of c and d is 2, c being at least 1. When M is a Group 3 or lanthanide metal, and b is 2, c is 1 and d is zero. When M is a Group 5 metal, and b is 2, the sum of c and d is 3, c being at least 2.

[00064] Also useful in this invention are compounds analogous to those of Formula (I) where one or more of the Cp groups are replaced by cyclic unsaturated charged groups isoelectronic with Cp, such as borabenzene or substituted borabenzene, azaborole or substituted azaborole, and various other isoelectronic Cp analogs. See for example Krishnamurti, et al., U.S. Patent No. 5,554,775 and 5,756,611.

[00065] In one group of metallocenes, b is 2, i.e., there are two cyclopentadienyl-moiety containing groups in the molecule, and these two groups can be the same or they can be different from each other.

[00066] Another sub-group of useful metallocenes which can be used in the practice of this invention are metallocenes of the type described in WO 98/32776. These metallocenes are characterized in that one or more cyclopentadienyl groups in the metallocene are substituted by one or more polyatomic groups attached via a N, O, S, or P atom or by a carbon-to-carbon double bond. Examples of such substituents on the cyclopentadienyl ring include -OR, -SR, -NR₂, -CH=, -CR=, and -PR₂, where R can be the same or different and is a substituted or unsubstituted C₁-C₁₆ hydrocarbyl group, a tri-C₁-C₈ hydrocarbylsilyl group, a tri-C₁-C₈ hydrocarbyloxysilyl group, a mixed C₁-C₈ hydrocarbyl and C₁-C₈ hydrocarbyloxysilyl group, a tri-C₁-C₈ hydrocarbylgermyl group, a tri-C₁-C₈ hydrocarbyloxygermyl group, or a mixed C₁-C₈ hydrocarbyl and C₁-C₈ hydrocarbyloxygermyl group.

[00067] Examples of metallocenes to which this invention is applicable include, but are not limited to:

bis(cyclopentadienyl)zirconium dimethyl;

bis(cyclopentadienyl)zirconium dichloride;

bis(cyclopentadienyl)zirconium monomethylmonochloride;

bis(cyclopentadienyl)titanium dichloride;

bis(cyclopentadienyl)titanium difluoride;

cyclopentadienylzirconium tri-(2-ethylhexanoate);

bis(cyclopentadienyl)zirconium hydrogen chloride;

bis(cyclopentadienyl)hafnium dichloride;

racemic and meso dimethylsilanylene-bis(methylcyclopentadienyl)hafnium dichloride;

racemic dimethylsilanylene-bis(indenyl)hafnium dichloride;

racemic ethylene-bis(indenyl)zirconium dichloride;
(η^5 -indenyl)hafnium trichloride;
(η^5 -C₅Me₅)hafnium trichloride;
racemic dimethylsilanylene-bis(indenyl)thorium dichloride;
racemic dimethylsilanylene-bis(4,7-dimethyl-1-indenyl)zirconium dichloride;
racemic dimethyl-silanylene-bis(indenyl)uranium dichloride;
racemic dimethylsilanylene-bis(2,3,5-trimethyl-1-cyclopentadienyl)zirconium dichloride;
racemic dimethyl-silanylene(3-methylcyclopentadienyl)hafnium dichloride;
racemic dimethylsilanylene-bis(1-(2-methyl-4-ethyl)indenyl) zirconium dichloride;
racemic dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride;
bis(pentamethylcyclopentadienyl)thorium dichloride;
bis(pentamethylcyclopentadienyl)uranium dichloride;
(tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride;
(tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane chromium dichloride;
(tert-butylamido)dimethyl(- η^5 -cyclopentadienyl)silanetitanium dichloride;
(tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanemethyltitanium bromide;
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyluranium dichloride;
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride;
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylcerium dichloride;
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride;
(ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylenetitanium dichloride;
(tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)-silanebenzylvanadium chloride;
(benzylamido)dimethyl(indenyl)silanetitanium dichloride;
(phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanebenzyltitanium chloride;
rac-dimethylsilylbis(2-methyl-1-indenyl)zirconium dimethyl;
rac-ethylenebis(1-indenyl)zirconium dimethyl;
bis(methylcyclopentadienyl)titanium dimethyl;
bis(methylcyclopentadienyl)zirconium dimethyl;
bis(n-butylcyclopentadienyl)zirconium dimethyl;
bis(dimethylcyclopentadienyl)zirconium dimethyl;
bis(diethylcyclopentadienyl)zirconium dimethyl;
bis(methyl-n-butylcyclopentadienyl)zirconium dimethyl;
bis(n-propylcyclopentadienyl)zirconium dimethyl;
bis(2-propylcyclopentadienyl)zirconium dimethyl;
bis(methylethylcyclopentadienyl)zirconium dimethyl;
bis(indenyl)zirconium dimethyl;
bis(methylindenyl)zirconium dimethyl;

dimethylsilylenebis(indenyl)zirconium dimethyl;
dimethylsilylenebis(2-methylindenyl)zirconium dimethyl;
dimethylsilylenebis(2-ethylindenyl)zirconium dimethyl;
dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dimethyl;
1,2-ethylenebis(indenyl)zirconium dimethyl;
1,2-ethylenebis(methylindenyl)zirconium dimethyl;
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)zirconium dimethyl;
dimethylsilylenebis(6-phenylindenyl)zirconium dimethyl;
bis(methylindenyl)zirconium benzyl methyl;
ethylenebis[2-(tert-butyl dimethylsiloxy)-1-indenyl] zirconium dimethyl;
dimethylsilylenebis(indenyl)chlorozirconium methyl;
5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium dimethyl;
dimethylsilylenebis(2-methylindenyl)hafnium dimethyl;
dimethylsilylenebis(2-ethylindenyl)hafnium dimethyl;
dimethylsilylenebis(2-methyl-4-phenylindenyl)hafnium dimethyl;
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)hafnium dimethyl;
bis(9-fluorenyl)(methyl)(vinyl)silane zirconium dimethyl;
bis(9-fluorenyl)(methyl)(prop-2-enyl)silane zirconium dimethyl;
bis(9-fluorenyl)(methyl)(but-3-enyl)silane zirconium dimethyl;
bis(9-fluorenyl)(methyl)(hex-5-enyl)silane zirconium dimethyl;
bis(9-fluorenyl)(methyl)(oct-7-enyl)silane zirconium dimethyl;
(cyclopentadienyl)(1-allylindenyl) zirconium dimethyl;
bis(1-allylindenyl)zirconium dimethyl;
(9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)zirconium dimethyl;
(9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)zirconium dimethyl;
bis(9-(prop-2-enyl)fluorenyl) zirconium dimethyl;
(9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) zirconium dimethyl;
bis(9-(cyclopent-2-enyl)(fluorenyl)zirconium dimethyl;
5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene zirconium dimethyl;
1-(9-fluorenyl)-1-(cyclopentadienyl)-1-(but-3-enyl)-1-(methyl)methane zirconium dimethyl;
5-(fluorenyl)-5-(cyclopentadienyl)-1-hexene hafnium dimethyl;
(9-fluorenyl)(1-allylindenyl)dimethylsilane zirconium dimethyl;
1-(2,7-di(alpha-methylvinyl)(9-fluorenyl)-1-(cyclopentadienyl)-1,1-dimethylmethane zirconium dimethyl;
1-(2,7-di(cyclohex-1-enyl)(9-fluorenyl))-1-(cyclopentadienyl)-1,1-methane zirconium dimethyl;
5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dimethyl;

5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dimethyl;
 bis(9-fluorenyl)(methyl)(vinyl)silane titanium dimethyl;
 bis(9-fluorenyl)(methyl)(prop-2-enyl)silane titanium dimethyl;
 bis(9-fluorenyl)(methyl)(but-3-enyl)silane titanium dimethyl;
 bis(9-fluorenyl)(methyl)(hex-5-enyl)silane titanium dimethyl;
 bis(9-fluorenyl)(methyl)(oct-7-enyl)silane titanium dimethyl;
 (cyclopentadienyl)(1-allylindenyl) titanium dimethyl;
 bis(1-allylindenyl)titanium dimethyl;
 (9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)hafnium dimethyl;
 (9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)hafnium dimethyl;
 bis(9-(prop-2-enyl)fluorenyl) hafnium dimethyl;
 (9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) hafnium dimethyl;
 bis(9-(cyclopent-2-enyl)(fluorenyl)hafnium dimethyl;
 5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene hafnium dimethyl;
 5-(fluorenyl)-5-(cyclopentadienyl)-1-octene hafnium dimethyl;
 (9-fluorenyl)(1-allylindenyl)dimethylsilane hafnium dimethyl;
 (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium(1,3-pentadiene);
 (cyclopentadienyl)(9-fluorenyl)diphenylmethane zirconium dimethyl;
 (cyclopentadienyl)(9-fluorenyl)diphenylmethane hafnium dimethyl;
 dimethylsilanylene-bis(indenyl) thorium dimethyl;
 dimethylsilanylene-bis(4,7-dimethyl-1-indenyl) zirconium dimethyl;
 dimethylsilanylene-bis(indenyl) uranium dimethyl;
 dimethylsilanylene-bis(2-methyl-4-ethyl-1-indenyl) zirconium dimethyl;
 dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dimethyl;
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dimethyl;
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane chromium dimethyl;
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dimethyl;
 (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dimethyl;
 [dimethylsilanediy]bis(indenyl)]scandium methyl; or any combination thereof.
 In many cases metallocenes such as those referred to above will exist as racemic mixtures, but pure enantiomeric forms or mixtures enriched in a given enantiomeric form can be employed in the present invention.

[00068] Other organometallic catalytic compounds with which the soluble aluminoxanate salt compositions can be used in forming the catalyst compositions of this invention are the late transition metal catalyst described, for example, in U.S. Patent Nos. 5,516,739 to Barborak, et al.; 5,561,216 to Barborak, et al.; 5,866,663 to Brookhart, et al; 5,880,241 to

Brookhart, et al; and 6,114,483 to Coughlin, et al. Such catalysts are sometimes referred to herein collectively as "a Brookhart-type late transition metal catalyst compound or complex".

[00069] Other transition metal catalyst compounds and catalyst complexes that can be used in the practice of this invention include catfluoro nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands such as described in Johnson et al. WO 96/23010; palladium and nickel catalysts containing selected bidentate phosphorus-containing ligands such as described in EP 381,495; catfluoro α -diimine-based nickel and palladium complexes such as described by Johnson et al. in *J. Am. Chem. Soc.*, **1995**, *117*, 6414, see also Brown et al. WO 97/17380; nickel complexes such as described by Johnson et al. in U.S. Patent No. 5,714,556; cobalt(III) cyclopentadienyl catalytic systems such as described by Schmidt et al. in *J. Am. Chem. Soc.*, **1985**, *107*, 1443, and by Brookhart et al. in *Macromolecules*, **1995**, *28*, 5378; anfluoro phosphorus, oxygen donors ligated to nickel(II) such as described by Klabunde in U.S. Pat Nos. 4,716,205, 4,906,754, 5,030,606, and 5,175,326; Group 8-10 transition metal complexes coordinated with a bidentate ligand such as described in WO 98/40374; transition metal complexes with bidentate ligands containing pyridine or quinoline moieties such as described in U.S. Patent No. 5,637,660; quinolinoxy or pyridinoxy-substituted Group 4 transition metal trihalides such as described in U.S. Patent No. 6,020,493; nickel complexes such as described by bis(ylide)nickel complexes such as described by Starzewski et al. in *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 63, and U.S. Patent No. 4,691,036; neutral N, O, P, or S donor ligands in combination with a nickel(0) compound and an acid such as described in WO 97/02298; aminobis(imino)phosphorane nickel catalysts such as described by Fink et al. in U.S. Patent No. 4,724,273.

[00070] Illustrative, non-limiting additional examples of various types of transition metal compounds that can be employed include the following:

2,6-bis-[1-(1-methylphenylimino)ethyl]pyridine iron(II) chloride;

2,6-bis[1-(1-ethylphenylimino)ethyl]pyridine iron(II) chloride;

2,6-bis[1-(1-isopropylphenylimino)ethyl]pyridine iron(II) chloride;

2,6-bis-(1-(2-methylphenylimino)ethyl)pyridine iron(II) chloride;

N,N'-di(trimethylsilyl)benzamidinato copper(II);

tridentate Schiff base complexes of cobalt and iron described by Mashima in *Shokubai* **1999**, vol. *41*, p. 58;

nickel compounds of the type described in U. S. Patent 5,880,323;

nickel(II) acetylacetonate;

bis(acetonitrile)dichloro palladium(II);

bis(acetonitrile)bis(tetrafluoroborate)palladium(II);

(2,2'-bipyridine)dichloro palladium(II);

bis(cyclooctadienyl) nickel(0);

palladium(II) acetylacetonate;
 bis(salicylaldiminato) complexes of the type described by Matsui *et. al.* in *Chemistry Letters* 2000, pp. 554-555;
 cobalt dioctoate;
 cobaltocene;
 (cyclopentadienyl)(triphenylphosphino)cobalt(II) diiodide;
 nickel compounds of the type described in JP 09-272709; or any combination thereof.

[00071] In one aspect of the present invention, transition metal compounds which can be used in forming the catalysts of this invention are transition metal compounds which can be represented by the formula:



where M is a transition metal of Group 4 to 8, of the Periodic Table of Elements, including the lanthanide series and actinide series, and Y is, independently, a halide or pseudohalide, n is the valence of M, and m is an integer of from 0 to n-1. Pseudohalide, which is a term of art, refers to anionic non-halogenides with salt-like characteristics. Non-limiting examples of suitable pseudohalide groups are oxyhalide groups, hydrocarbyloxy groups (—OR groups such as alkoxy, aryloxy, cycloalkoxy, arylalkoxy, etc.), amido groups (—NR₂), hydrocarbylthio groups (—SR groups), azides, cyanide, cyanate, thiocyanate, isocyanate, isothiocyanate, and the like. In one aspect of the present invention, M is a transition metal of Group 4 to 8 of the Periodic Table of Elements. In another aspect, M is a Group 4 metal. Examples of suitable transition metal compounds include, but are not limited to, transition metal halides and oxyhalides such as titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride, titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, hafnium oxychloride, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium triiodide, vanadium oxytrichloride, vanadium oxytribromide, niobium pentabromide, niobium pentachloride, niobium pentafluoride, tantalum pentabromide, tantalum pentachloride, tantalum pentafluoride, chromous bromide, chromic bromide, chromous chloride, chromic chloride, chromous fluoride, chromic fluoride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide, molybdenum dichloride, molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, molybdenum hexafluoride, lanthanum trichloride, cerous fluoride, cerous chloride, cerous bromide, cerous iodide, ceric fluoride, uranium trichloride, uranium tetrachloride, uranium

tribromide, uranium tetrabromide, thorium tetrachloride, thorium tetrabromide, or any combination thereof. Among suitable alkoxides and mixed halide/alkoxides of the transition metals which can be employed in the present invention include, but are not limited to, $\text{Ti}(\text{OCH}_3)_4$, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$, $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$, $\text{Ti}(\text{O-iso-C}_3\text{H}_7)\text{Cl}_3$, $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_{17}\text{H}_{18})_2\text{Br}_2$, $\text{Zr}(\text{OC}_2\text{H}_5)_4$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, $\text{Zr}(\text{OC}_5\text{H}_{11})_4$, $\text{ZrCl}_3(\text{OC}_2\text{H}_5)$, $\text{ZrCl}(\text{OC}_4\text{H}_9)_3$, $\text{Hf}(\text{OC}_4\text{H}_9)_4$, $\text{Hf}(\text{OC}_4\text{H}_9)_3\text{Cl}$, $\text{VO}(\text{OC}_2\text{H}_5)_3$, $\text{Cr}(\text{O-iso-C}_4\text{H}_9)_3$, $\text{Mo}(\text{OC}_2\text{H}_5)_3$, or any combination thereof. Other transition metal compounds which can be used include, but are not limited to, amides such as $\text{Ti}(\text{NMe}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Ti}(\text{NEt}_2)_4$, $\text{Zr}(\text{NEt}_2)_4$, and $\text{Ti}(\text{NBu}_2)_4$; or carboxylic acid salts such as titanium oxalate, cobalt acetate, chromium acetate, nickel formate, thallium oxalate, and uranyl formate. In one aspect of the present invention, the transition metal compounds are the halides, oxyhalides, alkoxides, or mixed halide-alkoxides of the Group 4 to 6 metals. In another aspect of the present invention, the transition metal compounds are the trivalent or tetravalent Group 4 metal halides and the vanadium oxyhalides. The Periodic Table of Elements referred to is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*.

Optional Support Materials

[00072] The catalyst composition can optionally be supported on any suitable organic or inorganic carrier. Support materials used in accordance with this invention can be any finely divided inorganic solid support, such as talc, clay, silica, alumina, silica-alumina, or any combination thereof. Support materials can also include particulate, organic resinous support materials including, but not limited to, spheroidal, particulate, or finely-divided polyethylene, polyvinylchloride, polystyrene, or any combination or modification thereof.

[00073] The specific particle size, surface area, and pore volume of the support material determine the amount of support material that is desirable to employ in preparing the catalyst compositions, as well as affect the properties of polymers formed with the aid of the catalyst compositions. These properties are frequently taken into consideration in choosing a support material for use in a particular aspect of the invention.

Preparation of the Catalyst Composition

[00074] This invention encompasses methods for preparing supported and unsupported catalyst compositions comprising contacting at least one soluble aluminoxanate salt composition and at least one complex of a transition metal of Groups 3 to 11 of the Periodic Table of Elements. In another aspect, the catalyst composition can be produced by contacting at least one ionic aluminoxanate compound, at least one organometallic compound having at least one long chain alkyl substituent, for example, an alkyl aluminum compound, at least one organic solvent, and at least one complex of a transition metal of

Groups 3 to 11 of the Periodic Table of Elements. In yet another aspect of the present invention, the catalyst composition can be produced by contacting at least one ionic aluminoxanate compound, at least one organometallic compound having at least one long chain alkyl substituent, for example, an alkyl aluminum compound, at least one organic solvent, at least one complex of a transition metal of Groups 3 to 11 of the Periodic Table of Elements, and at least one organic or inorganic support material. In these aspects, the supported or unsupported catalyst composition is obtained when the components are contacted in any sequence or order. For example, the components can be fed to a reactor or separate vessel separately, in any order, or any two or more can be premixed and fed as a mixture, with the remaining components being fed before, during, or after the mixture is fed to the reactor.

[00075] Unsupported catalyst compositions in accordance with the present invention can be produced by contacting the transition metal complex with the soluble aluminoxanate salt composition before, during, or after its formation. For example, before the soluble aluminoxanate salt composition is formed, the transition metal complex can be contacted with any one or any combination of (a) the ionic aluminoxanate composition; (b) the alkylaluminum compound; or (c) the organic solvent. Alternatively, the transition metal complex can be added at any time during the formation of the soluble aluminoxanate salt composition. Additionally, the transition metal complex can be contacted with the soluble aluminoxanate salt composition after it is formed.

[00076] Temperatures for the preparation of unsupported catalyst compositions are in a range of about -100°C to about 300°C. In another aspect, preparation temperatures are in a range of about 0°C to about 80°C. Typically, the preparation is carried out at temperatures in a range of 20°C to about 50°C, or at ambient room temperature. Holding times to allow for the completion of catalyst formation can range from about 10 seconds to about 60 minutes, depending on the reaction variables.

[00077] Supported catalyst compositions are similarly formed by contacting the support material with the catalyst composition before, during, or after its formation. Preparation can include contacting, in any order, the transition metal compound, a soluble aluminoxanate salt composition, and a support material in one or more suitable solvents or diluents. Suitable solvents and/or diluents include, but are not limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, or octane; cyclic and acyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, or methylcyclopentane; or aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, or xylene. Mixtures of different types of solvents and/or diluents can also be used, such as a mixture of one or more acyclic aliphatic hydrocarbons and one or more cycloaliphatic hydrocarbons; a mixture of one or more acyclic aliphatic hydrocarbons and

one or more aromatic hydrocarbons; a mixture of one or more cycloaliphatic hydrocarbons and one or more aromatic hydrocarbons; or a mixture of one or more acyclic aliphatic hydrocarbons, one or more cycloaliphatic hydrocarbons, and one or more aromatic hydrocarbons.

[00078] The support material can first be contacted with the soluble aluminoxanate salt composition to form a supported aluminoxanate which is subsequently contacted with the transition metal complex. Alternatively, the support material can first be contacted with the transition metal complex to form a supported complex which is subsequently contacted with a soluble aluminoxanate salt composition. In another aspect of this invention, the soluble aluminoxanate salt and the transition metal complex can be contacted together, and the resulting composition can be subsequently contacted with a support material. In further aspect of the present invention, the support material can be contacted with either the soluble aluminoxanate salt composition or the transition metal complex during its formation. For example, the support material can be contacted with one or more of the components used to form the soluble aluminoxanate or with one or more of the components used to form the transition metal complex.

[00079] Because of the sensitivity of the catalyst components and catalyst compositions to moisture and oxygen, these components and compositions are generally handled under a conventional inert atmosphere using substantially inert anhydrous materials, for example, in a moisture-free, oxygen-free environment such as argon, nitrogen, or helium. Temperatures for each stage of the preparation of supported catalyst compositions of this invention are in a range of about -100°C to about 300°C. In another aspect, preparation temperatures are in a range of about 0°C to about 80°C. Typically, the preparation is carried out temperatures in a range of 20°C to about 50°C, or at ambient room temperature. Holding times to allow for the completion of catalyst formation can range from about 10 seconds to about 60 minutes, depending on the reaction variables.

[00080] The concentration of transition metal compound on the support is typically in a range of about 0.01 wt% to about 50 wt%. In another aspect of the present invention, the concentration of transition metal compound on the support is in a range of about 0.1 wt% to about 20 wt%, based upon the weight of the support.

[00081] Modified supported catalysts can be prepared in accordance with this invention by combining, in any order, at least one transition metal compound, at least one soluble aluminoxanate salt composition, at least one modifier, and a support material, in a suitable solvent and/or diluent. A modifier can be defined as any compound containing a Lewis acidic or basic functionality. Examples of compounds containing a Lewis acidic or basic functionality include, but are not limited to, tetraethoxysilane, phenyltri(ethoxy)silane, bis-tert-butylhydroxytoluene (BHT), or N,N-dimethylaniline.

[00082] In one aspect of the present invention, the modified supported catalyst is formed by contacting a soluble aluminoxanate salt composition and the modifier in a suitable solvent to produce a slurry. A transition metal compound is subsequently added to the slurry. Suitable temperatures for these contacting steps are in a range of about -100°C to about 300°C, or, in another aspect of the present invention, in a range of about 0°C to about 100°C. Holding times to allow for the completion of the reaction can range from about 10 seconds to about 60 minutes, depending on the reaction variables. The mixture comprising the transition metal, modifier, and soluble aluminoxanate salt can then be contacted with the support material.

[00083] In the case of modified supported catalysts, the molar ratio of soluble aluminoxanate salt composition to transition metal compound is generally in a range of about 1:1 to about 20000:1, or, in another aspect of the present invention, in a range of about 10:1 to about 1000:1. The molar ratio of soluble aluminoxanate salt to modifier is in a range of about 1:1 to about 20000:1, or, in another aspect of the present invention, in a range of about 10:1 to about 1000:1. The concentration of transition metal compound on the support is typically in a range of 0.01 wt% to about 50 wt%, or, in another aspect of the present invention, in a range of about 0.1 wt% to about 20 wt%, based upon the weight of the support.

[00084] The amount of soluble aluminoxanate salt composition used varies depending upon the application and reaction conditions. Soluble aluminoxanate salt is typically used in an amount sufficient to produce molar ratio of aluminum atoms derived from the soluble aluminoxanate salt to transition metal is in a range of about 20:1 to about 2000:1. In another aspect, the molar ratio is in a range of about 20:1 to about 500:1.

Polymerization Process

[00085] This invention encompasses a method for polymerizing olefinic monomers comprising contacting at least one olefinic monomer and a catalyst system comprising a soluble aluminoxanate salt composition and at least one transition metal complex. Catalyst compositions in accordance with the present invention are useful for the homopolymerization or copolymerization of olefinic monomers, for example, α -olefin monomers, cyclic olefin monomers, or vinylaromatic monomers.

[00086] Polymerizations using the catalysts of this invention can be carried out in any manner known in the art. Such polymerization processes include, but are not limited to, slurry polymerizations, gas phase polymerizations, solution polymerizations, and the like, including multi-reactor combinations thereof. Thus, any polymerization zone known in the art to produce ethylene-containing polymers can be utilized. For example, a stirred reactor can be utilized for a batch process, or the reaction can be carried out continuously in a loop

reactor or in a continuous stirred reactor. The polymerization reactor can be any suitable type of reactor, for example, a gas phase reactor, tubular reactor, solution phase reactor, or a combination of two or more reactors.

[00087] The polymerization reaction typically occurs in an inert atmosphere, that is, in an atmosphere substantially free of oxygen and under substantially anhydrous conditions, as the reaction begins. Therefore a dry, inert atmosphere, for example, dry nitrogen or dry argon, is typically employed in the polymerization reactor. Conventional temperatures for polymerization are in a range of about 0°C to about 160°C and conventional pressures for polymerization are in a range of about 1 kg/cm² to about 50 kg/cm². Generally, the polymerization can be carried out at both ambient temperature and pressure. In some cases, in order to control the resulting polymer's properties, controlled admission of hydrogen gas is also suitable.

[00088] For slurry polymerizations, a particulate catalyst is typically dispersed in a suitable liquid reaction medium which can be composed of one or more ancillary solvents or an excess amount of liquid monomer. Suitable ancillary solvents include, but are not limited to, aliphatic and aromatic liquid hydrocarbons such as heptane, isooctane, decane, toluene, xylene, ethylbenzene, mesitylene, or any combination thereof. Slurry polymerization temperatures for this invention typically are in a range of about 0°C to about 160°C, with a polymerization reaction temperature more typically operating between about 40°C to about 110°C. The polymerization can take place under atmospheric, subatmospheric, or superatmospheric conditions, or any other polymerization reaction condition can be any pressure that does not adversely affect the polymerization reaction. Typical diluents include, but are not limited to, isobutane, pentane, isopentane, hexane, heptane, toluene, or any combination thereof.

[00089] Gas phase polymerizations are typically conducted at temperatures in a range of about 50°C to about 160°C, under superatmospheric pressures. However, the polymerization can take place at any temperature or pressure that does not adversely affect the polymerization reaction. These gas phase polymerizations can be performed in a stirred or fluidized bed of catalyst in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, hydrogen, and an inert diluent gas such as nitrogen can be introduced or recirculated to maintain the particles at the desired polymerization reaction temperature. An aluminum alkyl, such as triethylaluminum, can be added as a scavenger of water, oxygen, and other impurities. In such cases, the alkylaluminum is typically employed as a solution in a suitable dry liquid hydrocarbon solvent such as toluene or xylene. Concentrations of such solutions are typically in a range of about 5×10^{-5} molar (M), but solutions of greater or lesser

concentrations can be used. Polymer product can be withdrawn continuously or semi-continuously at a rate that maintains a constant product inventory in the reactor.

[00090] Polymerization reactions in accordance with the present invention are carried out using a catalytically effective amount of a novel catalyst composition of this invention. The amount of catalyst used depends on several factors, such as the type of polymerization being conducted, the polymerization conditions being used, and the type of reaction equipment in which the polymerization is being conducted. In one aspect of this invention, the catalyst composition is used in a range of about 0.000001 to about 0.01 percent by weight of transition, lanthanide, or actinide metal based on the total weight of the monomer(s) being polymerized.

[00091] When conducting polymerization reactions pursuant to this invention, conditions can be used for preparing unimodal or multimodal polymers. For example, multimodal polymers can be produced by using a mixture of different catalysts having different propagation and termination rate constants.

[00092] After polymerization and deactivation of the catalyst, the product polymer can be recovered from the polymerization reactor by any suitable means. When conducting the process with a slurry or dispersion of the catalyst in a liquid medium, the product is typically recovered by a physical separation technique, for example, decantation. The recovered polymer is generally washed with one or more suitable volatile solvents to remove residual polymerization solvent or other impurities, and then dried, typically under reduced pressure, with or without the addition of heat. When conducting the process as a gas phase polymerization, the product after removal from the gas phase reactor is typically freed of residual monomer by means of a nitrogen purge, and can possibly be used without further catalyst deactivation or catalyst removal.

[00093] Polymers produced in accordance with this invention can be homopolymers, typically of α -olefins such as ethylene, propylene, 1-butene, styrene, or any combination thereof. Polymers can also be copolymers of two or more monomers, one of which is typically an α -olefin. Monomers useful in forming copolymers include one or more different α -olefin, diolefin, cyclic olefin, acetylenic, or functional olefin monomers. Non-limiting examples of olefins that can be polymerized in the presence of a catalyst composition of the present invention include α -olefins having from 2 to about 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, or 1-octadecene. Typical diolefin monomers which can be used to form terpolymers with ethylene and propylene include, but are not limited to, butadiene, hexadiene, norbornadiene, or any combination thereof. Suitable acetylenic monomers include 1-heptyne or 1-octyne. In one aspect of the present invention,

ethylene can be copolymerized with at least one α -olefin having 3 to 8 carbon atoms, for example, propylene.

EXAMPLES

[00094] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of the invention. As discussed above and below, room temperature means a temperature in a range of about 25°C to about 30°C. Activator Conductivity in Tables III and IV is expressed as micro Mohs/centimeter ($\mu\text{S}/\text{cm}$).

GENERAL METHODS

NMR Characterization

Instrumentation

[00095] All spectra were obtained on Bruker DPX400 instruments operating at 400 MHz for proton NMR, 79.5 MHz for ^{29}Si NMR, and 104.3 MHz for ^{27}Al NMR. Proton spectra were obtained using a 5mm QNP probe, ^{29}Si spectra were obtained using a 10mm broadband observe probe, and ^{27}Al spectra were obtained on a 10 mm ^{27}Al probe having no ^{27}Al NMR background artifacts.

[00096] All spectra were obtained with conventional pulse sequences. Proton and ^{27}Al spectra were obtained with 1 pulse experiments, while ^{29}Si spectra were obtained with a DEPT45 sequence. In all cases probe tune and match were appropriately monitored.

Sample preparation

[00097] All samples were prepared in a dry nitrogen purge box. All solvents were dried over activated 4Å molecular sieves and stored in the purge box. For the MAO and DMAM•OMTS solid samples 1,3 dichlorobenzene with deuteromethylene chloride for NMR lock was used. In all cases the solid samples dissolved completely. For modified MAO and modified DMAM•OMTS samples, 1,2 dichlorobenzene with perdeuterobenzene for NMR lock was used.

EXAMPLE 1

Preparation of an Octamethyltrisiloxane-Complexed Dimethylaluminum Methylaluminoxanate (DMAM•OMTS)

[00098] A solution of about 30 wt% methylaluminoxane (MAO) in toluene (60 g, 308 mmol Al) was treated with octamethyltrisiloxane (OMTS, 3.65 g, 15.4 mmol) at room temperature. Clathrate formation occurred and two immiscible liquid phases were observed. The liquid

system was stirred at room temperature overnight. The upper layer was removed by decantation. The lower layer was washed with 3 samples of about 100 ml of toluene. After each washing process, the lower layer became denser. After the third wash, 2 samples of about 100 ml of cyclohexane were added to precipitate the solid ionic aluminoxanate composition (DMAM•OMTS). This solid product was filtered and washed with cyclohexane.

[00099] After thorough washing and precipitation as described above, the product was subjected to spectroscopic characterization. It was found that this product was an octamethyltrisiloxane-complexed dimethylaluminum methylaluminoxanate $[\text{Me}_2\text{Al}\cdot\text{OMTS}]^+(\text{MAO}\cdot\text{Me})^-$, which can also be termed an OMTS-complexed dimethylaluminum salt of a methylaluminoxane (DMAM•OMTS). A visual representation of this product is set forth in Figure 1.

EXAMPLE 2

Characterization of an Octamethyltrisiloxane-Complexed Dimethylaluminum Methylaluminoxanate (DMAM•OMTS)

[000100] The proton NMR spectra of DMAM•OMTS as produced in Example 1 and its MAO and OMTS precursors in 1,3 dichlorobenzene with deuteromethylene chloride for NMR lock are presented in Figure 2, where Spectrum A represents conventional MAO, Spectrum B represents OMTS, and Spectrum C represents DMAM•OMTS. Spectrum C clearly shows the presence of OMTS complexed to a dimethylaluminum species by comparative integration of the OMTS and $(\text{Me}_2\text{Al})^+$ peaks [(6:2):2]. Further, the OMTS peaks in Spectrum C are significantly shifted (at least about 0.2 ppm) as compared to Spectrum B for OMTS alone. Spectrum A, for conventional MAO, shows no hint of the features seen in Spectrum C.

[000101] Figure 3 compares the ^{29}Si NMR spectra of OMTS (Spectrum A) and DMAM•OMTS (Spectrum B) in 1,3 dichlorobenzene with deuteromethylene chloride for NMR lock. Conventional MAO contains no silicon species, and thus, generates no ^{29}Si NMR signals. Spectrum B shows two unusual downfield chemical shifts in the ^{29}Si NMR at about 29 and 39 ppm with respect to the tetramethylsilane (TMS) reference and a significant shifted (> about 5ppm) from OMTS alone. Theoretical calculations by Professor Jack Tossell of the University of Maryland have shown that the experimental ^{29}Si NMR chemical shifts are perfectly matched for the cationic species $[\text{Me}_2\text{Al}\cdot\text{OMTS}]^+$ of DMAM•OMTS.

[000102] Figure 4 compares the ^{27}Al NMR spectra of MAO (Spectrum A) and DMAM•OMTS (Spectrum B) in 1,3 dichlorobenzene with deuteromethylene chloride for NMR lock. Although DMAM•OMTS is ultimately derived from a conventional MAO, a significant difference in their chemical composition is clearly illustrated in Figure 4. For example, the

broad feature seen at about 0 parts per million (ppm) in Spectrum A is narrowed and shifted to about -20 ppm in Spectrum B. Further, the narrow feature at about 150 ppm in Spectrum A is significantly diminished and shifted slightly downfield in Spectrum B. The upfield peak in Spectrum B corresponds to the anionic aluminoxanate species and the downfield peak corresponds to the cationic four coordinate aluminum species.

EXAMPLE 3

Characterization of an 18-Crown-6 Ether-Complexed Dimethylaluminum Methylaluminoxanate (DMAM•18-CE-6)

[000103] A solution of MAO in toluene (20.5 g, 105.4 mmol Al) was treated with 18-Crown-6 ether (18-CE-6, 1.4 g, 5.26 mmol) at room temperature. Clathrate formation occurred and two immiscible liquid phases were observed. Additional toluene (about 60 g) was added because the lower clathrate layer was very thick. The liquid system was stirred at room temperature overnight. The upper layer was removed by decantation. The lower layer was washed with 3 samples of about 100 ml of toluene. The upper toluene layer was removed by decantation and the viscous lower layer was treated with 2 samples of about 100 ml of cyclohexane to precipitate the solid ionic aluminoxanate composition (DMAM•18-CE-6). This solid product was filtered, washed with cyclohexane, and vacuum dried.

[000104] Figure 5 compares the proton NMR spectra of MAO (Spectrum A) and DMAM•18-CE-6 (Spectrum B) in 1,3 dichlorobenzene with deuteromethylene chloride for NMR lock. Again, a significant difference in the chemical composition of MAO and DMAM•18-CE-6 is clearly illustrated in Figure 5.

EXAMPLE 4

Aluminoxanate salt compositions soluble in toluene

[000105] DMAM•OMTS was produced as described in Example 1 from a mixture of about 30% MAO in toluene (725 g, 3729 mmol Al) and OMTS (44.1 g, 186.5 mmol). The resulting clathrate composition was treated, without phase cut or wash, with tri-n-octylaluminum (TNOA, 47.6 g, 130.5 mmol). The two layers became one phase. The mixture was heated at about 80°C for about two hours and filtered to obtain a clear, colorless solution with an aluminum concentration of about 14.3 wt%. This composition did not show signs of solid or gel formation at room temperature or at about -20°C after 52 weeks. Although gel formation was not monitored past 52 weeks, it is believed that this composition will not show signs of solid or gel formation at these temperatures for longer periods of time.

EXAMPLE 5

Aluminoxanate salt compositions soluble in toluene

[000106] A solution of about 30 wt% MAO in toluene (725 g, 3729 mmol Al) was allowed to react with OMTS (44.1 g, 186.5 mmol) as described in Example 1. After phase cut and wash, the clathrate (lower) layer was treated with about 600 ml toluene and TNOA (47.6 g, 139.5 mmol). The resulting solution was heated at about 80°C for two hours to obtain a clear, colorless solution of soluble methylaluminoxanate salt in toluene, which did not show signs of solid or gel formation at room temperature after 52 weeks.

EXAMPLE 6

Solution stability of TNOA-modified DMAM•OMTS

[000107] DMAM•OMTS was produced as described in Example 1 from a mixture of about 30% MAO in toluene (725 g, 3729 mmol Al) and OMTS (44.1 g, 186.5 mmol). After phase cut and wash, the clathrate layer was treated with excess cyclohexane to obtain ionic methylaluminoxanate solids. The solids were then treated with about 800 ml toluene. The new washed clathrate was treated with TNOA (47.6 g, 139.5 mmol) and the mixture was heated at about 80°C for about two hours. A clear, colorless solution of soluble methylaluminoxanate salt in toluene was formed, which did not show signs of solid or gel formation at room temperature after 52 weeks.

COMPARATIVE EXAMPLE 7

Solution stability of TNOA-modified MAO compositions

[000108] A solution of about 30% MAO in toluene (129 g, 663 mmol Al) was treated with TNOA (8.47 g, 23.2 mmol Al). The amount of TNOA used is equivalent to the amount needed to render an analogous soluble aluminoxanate salt composition solution-stable at about -20°C. The mixture was heated at about 80°C for about two hours. The clear, colorless solution was filtered to afford TNOA-modified MAO solution in toluene, with an Al concentration of about 14.0 wt %. In sharp contrast to the analogous TNOA-modified DMAM•OMTS composition described in Example 6, this composition started to show signs of gel formation after ten weeks at room temperature.

EXAMPLE 8

Solution stability of TIBA-modified DMAM•OMTS

[000109] A solution of about 30% MAO in toluene (252.2 g, 1296.3 mmol Al) was allowed to react with OMTS (64.82 g, 15.33 mmol) as described in Example 1. The resulting two-phase clathrate composition was treated with triisobutylaluminum (TIBA, 25.72 g, 129.63 mmol). The two-layer solution became one single phase. The mixture was heated at about 80°C for about two hours. After filtration, a clear, colorless solution of soluble methylaluminoxanate salt in toluene was obtained, which did not show signs of solid or gel formation at room temperature after 52 weeks.

COMPARATIVE EXAMPLE 9

Solution stability of TIBA-modified MAO compositions

[000110] A solution of about 30% MAO in toluene (162 g, 833 mmol Al) was treated with TIBA (16.52 g, 83.27 mmol Al). The amount of TIBA used was equivalent to the amount needed to render an analogous soluble aluminoxanate salt composition solution-stable at about -20°C. The mixture was then filtered to obtain TIBA-modified MAO solution in toluene, with an Al concentration of about 14.2 wt%. In sharp contrast to the analogous TIBA-modified DMAM•OMTS composition described in Example 8, this composition started to show signs of gel formation after six weeks at room temperature.

EXAMPLE 10

Aluminoxanate salt compositions soluble in aliphatic hydrocarbons

[000111] DMAM•OMTS was produced as described in Example 1 from a mixture of about 30% MAO in toluene (719.2 g, 3696.6 mmol) and OMTS (43.72 g, 184.83 mmol). The resulting two-phase clathrate composition was treated without wash or phase cut with TNOA (94.44 g, 258.76 mmol). The mixture was heated at about 80°C for about two hours. The mixture was subsequently subjected to solvent swap by first removing toluene under reduced pressure. The resulting thick oil composition was treated with about 500 ml of isohexane, followed by vacuum distillation to remove the last traces of toluene. Again, a thick oil resulted. The oil was treated with about 707 g isohexane to obtain a clear, colorless solution of soluble methylaluminoxanate salt in isohexane, which did not show signs of solid or gel formation at room temperature or at about -20°C after 52 weeks.

EXAMPLE 11

Aluminoxanate salt compositions soluble in aliphatic hydrocarbons

[000112] A solution of about 30% MAO in toluene (719 g, 3696 mmol Al) was combined with OMTS (43.7 g, 184.8 mmol). After phase cut and wash, the clathrate layer was treated with excess isohexane to obtain ionic methylaluminoxanate solids. The resulting solids were suspended in about 800 g isohexane to produce a slurry. TNOA (94.4 g, 258.76 mmol) was added to the slurry and the slurry was heated at about 80°C for about two hours. The solution was filtered to obtain a clear, colorless solution of soluble methylaluminoxanate salt in isohexane, which did not show signs of solid or gel formation at room temperature or at about -20°C after about 52 weeks.

EXAMPLE 12

NMR characterization of modified DMAM•OMTS and modified MAO

[000113] TNOA-modified DMAM•OMTS and TNOA-modified MAO were prepared as in Examples 6 and 7. The ^{29}Si NMR spectra of these species in 1,2 dichlorobenzene with perdeuterobenzene for NMR lock are presented in Figure 6. The TNOA-modified MAO spectrum shows no silicon species or ^{29}Si NMR signals. The TNOA-modified DMAM•OMTS spectrum shows the characteristic 29 and 39-ppm shifts seen in the ^{29}Si NMR of DMAM•OMTS (Figure 3). However, as compared to the unmodified DMAM•OMTS spectrum, the TNOA-modified DMAM•OMTS spectrum shows that the 29 and 39-ppm peaks are split, indicating mixed alkyl groups on some of the cationic aluminum species.

[000114] TIBA-modified DMAM•OMTS and TIBA-modified MAO were prepared as in Examples 8 and 9. The ^{29}Si NMR spectra of these species in 1,2 dichlorobenzene with perdeuterobenzene for NMR lock are presented in Figure 7. As in Example 11, the TIBA-modified MAO spectrum shows no silicon species or ^{29}Si NMR signals. The TIBA-modified DMAM•OMTS spectrum also shows the characteristic 29 and 39-ppm shifts with split peaks, indicating mixed alkyl groups on some of the cationic aluminum species.

[000115] Figure 8 compares the proton NMR spectra for TNOA-modified DMAM•OMTS and TNOA-modified MAO in 1,2 dichlorobenzene with perdeuterobenzene for NMR lock. There are several noticeable differences in the spectra. For example, the TNOA-modified MAO spectrum does not show the peak corresponding to the OMTS cation complex present in the TNOA-modified DMAM•OMTS spectrum. The TNOA-modified MAO spectrum does not have any of the same sharp peak features seen in the TNOA-modified DMAM•OMTS spectrum. Further, the TNOA-modified MAO spectrum shows a peak corresponding to

trimethylaluminum, while the TNOA-modified DMAM•OMTS spectrum does not have such a feature.

[000116] Figure 9 compares the ^{27}Al NMR spectra for TNOA-modified DMAM•OMTS and TNOA-modified MAO in 1,2 dichlorobenzene with perdeuterobenzene for NMR lock. The broad feature seen at about 0 ppm in the TNOA-modified MAO spectrum is narrowed and shifted to about -20 ppm in the TNOA-modified DMAM•OMTS spectrum. A similar phenomenon was observed in the comparison of the ^{27}Al NMR spectra of MAO and DMAM•OMTS, shown in Figure 4.

EXAMPLE 13

Polymerization activity: Comparison of modified DMAM•OMTS and modified MAO

[000117] Comparative ethylene polymerizations were conducted using conventional MAO, modified MAO, and soluble methylaluminoxane salts of the present invention as co-catalysts. All polymerizations were carried out using *rac* ethylenebis(indenyl)zirconium(IV) dimethyl (ZDM) as the catalyst in an amount sufficient to produce a catalyst system having ratio of aluminum (Al) atoms to zirconium (Zr) atoms of about 50:1. In each trial, polymerizations were allowed to proceed for about 15 minutes at a temperature of about 70°C and an ethylene pressure of about 50 psi using isohexane as diluent. The results of the polymerization trials are shown in Table I.

Table I: Polymerization Activity

Trial #	Activator Solution	Polymer (g)	Activity kg polymer/g Zr/hour	Activity Kg polymer/mmol Zr/hour
1	30 wt% MAO in toluene (Control)	22.5	459	41.9
2	30 wt% MAO/ 3.5 wt% TNOA in toluene	30.3	622	56.7
3	20 wt% DMAM•OMTS/ 3.5 wt% TNOA in toluene	79.7	1626	148.3
4	20 wt% DMAM•OMTS/ 7.0 wt% TNOA in isohexane	67.3	1363	124.3
5	30 wt% MAO/ 10 wt% TIBA in toluene	24.3	494	45.1
6	30 wt% DMAM•OMTS/ 10 wt% TIBA in toluene	66.7	1360	124.1

[000118] As illustrated above, catalyst systems employing soluble aluminoxanate salts of the present invention as co-catalysts (Trials 3, 4, and 6) exhibit polymerization activities almost four times that of catalyst systems employing conventional MAO as co-catalyst (Trial 1). Further, catalyst systems employing the soluble aluminoxanate salts of the present invention as co-catalysts exhibit polymerization activities almost three times that of catalyst systems employing analogous modified MAO compositions as co-catalysts (Trials 2 and 5).

EXAMPLE 14

Solution stability: Comparison of MAO, modified MAO, and modified DMAM•OMTS

[000119] Aliquots of the activator solutions from Example 13 were placed in glass bottles in a substantially dry nitrogen box and stored at room temperature for at least 52 weeks. The stability of each activator solution is shown below in Table II.

Table II: Solution Stability

Trial #	Activator Solution	First Sign of Gel Formation (weeks)
1	30 wt% MAO in toluene (Control)	< 10
2	30 wt% MAO/3.5 wt% TNOA in toluene	< 20
3	20 wt% DMAM•OMTS/3.5 wt% TNOA in toluene	N/A [‡]
4	20 wt% DMAM•OMTS/7.0 wt% TNOA in isohexane	N/A [‡]
5	30 wt% MAO/10 wt% TIBA in toluene	< 20
6	30 wt% DMAM•OMTS/10 wt% TIBA in toluene	N/A [‡]

[‡] Trials 3, 4, and 6 did not exhibit gel formation after the 52 week observation period.

[000120] As illustrated by the data above, TNOA-modified and TIBA-modified DMAM•OMTS (Trials 3, 4, and 6) exhibit no gel formation at room temperature for at least 52 weeks. This date strongly suggests that TNOA-modified and TIBA-modified DMAM•OMTS will be stable at room temperature for even longer periods of time. In sharp contrast, conventional MAO and analogous modified MAOs exhibit gel formation after less than 10 weeks and less than 20 weeks at room temperature, respectively. Thus, soluble aluminoxanate compositions have greatly improved solution stability over both conventional MAO and analogous modified MAOs.

EXAMPLE 15

Conductivity: Comparison of MAO, modified MAO, and modified DMAM•OMTS

[000121] Comparative experiments were conducted to evaluate and compare the electrical conductivities of conventional MAO, modified MAO, and soluble methylaluminoxanate salts of the present invention. In these experiments, the activator solutions prepared in Example 13 were mixed with chlorobenzene in an amount sufficient to produce a sample solution having an aluminum content of about 2 wt%. The electrical conductivity of each of the six test solutions was determined at room temperature using a VWR Digital Conductivity Meter. The results are illustrated below in Table III.

Table III: Activator Conductivity

Trial #	Activator Solution	Activator Conductivity ($\mu\text{S}/\text{cm}$)
1	30 wt% MAO in toluene (Control)	1.7
2	30 wt% MAO/3.5 wt% TNOA in toluene	2.6
3	20 wt% DMAM•OMTS/3.5 wt% TNOA in toluene	46.9
4	20 wt% DMAM•OMTS/7.0 wt% TNOA in isohexane	46.7
5	30 wt% MAO/10 wt% TIBA in toluene	1.4
6	30 wt% DMAM•OMTS/10 wt% TIBA in toluene	42.9

[000122] As indicated by the conductivity measurements above, even though the soluble aluminoxanate compositions of the present are ultimately derived from conventional MAOs, they have significantly different chemical compositions. This difference is accentuated by the inherent conductivity of soluble aluminoxanate compositions, while MAO compositions are essentially non-conducting. Further, analogous modification of MAO with alkylaluminum compounds results in compositions which are non-conducting, and thus, different from the soluble aluminoxanate salt compositions of this invention.

EXAMPLE 16

Conductivity: Comparison of MAO, modified MAO, and modified DMAM•OMTS

[000123] Comparative experiments were conducted as in Example 15 to evaluate and compare the electrical conductivities of conventional MAO, modified MAO, and soluble methylaluminoxanate salts of the present invention, as well as catalyst compositions formed using each of these activators. In these experiments, the solvent was removed from the activator solutions to unmask any potential solvent interference with the conductivity measurements. Catalyst systems were prepared by combining each activator (after solvent removal) with *rac* ethylenebis(indenyl)zirconium(IV) dimethyl (ZDM) in an amount sufficient to produce a catalyst system having ratio of aluminum (Al) atoms to zirconium (Zr) atoms of about 50:1. As in Example 13, the activators and catalyst systems were added to chlorobenzene in an amount sufficient to produce a sample solution having an aluminum content of about 2 wt%. The electrical conductivity of each sample solution was determined at room temperature using a VWR Digital Conductivity Meter. The results are illustrated below in Table IV.

Table IV: Activator and Catalyst Conductivity

Activator	Activator Conductivity ($\mu\text{S/cm}$)	Catalyst Conductivity ($\mu\text{S/cm}$)	Conductivity Change ($\Delta \mu\text{S/cm}$)
MAO	1.5	23.5	22
MAO/TNOA	1.8	31.3	29.5
DMAM•OMTS	48.0	46.8	-1.2
DMAM•OMTS/TNOA	55.5	63.2	7.7

[000124] The activator conductivity results shown above were similar to the measurements obtained in Example 15. It is interesting to note that TNOA-modified DMAM•OMTS is actually more conductive than its insoluble ionic precursor, DMAM•OMTS. Further, when combined with ZDM, TNOA-modified DMAM•OMTS yields a catalyst system having the higher conductivity than catalyst systems formed using MAO or modified MAO. This higher catalyst system conductivity translates to a higher polymerization activity, as shown in Table I. Thus, it is speculated that the ionic character of aluminoxanate salts contributes to their ability to effectively activate transition metal catalysts.

CLAIMS

1. A soluble aluminoxanate salt composition comprising the contact product of:
 - (a) at least one ionic aluminoxanate having the general formula



wherein:

L is a stabilizing ligand,

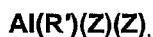
R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms,

AO is an aluminoxane moiety,

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide, and

m is 1, 2, or 3, inclusive;

- (b) at least one alkylaluminum compound having the general formula



wherein:

R' is an alkyl group having from about four to about twenty carbon atoms, and

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms; and

- (c) at least one inert organic solvent.

2. A composition according to Claim 1, wherein the inert organic solvent is an aliphatic solvent, an aromatic solvent, a halogenated solvent, or any combination thereof.

3. A composition according to Claim 1, wherein L is a monosiloxane, a polysiloxane, a monoether, a polyether, a monothioether, a polythioether, or a multidentate ligand comprising oxygen coordinating atoms, nitrogen coordinating atoms, phosphorous coordinating atoms, sulfur coordinating atoms, or any combination thereof.

4. A composition according to Claim 1, wherein

L is a polysiloxane, a polyether, an oxygen crown ether ligand, a nitrogen crown ether ligand, or a nitrogen and oxygen crown ether ligand;

R is an alkyl group having from one to about eight carbon atoms; and

X is fluoride or an alkyl group having from one to about eight carbon atoms.

5. A composition according to Claim 1, wherein AO is an aluminoxane having at least one hydrocarbyl aluminum moiety having from one to about twenty carbon atoms.

6. A composition according to Claim 1, wherein AO is a hydrocarbylaluminoxane selected from alkylaluminoxanes, cycloalkylaluminoxanes, arylaluminoxanes, aralkylaluminoxanes, or any combination thereof.

7. A composition according to Claim 1, wherein the ratio of aluminum atoms derived from the ionic aluminoxanate to aluminum atoms derived from the alkylaluminum compound is in a range of about 2:1 to about 1000:1.

8. A supported composition comprising the composition of Claim 1 and an organic or inorganic support material.

9. A composition according to Claim 8, wherein the inorganic support material is talc, clay, modified clay, silica, alumina, silica-alumina, magnesia, titania, zirconia, magnesium halides, aluminum silicates, kaolinite, attapulgite, montmorillonite, illite, bentonite, halloysite, or any combination thereof.

10. A composition according to Claim 8, wherein the organic support material is spheroidal, particulate, or finely-divided polyethylene, polyvinylchloride, polystyrene, or any combination thereof.

11. A catalyst composition comprising the composition of Claim 1 and a complex of a transition metal of Group 3, 4, 5, 6, 7, 8, 9, 10, or 11 of the Periodic Table of Elements, including the lanthanide series and the actinide series.

12. A catalyst composition according to Claim 11, further comprising an organic or inorganic support material.

13. A catalyst composition comprising the contact product of
(a) at least one soluble aluminoxanate salt composition having the general formula



wherein:

L is a stabilizing ligand,

R is a hydrocarbyl group having from one to about twenty carbon atoms,

R' is an alkyl group having from about four to about twenty carbon atoms,

AO is an aluminoxane moiety,

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide; and

m is 1, 2, or 3, inclusive; and

(b) at least one complex of a transition metal of Group 3, 4, 5, 6, 7, 8, 9, 10, or 11 of the Periodic Table of Elements, including the lanthanide series and the actinide series.

14. A catalyst composition according to Claim 13, further comprising a support material.

15. A catalyst composition according to Claim 13, further comprising an inert organic solvent.

16. A soluble methylaluminoxanate salt composition having the general formula



wherein:

L is a stabilizing ligand,

Me is a methyl group,

R' is an alkyl group having from about four to about twenty carbon atoms,

MAO is a methylaluminoxane moiety, and

m is 1, 2, or 3, inclusive.

17. A composition according to Claim 16 further comprising at least one inert organic solvent.

18. A catalyst composition comprising the composition of Claim 16 and a complex of a transition metal of Group 3, 4, 5, 6, 7, 8, 9, 10, or 11 of the Periodic Table of Elements, including the lanthanide series and the actinide series.

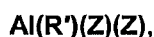
19. A process to produce a soluble aluminoxanate salt composition comprising contacting, in an environment that is substantially inert and anhydrous,

(a) at least one ionic aluminoxanate having the general formula



(b) at least one inert organic solvent; and

(c) at least one alkylaluminum compound having the general formula



wherein:

L is a stabilizing ligand,

R is, independently, a hydrocarbyl group having from one to about twenty carbon atoms,

R' is an alkyl group having from about four to about twenty carbon atoms,

AO is an aluminosiloxane moiety,

X is a hydrocarbyl group having from one to about twenty carbon atoms, a halide, or a pseudohalide,

Z is, independently, a halide, a pseudohalide, or an alkyl group having from about three to about twenty carbon atoms, and

m is 1, 2, or 3, inclusive.

20. A process according to Claim 19, wherein the inert organic solvent is an aliphatic solvent, wherein (a) and (b) are first contacted together to form a slurry, and wherein the slurry is subsequently contacted with (c).

21. A process according to Claim 19, wherein the inert organic solvent is an aromatic solvent, wherein (a) and (b) are first contacted together to form a liquid clathrate, and wherein the liquid clathrate is subsequently contacted with (c).

22. A process according to Claim 19, wherein L is a monosiloxane, a polysiloxane, a monoether, a polyether, a monothioether, a polythioether, or a multidentate ligand comprising oxygen coordinating atoms, nitrogen coordinating atoms, phosphorous coordinating atoms, sulfur coordinating atoms, or any combination thereof.

23. A process according to Claim 19, wherein AO is a hydrocarbylaluminosiloxane selected from alkylaluminosiloxanes, cycloalkylaluminosiloxanes, arylaluminosiloxanes, aralkylaluminosiloxanes, or any combination thereof.

24. A process according to Claim 19, further comprising obtaining the ionic aluminosiloxanate by removing a second aromatic solvent from an aluminosiloxanate-containing liquid clathrate.

25. A process for producing a polyolefin polymer comprising contacting, under polymerization conditions, at least one olefinic monomer and at least one catalyst composition of Claim 13, 19, 20, 29, 30, or 34.

26. A composition according to Claim 1, wherein the composition has enhanced ionic character as compared to a corresponding conventional aluminoxane, as measured by electrical conductivity.

27. A composition according to Claim 1, wherein the composition has enhanced stability in aliphatic and aromatic solvents as compared to a corresponding conventional aluminoxane.

28. A catalyst composition according to Claim 19 or 29, wherein the catalyst composition has enhanced ionic character as compared to a corresponding catalyst composition employing a conventional aluminoxane, as measured by electrical conductivity.

FIGURE 1

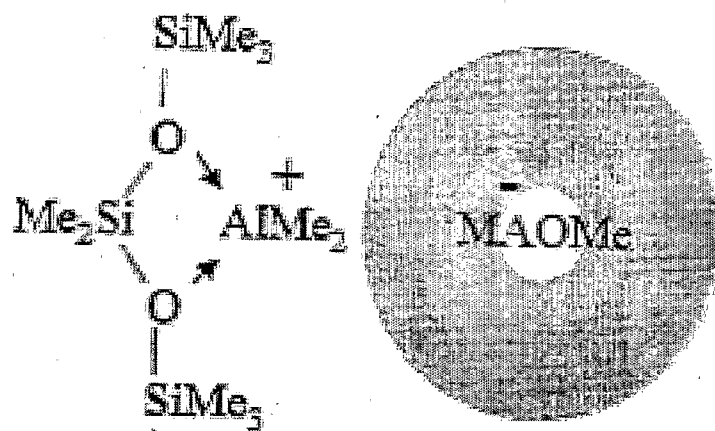


FIGURE 2

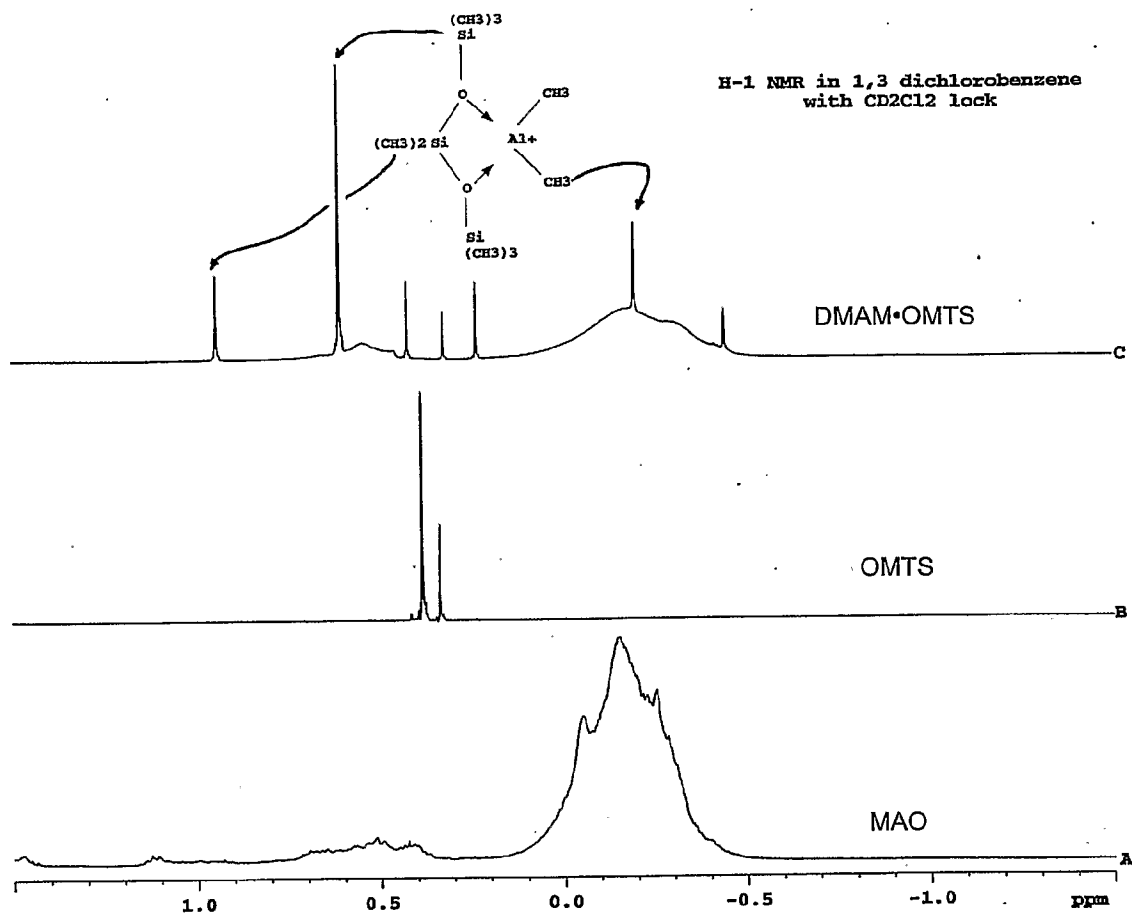


FIGURE 3

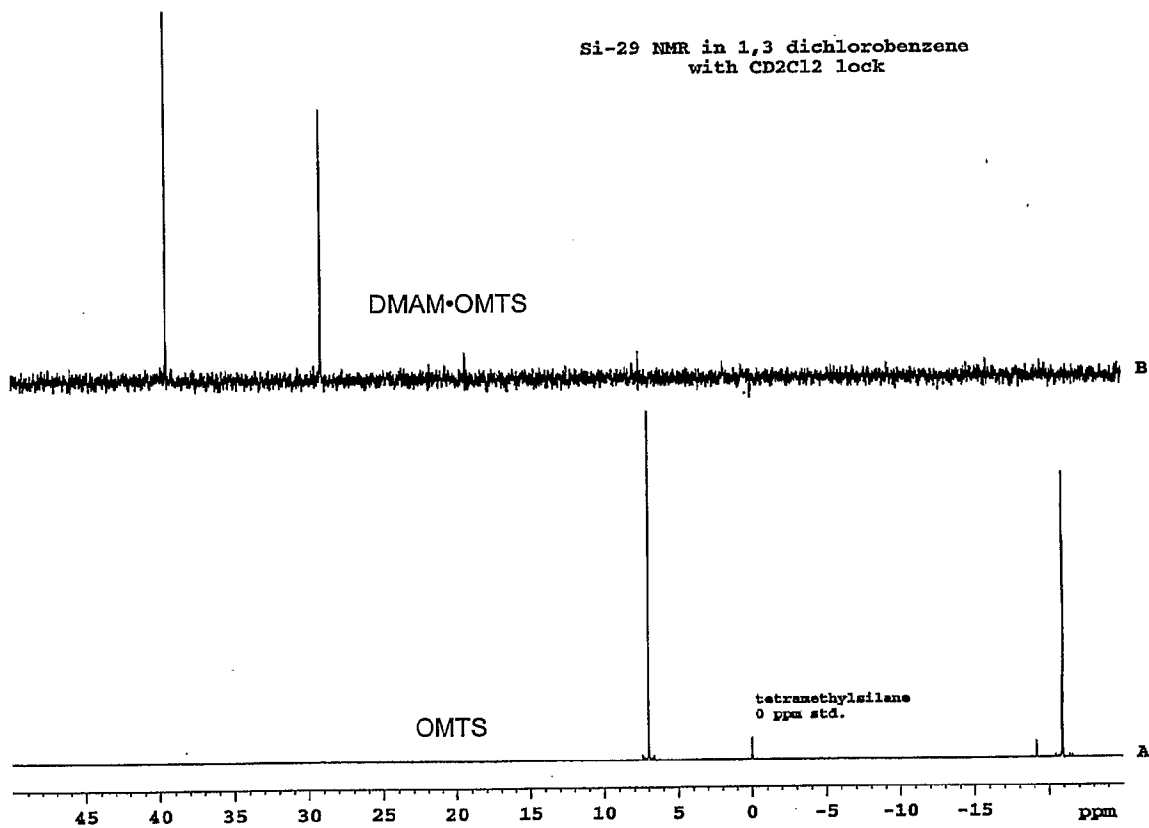


FIGURE 4

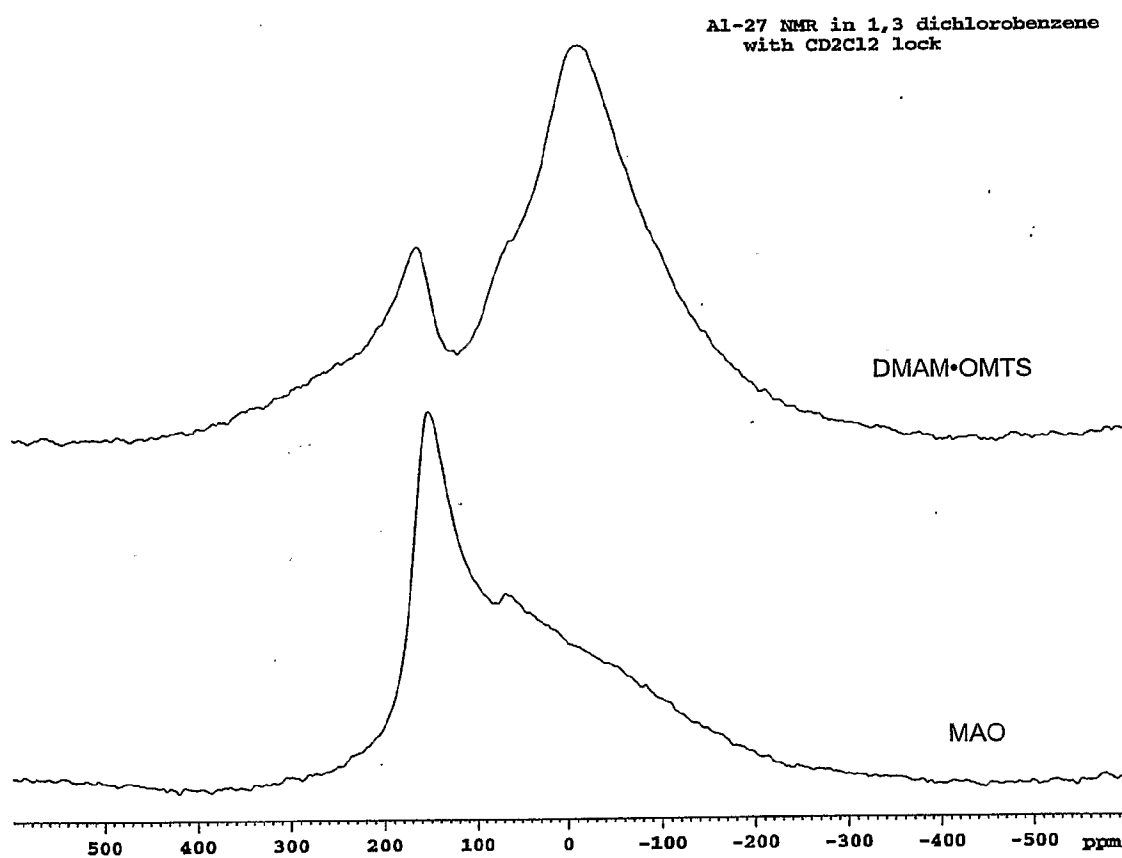


FIGURE 5

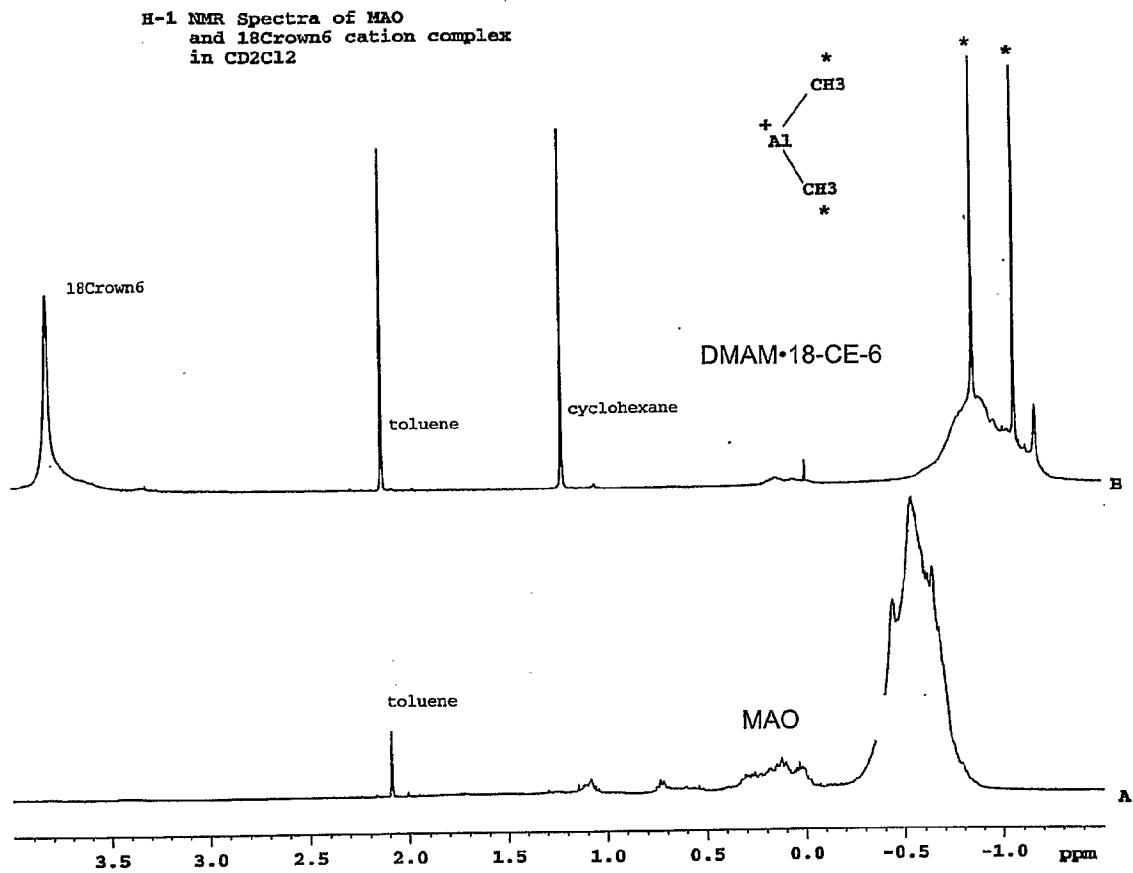


FIGURE 6

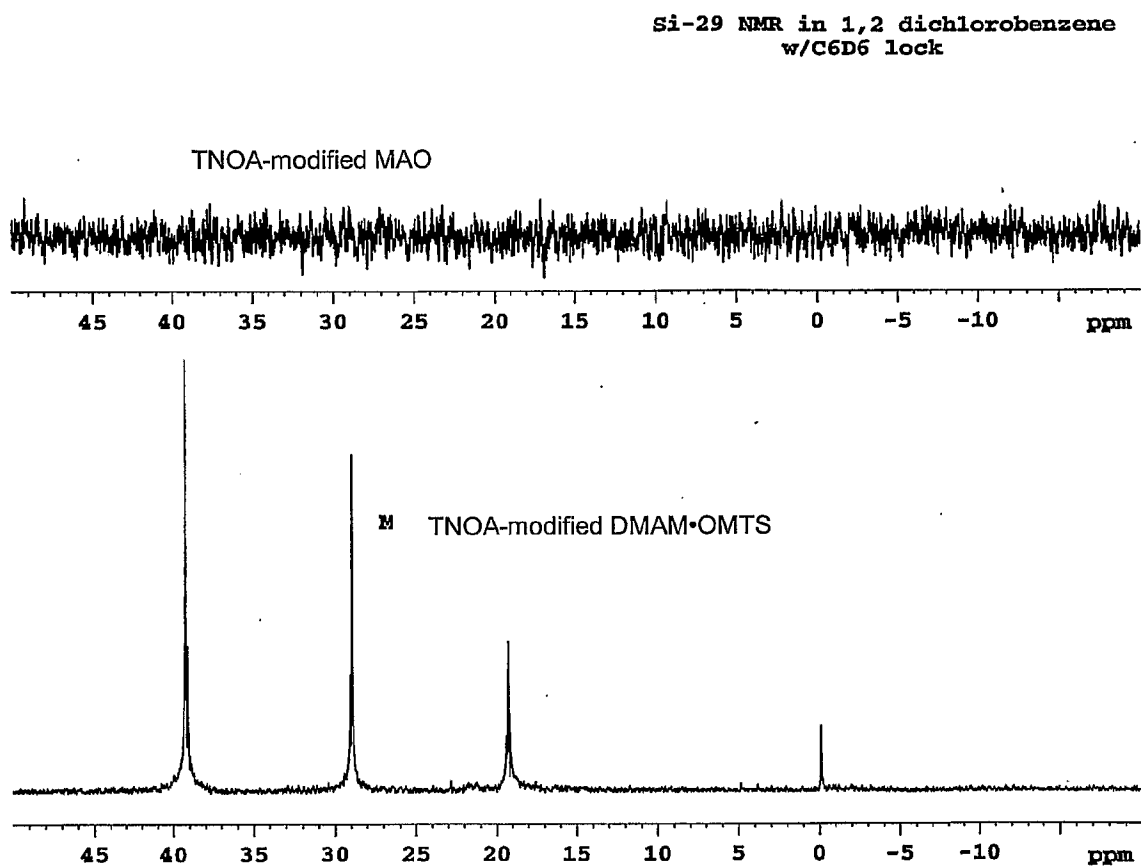


FIGURE 7

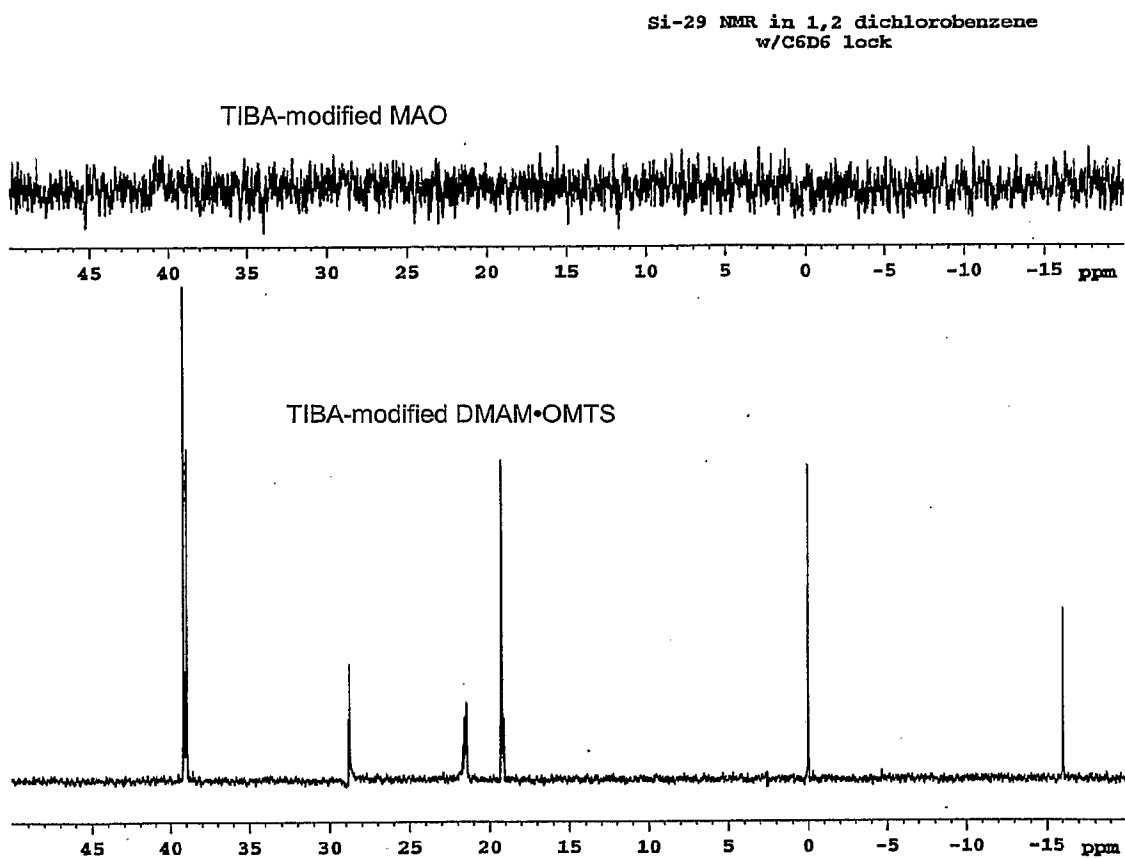


FIGURE 8

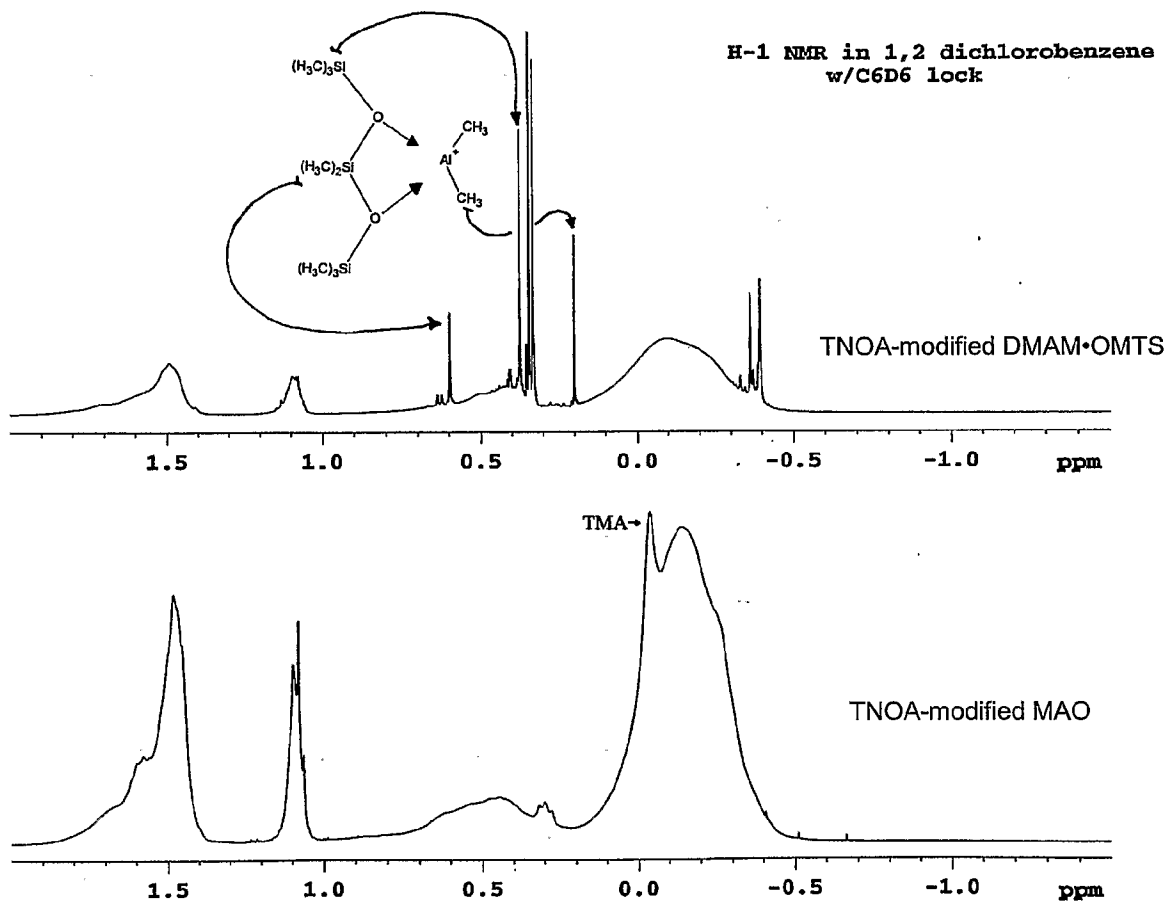


FIGURE 9

