

Title: Improved Process to Prepare Catalyst from *In-Situ* Formed Alumoxane5 **Cross Reference to Related Applications**

[0001] This application claims the benefit of and priority to US Provisional Application No. 63/117328 filed November 23, 2020, the disclosure of which is incorporated herein by reference.

Field

10 [0002] The present disclosure relates to processes for forming alumoxanes and catalyst systems thereof for olefin polymerization.

Background

[0003] Polyolefins are widely used commercially because of their robust physical properties. For example, various types of polyethylenes, including high density, low density, 15 and linear low density polyethylenes, are examples of commercially useful polyolefins. Polyolefins are typically prepared with a catalyst (mixed with one or more other components to form a catalyst system) which promotes polymerization of olefin monomers in a reactor, such as a gas phase reactor.

[0004] Methylalumoxane (MAO) is a popular activator that may be used in a catalyst 20 system. For example, MAO may be supported on silica to activate a single site catalyst precursor, e.g., a metallocene, to form an active solid catalyst used in a commercial gas phase reactor to produce single-site polyolefin resins. Commercial MAO is commonly sold as a toluene solution because an aromatic solvent can dissolve MAO without causing issues observed with other solvents. However, polyolefin products are often used as plastic 25 packaging for food products, and the amount of non-polyolefin compounds, such as toluene, present in the polyolefin products should be minimized.

[0005] In addition, MAO is challenging to prepare. MAO is typically formed from the low temperature reaction of trimethylaluminum (TMA) and water in toluene. This reaction is very exothermic and involves precautions when performing the reaction. The commercially 30 available MAO has a short shelf life, typically less than one week under ambient conditions and less than twelve months in cold storage, after which the MAO undergoes compositional changes, e.g. gelation, even in cold storage.

[0006] Therefore, there is a need for processes for forming more stable catalyst systems including the MAO activator.

- [0007] References for citing in an Information Disclosure Statement (37 CFR 1.97(h)):
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Summary

- [0008] The present disclosure relates to processes for forming alumoxanes and catalyst
 systems therefrom for olefin polymerization.
- 30 [0009] In at least one embodiment, a process for preparing a supported alumoxane
 precursor includes forming a solution by, in an aliphatic hydrocarbon fluid, combining at least
 one hydrocarbyl aluminum with at least one non-hydrolytic oxygen-containing compound and
 a support material, wherein the molar ratio of aluminum to non-hydrolytic oxygen in the

solution is greater than or equal to 1.5, wherein the aliphatic hydrocarbon fluid has a boiling point of less than about 70 degrees Celsius, and wherein the combining is conducted at a temperature of less than about 70 degrees Celsius. The process includes distilling the solution at a pressure of greater than or equal to 0.5 atm to form a supported alumoxane precursor, wherein the supported alumoxane precursor comprises from about 1 wt% to about 50 wt% of the aliphatic hydrocarbon fluid based on the total weight of the supported alumoxane precursor. The process further includes heating the supported alumoxane precursor to a temperature greater than the boiling point of the aliphatic hydrocarbon and less than about 160 degrees Celsius to form a supported alumoxane.

10 **Brief Description of the Figures**

[0010] Fig. 1 depicts the vinyl region of the ^1H NMR (C_6D_6) spectrum of the catalyst precursor prepared in Comparative 4a.

[0011] Fig. 2 depicts the vinyl region of the ^1H NMR (C_6D_6) spectrum of the concentrated precursor prepared in Example 5a.

15 [0012] Fig. 3 depicts the ^1H NMR (C_6D_6) spectrum of the concentrated precursor prepared in Example 5a.

[0013] Fig. 4 depicts the vinyl Region of an ^1H NMR (C_6D_6) spectrum of the concentrated precursor prepared in Example 5a before and after addition of hemialkoxide $\text{Me}_2\text{Al}(\mu\text{-Me})(\mu\text{-OCMe}_2\text{CMe=CH}_2)\text{AlMe}_2$.

20 [0014] Fig. 5 depicts an X-Ray Crystallographic spectrum (Oak Ridge Thermal Ellipsoid Plot ORTEP structure)) of the $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$ prepared in Example 15a.

[0015] Fig. 6 depicts the ^1H NMR (C_6D_6) spectrum of the $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$ prepared in Example 15a.

Detailed Description

25 [0016] The present disclosure relates to processes for forming alumoxanes and catalyst systems thereof for olefin polymerization. Processes of the present disclosure can provide supported alumoxane precursors having improved stability and shelf life, as compared to supported methylalumoxane in toluene. In addition, supported alumoxane precursors of the present disclosure can be heat treated to form supported alumoxanes without compromising catalyst activity when the supported alumoxanes are used in catalyst systems for olefin polymerizations. Supported alumoxane precursors can be formed without the use of toluene, which can provide polyolefins that are substantially free of toluene and suitable for use in packaging applications, such as food packaging.

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[0017] For purposes of the present disclosure, the numbering scheme for the Periodic Table Groups is used as described in *Chemical and Engineering News*, v.63(5), pg. 27 (1985). Therefore, a "Group 4 metal" is an element from group 4 of the Periodic Table, e.g., Hf, Ti, or Zr.

5 [0018] As used herein, a "composition" can include the components of the composition and/or one or more reaction product(s) of the components. "Catalyst productivity" is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W g of catalyst (cat), over a period of time of T hours; and may be expressed by the following formula: $P/(T \times W)$ and expressed in units of $\text{gP/gcat} \cdot \text{hr}^{-1}$. "Conversion" is
10 the amount of monomer that is converted to polymer product, and is reported as mole percent (mol%) and is calculated based on the polymer yield (weight) and the amount of monomer fed into the reactor. "Catalyst activity" is a measure of how active the catalyst is and is reported as the mass of product polymer (P) produced per mole of catalyst (cat) used ($\text{kgP/molcat} \cdot \text{h}$). For calculating catalyst activity, also referred to as catalyst productivity, only
15 the weight of the transition metal component of the catalyst is used.

[0019] An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized
20 form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A
25 "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. An "ethylene polymer" or "ethylene
30 copolymer" is a polymer or copolymer comprising at least 50 mol% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at least 50 mole% propylene derived units, and so on.

[0020] As used herein, and unless otherwise specified, the term " C_n " means

hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

[0021] The term “hydrocarbon” means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n. Likewise, a “C_m-C_y” group or compound refers to a group or compound comprising carbon atoms at a total number thereof in the range from m to y. Thus, a C₁-C₅₀ alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0022] The terms “group,” “radical,” and “substituent” may be used interchangeably.

10 [0023] The terms “hydrocarbyl radical,” “hydrocarbyl group,” or “hydrocarbyl” may be used interchangeably and are defined to mean a group consisting of hydrogen and carbon atoms only. Preferred hydrocarbyls are C₁-C₁₀₀ radicals that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, aryl groups, such as phenyl, benzyl naphthyl, and the like.

[0024] Unless otherwise indicated, (e.g., the definition of “substituted hydrocarbyl”, etc.), the term “substituted” means that at least one hydrogen atom has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic (or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0025] The term “substituted hydrocarbyl” means a hydrocarbyl radical in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with at least one heteroatom (such as halogen, e.g., Br, Cl, F or I) or heteroatom-containing group (such as a functional group, e.g., -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may

join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic (or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0026] The terms “alkyl radical,” and “alkyl” are used interchangeably throughout this disclosure. For purposes of this disclosure, “alkyl radical” is defined to be C₁-C₁₀₀ alkyls that may be linear, branched, or cyclic. Examples of such radicals can include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like including their substituted analogues. Substituted alkyl radicals are radicals in which at least one hydrogen atom of the alkyl radical has been substituted with at least a non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic (or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0027] The terms “alkoxy” or “aryloxy” mean an alkyl or aryl group bound to an oxygen atom, such as an alkyl ether or aryl ether group/radical connected to an oxygen atom and can include those where the alkyl group is a C₁ to C₁₀ hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. Examples of suitable alkoxy and aryloxy radicals can include methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, phenoxy, and the like.

[0028] The term “aryl” or “aryl group” means an aromatic ring (typically made of 6 carbon atoms) and the substituted variants thereof, such as phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise, heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. As used herein, the term “aromatic” also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic.

[0029] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl) reference to one member of the group (e.g., n-butyl) shall expressly disclose the remaining isomers (e.g., iso-butyl, sec-butyl, and

tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (e.g., butyl) expressly discloses all isomers (e.g., n-butyl, iso-butyl, sec-butyl, and tertbutyl).

[0030] A "metallocene" catalyst compound is a transition metal catalyst compound
5 having one, two or three, typically one or two, substituted or unsubstituted cyclopentadienyl ligands bound to the transition metal, typically a metallocene catalyst is an organometallic compound containing at least one π -bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety). Substituted or unsubstituted cyclopentadienyl ligands include substituted or unsubstituted indenyl, fluorenyl, tetrahydro-*s*-indacenyl, tetrahydro-*as*-
10 indenyl, benz[*f*]indenyl, benz[*e*]indenyl, tetrahydrocyclopenta[*b*]naphthalene, tetrahydrocyclopenta[*a*]naphthalene, and the like.

[0031] As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity index
15 (PDI), is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol (g mol^{-1}).

[0032] The following abbreviations may be used herein: Me is methyl, MAA is methacrylic acid, TMA is trimethylaluminum, MAO is methylalumoxane, TIBAL (also referred to as TIBA) is triisobutylaluminum, THF (also referred to as thf) is tetrahydrofuran,
20 RT is room temperature (and is 23 degrees Celsius unless otherwise indicated).

[0033] A "catalyst system" is a combination of at least one catalyst compound, at least one activator, an optional co-activator, and an optional support material. When "catalyst system" is used to describe such a pair before activation, it means the unactivated catalyst complex (precatalyst) together with an activator and, optionally, a co-activator. When it is
25 used to describe such a pair after activation, it means the activated complex and the activator or other charge-balancing moiety. The transition metal compound may be neutral as in a precatalyst, or a charged species with a counter ion as in an activated catalyst system. For purposes herein, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of
30 the component is the form that reacts with the monomers to produce polymers. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer.

[0034] In the description herein, the catalyst may be described as a catalyst, a catalyst precursor, a pre-catalyst compound, catalyst compound or a transition metal compound, and

these terms are used interchangeably.

[0035] For purposes herein, particle size (PS) or diameter, and distributions thereof, are determined by laser diffraction using a MASTERSIZER 3000 (range of 1 to 3500 μm) available from Malvern Instruments, Ltd., Worcestershire, England, or an LS 13 320 MW with a micro liquid module (range of 0.4 to 2000 μm) available from Beckman Coulter, Inc., Brea, California. Average PS refers to the distribution of particle volume with respect to particle size.

[0036] For purposes herein, the surface area (SA, also called the specific surface area or BET surface area), pore volume (PV), and pore diameter (PD) of catalyst support materials are determined by the Brunauer-Emmett-Teller (BET) method and/or Barrett-Joyner-Halenda (BJH) method using adsorption-desorption of nitrogen (temperature of liquid nitrogen: 77 K) with a MICROMERITICS TRISTAR II 3020 instrument or MICROMERITICS ASAP 2420 instrument after degassing of the powders for 4 to 8 hours at 100 to 300°C for raw/calcined silica or 4 hours to overnight at 40°C to 100°C for silica supported alumoxane. More information regarding the method can be found, for example, in "Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density," S. Lowell et al., Springer, 2004. PV refers to the total PV, including both internal and external PV.

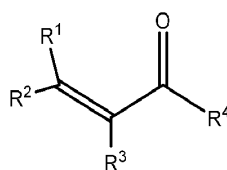
[0037] One way to determine the spatial distribution of alumoxane or alumoxane precursor of the present disclosure within the pores of a support material composition is to determine the ratio of Al/Si in the uncrushed to crushed material where support material is a supported alumoxane precursor, alumoxane or catalyst on silica. For example, when the support material composition is SiO_2 , the composition can have an uncrushed (Al/Si)/crushed (Al/Si) value of from about 1 to about 4, such as from about 1 to about 3, for example from about 1 to about 2, such as about 1, as determined by X-ray Photoelectron Spectroscopy. As used herein, the term "crushed" is defined as a support material that has been ground into fine particles via mortar and pestle. As used herein, the term "uncrushed" is defined as a material that has not been ground into fine particles via mortar and pestle. To measure an uncrushed (Al/Si)/crushed (Al/Si) value, an X-ray Photoelectron spectrum is obtained for a support material. The metal content of the outer surface of the support material is determined as a wt% of the outer surface using the spectrum. Then, the catalyst system is ground into fine particles using a mortar and a pestle. A subsequent X-ray Photoelectron spectrum is obtained for the fine particles, and metal content of the fine particle surfaces is determined as a wt% using the subsequent X-Ray Photoelectron spectrum. The wt% value determined for the

uncrushed support material is divided by the wt% value for the crushed supported alumoxane precursor (*i.e.*, the fine particles) to provide an uncrushed/crushed value. A value of 1 indicates completely uniform metal distribution on the outer surface and surfaces within void spaces within the catalyst system. A value of greater than 1 indicates a greater amount of metal on the outer surface of the support material composition than in the voids of the support material composition. A value of less than 1 indicates a greater amount of metal on the surface of the support material composition within the voids than metal on the outer surface of the support material composition.

Alumoxane Precursor

[0038] In at least one embodiment, an alumoxane precursor may be formed by combining at least one non-hydrolytic oxygen-containing compound to at least one hydrocarbyl aluminum in an aliphatic hydrocarbon fluid, which acts as a solvent, at a temperature of less than about 70 degrees.

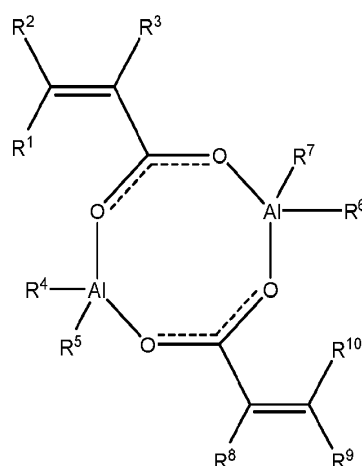
[0039] In at least one embodiment, the at least one non-hydrolytic oxygen-containing compound may comprise a compound represented by the Formula (I):



(I)

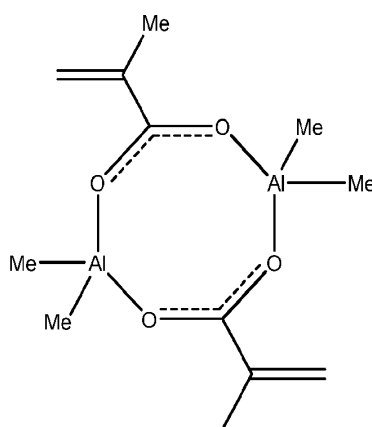
where R^1 and R^2 independently are hydrogen or a hydrocarbyl group (preferably C_1 to C_{20} alkyl, alkenyl or C_5 to C_{20} aryl group, such as selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or phenyl), R^3 is a hydrocarbyl group, optionally R^1 , R^2 , or R^3 may be joined together to form a ring, and R^4 is -OH (hydroxide), $-\text{OC}(\text{O})\text{CR}^3=\text{CR}^1\text{R}^2$, OCR^3 , -F, or -Cl. In at least one embodiment, the at least one non-hydrolytic oxygen-containing compound comprises an alkylacrylic acid represented by the formula $\text{R}^*- \text{C}(=\text{CH}_2)\text{COOH}$, where each R^* is a C_1 to C_{20} alkyl group (such as selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl). In at least one embodiment, the at least one non-hydrolytic oxygen-containing compound comprises methacrylic acid. In at least one embodiment, the at least one non-hydrolytic oxygen-containing compound comprises benzoic acid.

[0040] In at least one embodiment, the at least one non-hydrolytic oxygen-containing compound may comprise a compound represented by the Formula (II):



(II),

where R^1 , R^2 , R^9 , and R^{10} independently are hydrogen or a hydrocarbyl group; R^3 and R^8 is a hydrocarbyl group; optionally R^1 , R^2 , or R^3 may be joined together to form a ring; optionally R^8 , R^9 , or R^{10} may be joined together to form a ring; and each of R^4 , R^5 , R^6 , and R^7 is independently a C₂-C₂₀ hydrocarbyl group, a methyl group, hydrogen, or a heteroatom containing group. Often, each of R^4 , R^5 , R^6 , and R^7 is methyl. Alternatively, at least three members of the group consisting of R^4 , R^5 , R^6 and R^7 are methyl, such as R^4 , R^5 , and R^6 or R^4 , R^5 , and R^7 . Often, the non-hydrolytic oxygen-containing compounds comprises a plurality of compounds represented by the Formula (II). In such aspects, R^4 , R^5 , R^6 , and R^7 is at least about 85% methyl, up to about 15% C₂-C₂₀ hydrocarbyl group or a heteroatom containing group, and up to about 10 mol% hydrogen based on the total amount of moles of R^4 , R^5 , R^6 , and R^7 in the plurality of compounds. Preferably, the compound represented by the Formula (II) comprises the reaction product of trimethylaluminum (TMA) and an unsaturated carboxylic acid. In at least one embodiment, the compound is represented by the Formula (III).



(III)

- [0041] In at least one embodiment, the at least one hydrocarbyl aluminum comprises a compound is represented by the formula $R^1R^2R^3Al$, wherein each of R^1 , R^2 , and R^3 is independently a C_1 to C_{20} alkyl group (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl). Often, the at least one hydrocarbyl aluminum comprises a plurality of compounds represented by the foregoing formula $R^1R^2R^3Al$. In such aspects, R^1 , R^2 , and R^3 is at least about 85% methyl, up to about 15 mol% C_1 - C_{20} hydrocarbyl group or a heteroatom containing group, and from 0 to 10 mol% hydrogen based on the total amount of moles of R^1 , R^2 , and R^3 in the plurality of compounds. In at least one embodiment, the at least one hydrocarbyl aluminum comprises trimethylaluminum.
- [0042] Generally, the at least one hydrocarbyl aluminum is introduced in excess of the at least one non-hydrolytic oxygen-containing compound. Without wishing to be bound by theory, it is believed that adding the hydrocarbyl aluminum in excess of the non-hydrolytic oxygen-containing compound ensures that the surface of the support material particles described herein may be coated with both the alumoxane precursor and the hydrocarbyl aluminum to form a supported alumoxane precursor. It is further believed that heating of the supported alumoxane precursor can cause the hydrocarbyl aluminum to react with the alumoxane precursor to form the supported alumoxane described herein. Generally, the at least one hydrocarbyl aluminum is introduced at a concentration such that the molar ratio of aluminum to non-hydrolytic oxygen in the solution is greater than or equal to 1.5. Often, the at least one hydrocarbyl aluminum may be introduced at a concentration of greater than or equal to 3 molar equivalents of the at least one non-hydrolytic oxygen-containing compound. For example, the molar ratio of the at least one non-hydrolytic oxygen-containing compound to the at least one hydrocarbyl aluminum can be from about 1:3 to about 1:9, such as from about 1:3 to about 1:5. Alternatively, in aspects where the at least one non-hydrolytic oxygen-containing compound comprises a compound of the Formula (II) or Formula (III), the at least one hydrocarbyl aluminum is introduced at a concentration of greater than or equal to 2 molar equivalents of the at least one non-hydrolytic oxygen-containing compound. For example, the molar ratio of the at least one non-hydrolytic oxygen-containing compound to the at least one hydrocarbyl aluminum in such aspects can be from about 1:2 to about 1:9, such as from about 1:2 to about 1:5. Often, the molar ratio of the at least one hydrocarbyl aluminum to the at least one non-hydrolytic oxygen containing compound is greater than or equal to $[A*B + 0.5(C*D)]/B$, wherein A is 2 or 3; B is the moles of the non-hydrolytic oxygen containing compound; C is the moles of hydrocarbyl aluminum chemisorbed to the

surface of the support material in the absence of the non-hydrolytic oxygen containing compound per gram of the support material; and D is the grams of the support material. In such aspects, A is generally 2 if the at least one non-hydrolytic oxygen containing compound comprises a compound represented by the Formula (II), and A is generally 3 if the at least one non-hydrolytic oxygen containing compound comprises a compound represented by the Formula (I). Further, in such aspects, B/D is generally greater than or equal to about 1.5 mmol/g.

[0043] Generally, suitable aliphatic hydrocarbon fluids include aliphatic hydrocarbon fluid has a boiling point of less than about 70 degrees Celsius, such as from about 20 degrees Celsius to about 70 degrees Celsius. The boiling point of the aliphatic hydrocarbon fluid may be lower than the boiling point of the hydrocarbyl aluminum. In at least one embodiment, the boiling point of the aliphatic solvent is at least 40 degrees Celsius lower than the boiling point of the hydrocarbyl aluminum, such as at least 50 degrees Celsius lower or at least 60 degrees Celsius lower. Suitable aliphatic hydrocarbon fluids include, but are not limited to, propane, butanes, pentanes, hexanes, heptanes, octanes, nonanes, decanes, undecanes, dodecanes, tridecanes, tetradecanes, pentadecanes, hexadecanes, or combination(s) thereof; preferable aliphatic hydrocarbon fluids can include normal paraffins (such as NORPAR® hydrocarbon fluids available from ExxonMobil Chemical Company in Houston, TX), isoparaffins (such as ISOPAR® hydrocarbon fluids available from ExxonMobil Chemical Company in Houston, TX), and combinations thereof. For example, the aliphatic hydrocarbon fluid can be selected from C₃ to C₁₂ linear, branched or cyclic alkanes. In some embodiments, the aliphatic hydrocarbon fluid is substantially free of aromatic hydrocarbons. Preferably, the aliphatic hydrocarbon fluid is essentially free of toluene. Useful aliphatic hydrocarbon fluids are ethane, propane, n-butane, 2-methylpropane, n-pentane, cyclopentane, 2-methylbutane, 2-methylpentane, n-hexane, cyclohexane, methylcyclopentane, 2,4-dimethylpentane, n-heptane, 2,2,4-trimethylpentane, methylcyclohexane, octane, nonane, decane, or dodecane, and mixture(s) thereof. In at least one embodiment, aromatics are present in the aliphatic hydrocarbon fluid at less than 1 wt%, such as less than 0.5 wt%, such as at 0 wt% based upon the weight of the hydrocarbon fluid. In at least one embodiment, the aliphatic hydrocarbon fluid is n-pentane and/or 2-methylpentane.

[0044] The combination of the at least one hydrocarbyl aluminum with the at least one non-hydrolytic oxygen-containing compound and a support material is generally conducted at a temperature of less than about 70 degrees Celsius. Often, the combination may be done at

the reflux temperature of the aliphatic hydrocarbon fluid. The reflux temperature is based on the boiling point of the aliphatic hydrocarbon fluid, such as from about 20 degrees Celsius to about 70 degrees Celsius or from about 25 degrees Celsius to about 70 degrees Celsius.

[0045] Typically, the at least one non-hydrolytic oxygen-containing compound is
5 combined with the at least one hydrocarbyl aluminum prior to combining with the support material. Often, the at least one non-hydrolytic oxygen-containing compound may be dissolved in an aliphatic hydrocarbon fluid prior to combining with the at least one hydrocarbyl aluminum, which may also be dissolved in an aliphatic hydrocarbon fluid. In such aspects, the aliphatic hydrocarbon fluid in which the at least one non-hydrolytic oxygen-
10 containing compound and the at least one hydrocarbyl aluminum are dissolved may be the same or different. In at least one embodiment, an alumoxane precursor in solution can be prepared by addition of a solution of methylacrylic acid (MAA) in pentane to a solution of trimethylaluminum (TMA) in pentane at a rate sufficient to maintain a controlled reflux (i.e., maintaining the reaction temperature at about 36.1 degrees Celsius, which is the boiling point
15 of pentane). In such aspects, the MAA may be introduced to the TMA at a molar ratio from about 1:3 to about 1:5.

Support Materials

[0046] In embodiments herein, a support material may be utilized. In at least one embodiment, the support material is a porous support material, for example, talc, or inorganic
20 oxides. Other support materials include zeolites, clays, organoclays, or any other suitable organic or inorganic support material and the like, or mixtures thereof.

[0047] In at least one embodiment, the support material is an inorganic oxide. Suitable inorganic oxide materials for use in catalyst systems herein include Groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may
25 be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be used, for example, functionalized polyolefins, such as polypropylene. Support materials may include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-
30 alumina, silica-titania, and the like. Support materials may include Al_2O_3 , ZrO_2 , SiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{TiO}_2$, silica clay, silicon oxide/clay, or mixtures thereof. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene, polypropylene, and polystyrene with

functional groups that are able to absorb water, e.g., oxygen or nitrogen containing groups such as -OH, -RC=O, -OR, and -NR₂. Particularly useful supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, silica clay, silicon oxide clay, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and the like. In at least one embodiment, the support material is selected from Al₂O₃, ZrO₂, SiO₂, SiO₂/Al₂O₃, silica clay, silicon oxide/clay, or mixtures thereof. The support material may be fluorided.

[0048] As used herein, the phrases "fluorided support" and "fluorided support composition" mean a support, desirably particulate and porous, which has been treated with at least one inorganic fluorine containing compound. For example, the fluorided support composition can be a silicon dioxide support wherein a portion of the silica hydroxyl groups has been replaced with fluorine or fluorine containing compounds. Suitable fluorine containing compounds include, but are not limited to, inorganic fluorine containing compounds and/or organic fluorine containing compounds.

[0049] Fluorine compounds suitable for providing fluorine for the support may be organic or inorganic fluorine compounds and are desirably inorganic fluorine containing compounds. Such inorganic fluorine containing compounds may be any compound containing a fluorine atom as long as it does not contain a carbon atom. Particularly desirable are inorganic fluorine-containing compounds selected from NH₄BF₄, (NH₄)₂SiF₆, NH₄PF₆, NH₄F, (NH₄)₂TaF₇, NH₄NbF₄, (NH₄)₂GeF₆, (NH₄)₂SmF₆, (NH₄)₂TiF₆, (NH₄)₂ZrF₆, MoF₆, ReF₆, GaF₃, SO₂ClF, F₂, SiF₄, SF₆, ClF₃, ClF₅, BrF₅, IF₇, NF₃, HF, BF₃, NHF₂, NH₄HF₂, and combinations thereof. In at least one embodiment, ammonium hexafluorosilicate and ammonium tetrafluoroborate are used.

[0050] In at least one embodiment, the support material comprises a support material treated with an electron-withdrawing anion. The support material can be silica, alumina, silica-alumina, silica-zirconia, alumina-zirconia, aluminum phosphate, heteropolytungstates, titania, magnesia, boria, zinc oxide, mixed oxides thereof, or mixtures thereof; and the electron-withdrawing anion is selected from fluoride, chloride, bromide, phosphate, triflate, bisulfate, sulfate, or any combination thereof.

[0051] An electron-withdrawing component can be used to treat the support material. The electron-withdrawing component can be any component that increases the Lewis or Brønsted acidity of the support material upon treatment (as compared to the support material that is not treated with at least one electron-withdrawing anion). In at least one embodiment,

the electron-withdrawing component is an electron-withdrawing anion derived from a salt, an acid, or other compound, such as a volatile organic compound, that serves as a source or precursor for that anion. Electron-withdrawing anions can be sulfate, bisulfate, fluoride, chloride, bromide, iodide, fluorosulfate, fluoroborate, phosphate, fluorophosphate, trifluoroacetate, triflate, fluoro-zirconate, fluorotitanate, phospho-tungstate, or mixtures thereof, or combinations thereof. An electron-withdrawing anion can be fluoride, chloride, bromide, phosphate, triflate, bisulfate, or sulfate, and the like, or any combination thereof, at least one embodiment of this disclosure. In at least one embodiment, the electron-withdrawing anion is sulfate, bisulfate, fluoride, chloride, bromide, iodide, fluorosulfate, fluoroborate, phosphate, fluorophosphate, trifluoroacetate, triflate, fluoro-zirconate, fluorotitanate, or combinations thereof.

[0052] Thus, for example, the support material suitable for use in the catalyst systems of the present disclosure can be one or more of fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, and the like, or combinations thereof. In at least one embodiment, the activator-support can be, or can comprise, fluorided alumina, sulfated alumina, fluorided silica-alumina, sulfated silica-alumina, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or combinations thereof. In another embodiment, the support material includes alumina treated with hexafluorotitanic acid, silica-coated alumina treated with hexafluorotitanic acid, silica-alumina treated with hexafluorozirconic acid, silica-alumina treated with trifluoroacetic acid, fluorided boria-alumina, silica treated with tetrafluoroboric acid, alumina treated with tetrafluoroboric acid, alumina treated with hexafluorophosphoric acid, or combinations thereof. Further, any of these activator-supports optionally can be treated with a metal ion.

[0053] Nonlimiting examples of cations suitable for use in the present disclosure in the salt of the electron-withdrawing anion include ammonium, trialkyl ammonium, tetraalkyl ammonium, tetraalkyl phosphonium, H^+ , $[H(OEt)_2]^+$, $[HNR_3]^+$ ($R = C_1-C_{20}$ hydrocarbyl group, which may be the same or different) or combinations thereof.

[0054] Further, combinations of one or more different electron-withdrawing anions, in varying proportions, can be used to tailor the specific acidity of the support material to a

desired level. Combinations of electron-withdrawing components can be contacted with the support material simultaneously or individually, and in any order that provides a desired chemically-treated support material acidity. For example, in at least one embodiment, two or more electron-withdrawing anion source compounds in two or more separate contacting steps.

[0055] In one embodiment of the present disclosure, one example of a process by which a chemically-treated support material is prepared is as follows: a selected support material, or combination of support materials, can be contacted with a first electron-withdrawing anion source compound to form a first mixture; such first mixture can be calcined and then contacted with a second electron-withdrawing anion source compound to form a second mixture; the second mixture can then be calcined to form a treated support material. In such a process, the first and second electron-withdrawing anion source compounds can be either the same or different compounds.

[0056] The method by which the oxide is contacted with the electron-withdrawing component, typically a salt or an acid of an electron-withdrawing anion, can include, but is not limited to, gelling, co-gelling, impregnation of one compound onto another, and the like, or combinations thereof. Following a contacting method, the contacted mixture of the support material, electron-withdrawing anion, and optional metal ion, can be calcined.

[0057] According to another embodiment of the present disclosure, the support material can be treated by a process comprising: (i) contacting a support material with a first electron-withdrawing anion source compound to form a first mixture; (ii) calcining the first mixture to produce a calcined first mixture; (iii) contacting the calcined first mixture with a second electron-withdrawing anion source compound to form a second mixture; and (iv) calcining the second mixture to form the treated support material.

[0058] It is preferred that the support material, most preferably an inorganic oxide, has a surface area between about 10 m²/g and about 700 m²/g, pore volume between about 0.1 cc/g and about 4.0 cc/g and average particle size between about 5 μm and about 500 μm. In at least one embodiment, the surface area of the support material is between about 50 m²/g and about 500 m²/g, pore volume between about 0.5 cc/g and about 3.5 cc/g and average particle size between about 10 μm and about 200 μm. The surface area of the support material may be between about 100 m²/g and about 400 m²/g, pore volume between about 0.8 cc/g and about 3.0 cc/g and average particle size between about 5 μm and about 100 μm. The average pore size of the support material may be between about 10 Å and about 1000 Å, such as

between about 50 Å and about 500 Å, such as between about 75 Å and about 350 Å. In at least one embodiment, the support material is a amorphous silica with surface area=300-400 m²/gm; pore volume of 0.9-1.8 cm³/gm. In at least one embodiment, the supported material may optionally be a sub-particle containing silica with average sub-particle size in the range of 0.05 to 5 micron, e.g., from the spray drying of average particle size in the range of 0.05 to 5 micron small particle to form average particle size in the range 5 to 200 micron large main particles. In at least one embodiment, the supported material may optionally have pores with pore diameter = or > 100 angstrom at least 20% of the total pore volume defined by BET method. Non-limiting example silicas are Grace Davison's 952, 955, and 948; PQ Corporation's ES70 series, PD 14024, PD16042, and PD16043; Asahi Glass Chemical (AGC)'s D70-120A, DM-H302, DM-M302, DM-M402, DM-L302, and DM-L402; Fuji's P-10/20 or P-10/40; and the like.

[0059] The support material, such as an inorganic oxide, optionally has a surface area of from 50 m²/g to 800 m²/g, a pore volume in the range of from 0.5 cc/g to 5.0 cc/g and an average particle size in the range of from 1 µm to 200 µm.

[0060] The support material should be dry, that is, substantially free of absorbed water. Drying of the support material can be effected by heating or calcining at 100 degrees Celsius to 1,000 degrees Celsius, such as at least about 600 degrees Celsius. When the support material is silica, it is heated to at least 200 degrees Celsius, such as 200 degrees Celsius to 900 degrees Celsius, such as at about 600 degrees Celsius; and for a time of 1 minute to about 100 hours, from 12 hours to 72 hours, or from 24 hours to 60 hours. The calcined support material should have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems of the present disclosure. The calcined support material is then contacted with at least one polymerization catalyst comprising at least one catalyst compound and an activator.

Supported Alumoxane Precursor

[0061] A supported alumoxane precursor may be formed by coating particles of a support material, such as silica, with an alumoxane precursor. In one embodiment, the supported precursor may be formed by mixing the alumoxane precursor and an alkylaluminum in an aliphatic hydrocarbon fluid, followed by removing at least a portion of the aliphatic hydrocarbon fluid by distilling the solution at a pressure of greater than about 0.5 atm. Generally, the aliphatic hydrocarbon fluid is preferentially removed over the unreacted hydrocarbyl aluminum present in the solution. For example, typically the concentration of the

unreacted hydrocarbyl aluminum present in the solution is maintained during the distillation because the boiling point of the hydrocarbyl aluminum is greater than that of the aliphatic hydrocarbon fluid. Generally, supported alumoxane precursor comprises from about 1 wt% to about 50 wt% of the aliphatic hydrocarbon fluid based on the total weight of the supported alumoxane precursor. For example, the supported alumoxane precursor may include from about 1 wt% to about 40 wt% of the aliphatic hydrocarbon fluid based on the total weight of the supported alumoxane precursor, such as from about 1 wt% to about 30 wt%, or from about 1 wt% to about 20 wt%.

[0062] The particles of the support material can be coated with both the alumoxane precursor and the alkylaluminum. In at least one embodiment, the alumoxane precursor is evenly distributed on the support material and covers over 50% of the surface area of the support material. By introducing the alkylaluminum in excess of the non-hydrolytic oxygen compound as described herein, both the alkylaluminum and the alumoxane precursor are typically present on the surface of the particles. Subsequent heating of the particles can cause the alkylaluminum to react with the alumoxane precursor to form alkylalumoxane, such as MAO. In at least one embodiment, the total amount of the supported alumoxane precursor includes from about 1 wt% to about 90 wt% of the alkylaluminum. In at least one embodiment, the molar ratio of the alkylaluminum to the alumoxane precursor in the supported alumoxane precursor ranges from about 1:10 to about 10:1, such as about 4:1. The supported alumoxane precursor is stable at ambient and cold temperatures, such as less than about 25 degrees Celsius and is easy to store and ship.

Supported Alumoxane

[0063] The supported alumoxane may be formed by heating the supported alumoxane precursor to a temperature greater than the boiling point of the aliphatic hydrocarbon fluid and less than about 160 degrees Celsius, such as from about 70 degrees Celsius to about 120 degrees Celsius. In at least one example, the supported alumoxane is SMAO. Often, heating the supported precursor produces volatile compounds and derivatives thereof. In such aspects, the methods described herein may include removing at least a portion of the volatile compounds and derivatives thereof. Thus, the methods described herein include forming an alumoxane precursor, forming a supported alumoxane precursor, and forming the supported alumoxane. Conventional methods for forming the supported alumoxane include forming an intermediate MAO, which is difficult to store and ship. The shelf lives of an alumoxane precursor and a supported alumoxane precursor of the present disclosure can be longer than

that of MAO. In addition, it is easier to ship the alumoxane precursor and the supported alumoxane precursor compared to shipping MAO due to the stability of the alumoxane precursor and the supported alumoxane precursor.

Catalyst Compounds

5 [0064] In at least one embodiment, the present disclosure provides a catalyst system comprising a catalyst compound having a metal atom. The catalyst compound can be a metallocene catalyst compound. The metal can be a Group 3 through Group 12 metal atom, such as Group 3 through Group 10 metal atoms, or lanthanide Group atoms. The catalyst compound having a Group 3 through Group 12 metal atom can be monodentate or
10 multidentate, such as bidentate, tridentate, or tetradentate, where a heteroatom of the catalyst, such as phosphorous, oxygen, nitrogen, or sulfur is chelated to the metal atom of the catalyst. Non-limiting examples include bis(phenolate)s. In at least one embodiment, the Group 3 through Group 12 metal atom is selected from Group 5, Group 6, Group 8, or Group 10 metal atoms. In at least one embodiment, a Group 3 through Group 10 metal atom is selected from
15 Cr, Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni. In at least one embodiment, a metal atom is selected from Groups 4, 5, and 6 metal atoms. In at least one embodiment, a metal atom is a Group 4 metal atom selected from Ti, Zr, or Hf. The oxidation state of the metal atom can range from 0 to +7, for example +1, +2, +3, +4, or +5, for example +2, +3 or +4.

20 [0065] A catalyst compound of the present disclosure can be a chromium or chromium-based catalyst. Chromium-based catalysts include chromium oxide (CrO_3) and silylchromate catalysts. Chromium catalysts have been the subject of much development in the area of continuous fluidized-bed gas-phase polymerization for the production of polyethylene polymers. Such catalysts and polymerization processes have been described, for example, in
25 US Patent Application Publication No. 2011/0010938 and US Patent Nos. 6,833,417, 6,841,630, 6,989,344, 7,202,313, 7,504,463, 7,563,851, 7,915,357, 8,101,691, 8,129,484, and 8,420,754.

[0066] Metallocene catalyst compounds as used herein include metallocenes comprising Group 3 to Group 12 metal complexes, preferably, Group 4 to Group 6 metal complexes, for
30 example, Group 4 metal complexes. The metallocene catalyst compound of catalyst systems of the present disclosure may be unbridged metallocene catalyst compounds represented by the formula: $\text{Cp}^{\text{A}}\text{Cp}^{\text{B}}\text{M}^{\text{X}}_n$, wherein each Cp^{A} and Cp^{B} is independently selected from cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, one or both Cp^{A} and Cp^{B}

- may contain heteroatoms, and one or both Cp^A and Cp^B may be substituted by one or more R'' groups. M' is selected from Groups 3 through 12 atoms and lanthanide Group atoms. X' is an anionic leaving group. n is 0 or an integer from 1 to 4. R'' is selected from alkyl, lower alkyl, substituted alkyl, heteroalkyl, alkenyl, lower alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, lower alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, lower alkoxy, aryloxy, alkylthio, lower alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylène, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, lower hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.
- 10 **[0067]** In at least one embodiment, each Cp^A and Cp^B is independently selected from cyclopentadienyl, indenyl, fluorenyl, cyclopentaphenanthrenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7-H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenindenyl, thiophenofluorenyl, and
- 15 hydrogenated versions thereof.
- [0068]** The metallocene catalyst compound may be a bridged metallocene catalyst compound represented by the formula: $Cp^A(A)Cp^BM'X'_n$, wherein each Cp^A and Cp^B is independently selected from cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl. One or both Cp^A and Cp^B may contain heteroatoms, and one or both Cp^A
- 20 and Cp^B may be substituted by one or more R'' groups. M' is selected from Groups 3 through 12 atoms and lanthanide Group atoms. X' is an anionic leaving group. n is 0 or an integer from 1 to 4. (A) is selected from divalent alkyl, divalent lower alkyl, divalent substituted alkyl, divalent heteroalkyl, divalent alkenyl, divalent lower alkenyl, divalent substituted alkenyl, divalent heteroalkenyl, divalent alkynyl, divalent lower alkynyl, divalent substituted alkynyl, divalent heteroalkynyl, divalent alkoxy, divalent lower alkoxy, divalent aryloxy, divalent alkylthio, divalent lower alkylthio, divalent arylthio, divalent aryl, divalent substituted aryl, divalent heteroaryl, divalent aralkyl, divalent aralkylene, divalent alkaryl, divalent alkarylène, divalent haloalkyl, divalent haloalkenyl, divalent haloalkynyl, divalent heteroalkyl, divalent heterocycle, divalent heteroaryl, a divalent heteroatom-containing group,
- 25 divalent hydrocarbyl, divalent lower hydrocarbyl, divalent substituted hydrocarbyl, divalent heterohydrocarbyl, divalent silyl, divalent boryl, divalent phosphino, divalent phosphine, divalent amino, divalent amine, divalent ether, divalent thioether. R'' is selected from alkyl, lower alkyl, substituted alkyl, heteroalkyl, alkenyl, lower alkenyl, substituted alkenyl,
- 30

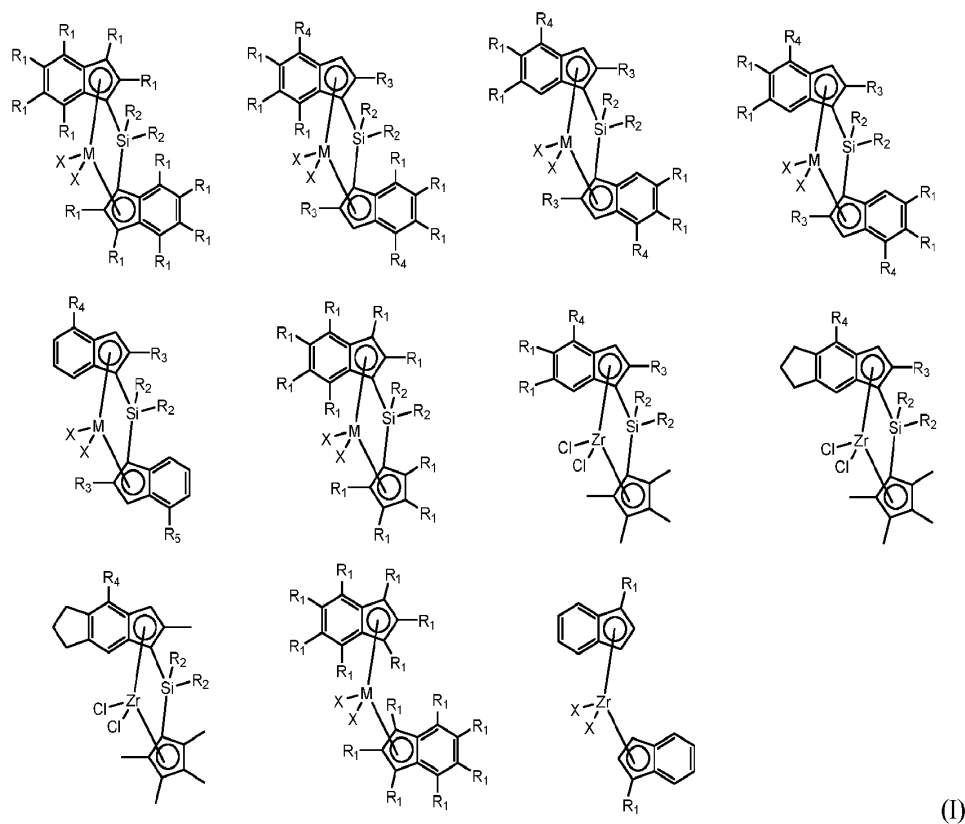
heteroalkenyl, alkynyl, lower alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, lower alkoxy, aryloxy, alkylthio, lower alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, lower hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, germanium, ether, and thioether.

[0069] In at least one embodiment, each of Cp^A and Cp^B is independently selected from cyclopentadienyl, n-propylcyclopentadienyl, indenyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, and n-butylcyclopentadienyl.

10 [0070] (A) may be O, S, NR' , or SiR'_2 , where each R' is independently hydrogen or C_1 - C_{20} hydrocarbyl.

[0071] In at least one embodiment $Cp^ACp^BM^*X_n$ is (n-propylcyclopentadienyl) $_2$ HfMe $_2$, (1,3-methyl, butylcyclopentadienyl)ZrCl $_2$, (1,3-methyl, butylcyclopentadienyl)ZrCl $_2$, (1,3-methyl, butylcyclopentadienyl)ZrMe $_2$, Me $_2$ Si(tetrahydroindenyl)ZrCl $_2$,
15 Me $_2$ Si(tetrahydroindenyl)ZrMe $_2$, Me $_2$ Si(CpCH $_2$ SiMe $_3$) $_2$ HfCl $_2$, Me $_2$ Si(CpCH $_2$ SiMe $_3$) $_2$ HfMe $_2$.

[0072] In additional embodiments, the metallocene may have the structures I:

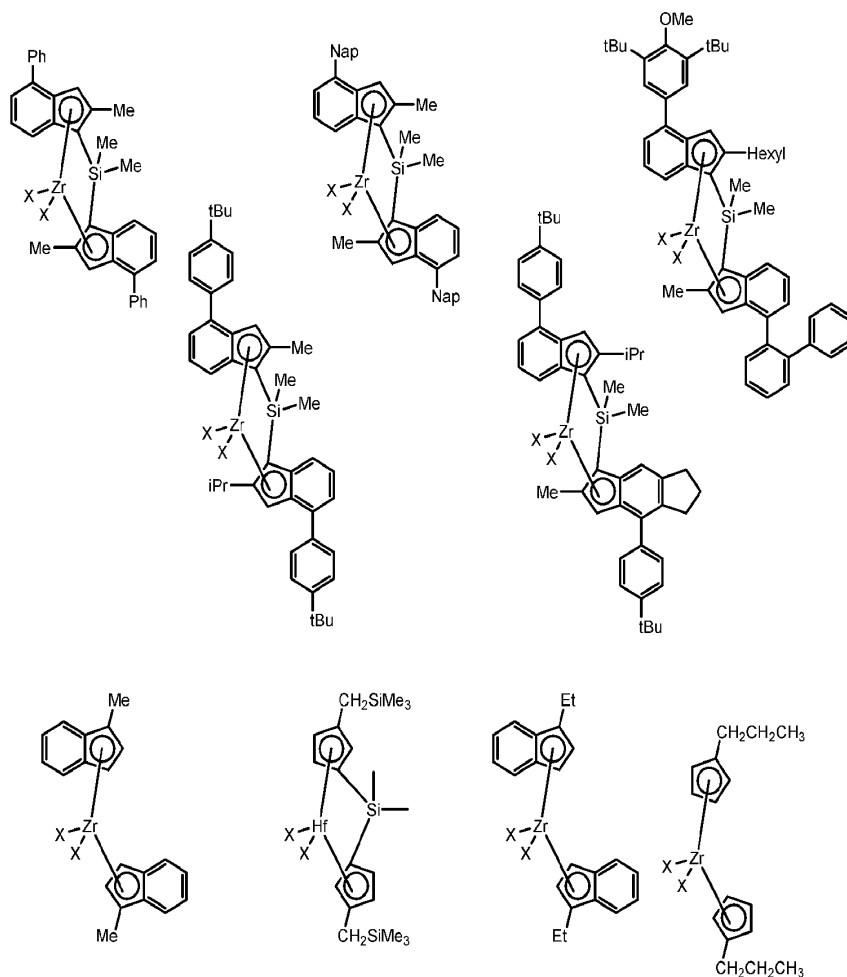


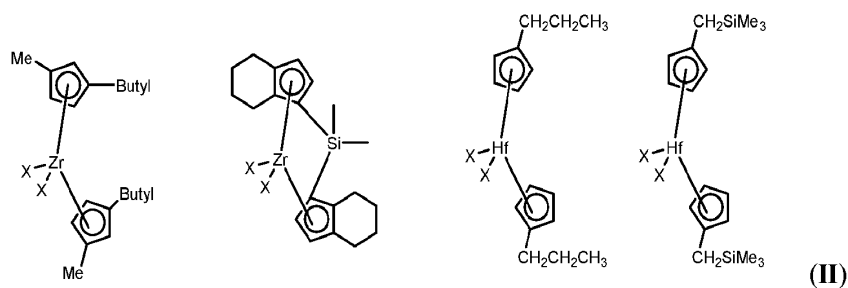
Where the metallocenes have substituted cyclopentadienyl rings, they may be comprised of racemic or meso geometries. R_1 is hydrogen, hydrocarbyl or substituted hydrocarbyl groups. R_1 may be the same or different. Two or more R_1 may join together to form a ring. R_2 is a hydrocarbyl or substituted hydrocarbyl group. Two R_2 may join together to form a ring. An

5 R_1 and R_2 may also join together to form a ring. R_3 is an alkyl group. R_4 is an alkyl, substituted alkyl, aryl, or substituted aryl group. X is an anionic leaving group such as fluoride, chloride, alkoxide, methyl, allyl, benzyl, trimethylsilylmethyl. Two X may also be joined together such as in butadienyl type ligands.

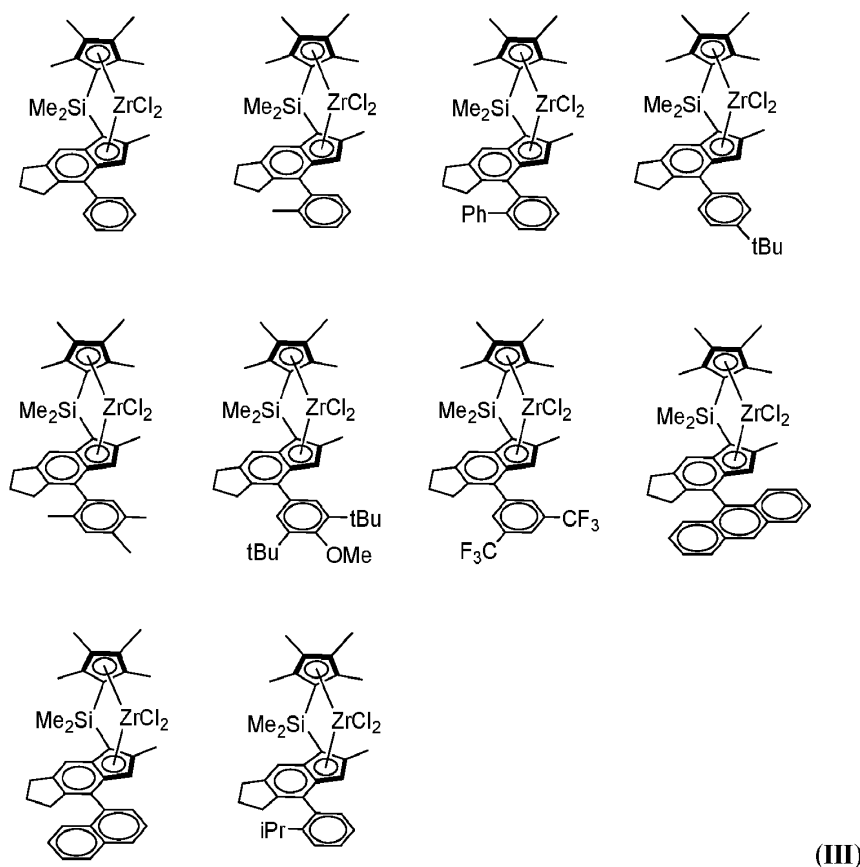
[0073] In additional embodiments, the metallocene catalyst compounds are represented

10 by (II):





[0074] In additional embodiments, the metallocene catalyst compounds are represented by (III):



5 [0075] In another embodiment, the metallocene catalyst compound is represented by the formula:



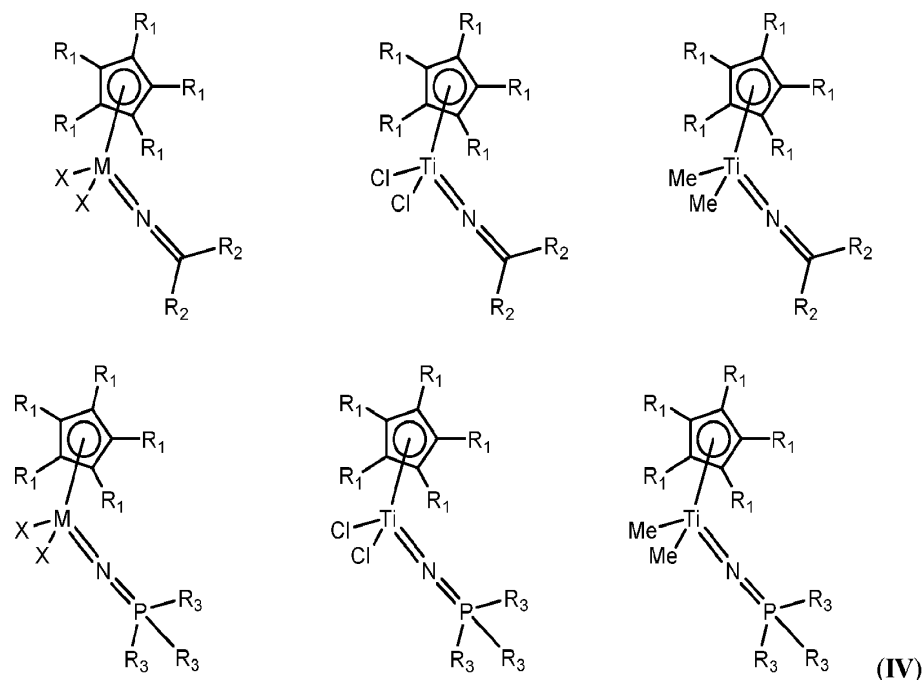
where Cp is independently a substituted or unsubstituted cyclopentadienyl ligand or substituted or unsubstituted ligand isolobal to cyclopentadienyl. M is a Group 4 transition metal. G is a heteroatom group represented by the formula JR^*_z where J is N, P, O or S, and
 10 R^* is a linear, branched, or cyclic C_1 - C_{20} hydrocarbyl. z is 1 or 2. T is a bridging group. y is

0 or 1. X is a leaving group. $m=1$, $n=1, 2$ or 3 , $q=0, 1, 2$ or 3 , and the sum of $m+n+q$ is equal to the oxidation state of the transition metal.

[0076] In at least one embodiment, J is N, and R* is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, cyclooctyl, cyclododecyl, decyl, undecyl, dodecyl, adamantyl or an isomer thereof.

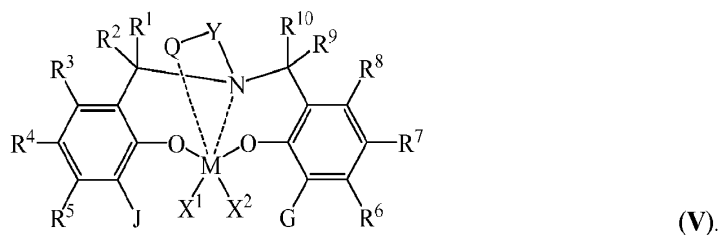
[0077] The metallocene catalyst compound may be selected from:
 bis(1-methyl, 3-n-butyl cyclopentadienyl) zirconium dichloride;
 dimethylsilyl bis(tetrahydroindenyl) zirconium dichloride;
 bis(n-propylcyclopentadienyl) hafnium dimethyl;
 10 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl;
 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dichloride;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)titanium dimethyl;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido)titanium dichloride;
 $\mu-(\text{CH}_3)_2\text{Si}(\text{cyclopentadienyl})(1\text{-adamantylamido})\text{M}(\text{R})_2$;
 15 $\mu-(\text{CH}_3)_2\text{Si}(3\text{-tertbutylcyclopentadienyl})(1\text{-adamantylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2(\text{tetramethylcyclopentadienyl})(1\text{-adamantylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2\text{Si}(\text{tetramethylcyclopentadienyl})(1\text{-adamantylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2\text{C}(\text{tetramethylcyclopentadienyl})(1\text{-adamantylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2\text{Si}(\text{tetramethylcyclopentadienyl})(1\text{-tertbutylamido})\text{M}(\text{R})_2$;
 20 $\mu-(\text{CH}_3)_2\text{Si}(\text{fluorenyl})(1\text{-tertbutylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2\text{Si}(\text{tetramethylcyclopentadienyl})(1\text{-cyclododecylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{C}_6\text{H}_5)_2\text{C}(\text{tetramethylcyclopentadienyl})(1\text{-cyclododecylamido})\text{M}(\text{R})_2$;
 $\mu-(\text{CH}_3)_2\text{Si}(\eta^5\text{-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl})(\text{tertbutylamido})\text{M}(\text{R})_2$;
 where M is selected from Ti, Zr, and Hf; and R is selected from halogen or C_1 to C_5 alkyl.

[0078] In further embodiments, the catalyst compounds are represented by (IV):



where R_1 is hydrogen, hydrocarbyl or substituted hydrocarbyl groups. R_1 may be the same or different. Two or more R_1 may join together to form a ring. R_2 and R_3 are a hydrocarbyl or substituted hydrocarbyl group. X is an anionic leaving group such as fluoride, chloride, alkoxide, methyl, allyl, benzyl, trimethylsilylmethyl. Two X may also be joined together such as in butadienyl type ligands.

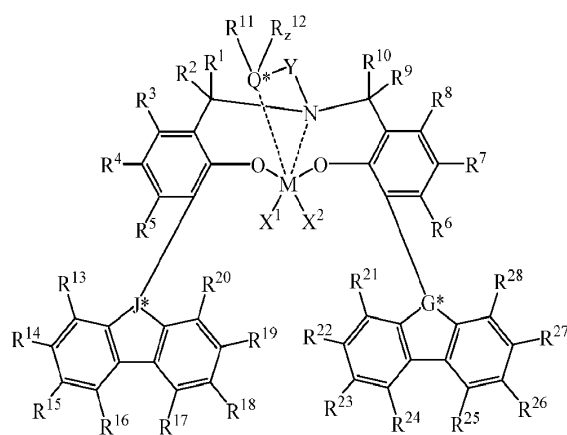
[0079] In at least one embodiment, the catalyst compound is a bis(phenolate) catalyst compound represented by Formula (V):



M is a Group 4 metal. X^1 and X^2 are independently a univalent C_1 - C_{20} hydrocarbyl, C_1 - C_{20} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or X^1 and X^2 join together to form a C_4 - C_{62} cyclic or polycyclic ring structure. R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or two or more of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , or R^{10} are joined together to form a C_4 - C_{62} cyclic or polycyclic ring structure, or a combination thereof. Q is a neutral donor group. J is heterocycle, a substituted or

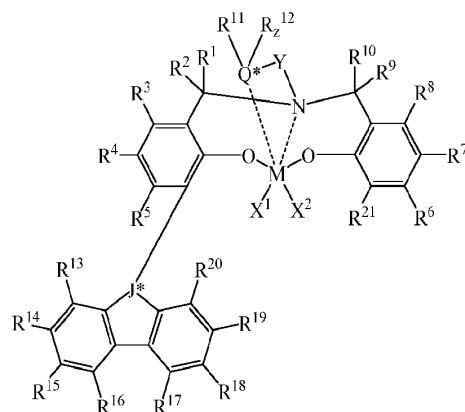
unsubstituted C₇-C₆₀ fused polycyclic group, where at least one ring is aromatic and where at least one ring, which may or may not be aromatic, has at least five ring atoms. G is as defined for J or may be hydrogen, C₂-C₆₀ hydrocarbyl, C₁-C₆₀ substituted hydrocarbyl, or may independently form a C₄-C₆₀ cyclic or polycyclic ring structure with R⁶, R⁷, or R⁸ or a combination thereof. Y is divalent C₁-C₂₀ hydrocarbyl or divalent C₁-C₂₀ substituted hydrocarbyl or (-Q*-Y-) together form a heterocycle. Heterocycle may be aromatic and/or may have multiple fused rings.

[0080] In at least one embodiment, the catalyst compound represented by Formula (V) is represented by Formula (VI) or Formula (VII):



(VI),

or

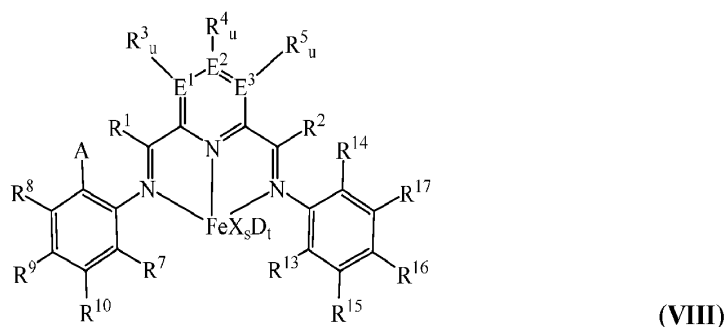


(VII).

M is Hf, Zr, or Ti. X¹, X², R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, and Y are as defined for Formula (V). R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, and R²⁸ is independently a hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a functional group comprising elements from Groups 13 to 17, or two or more of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴,

- R^{25} , R^{26} , R^{27} , and R^{28} may independently join together to form a C_4 - C_{62} cyclic or polycyclic ring structure, or a combination thereof. R^{11} and R^{12} may join together to form a five- to eight-membered heterocycle. Q^* is a group 15 or 16 atom. z is 0 or 1. J^* is CR'' or N , and G^* is CR'' or N , where R'' is C_1 - C_{20} hydrocarbyl or carbonyl-containing C_1 - C_{20} hydrocarbyl.
- 5 $z = 0$ if Q^* is a group 16 atom, and $z = 1$ if Q^* is a group 15 atom.

[0081] In at least one embodiment the catalyst is an iron complex represented by Formula (VIII):



wherein:

- 10 A is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$,
 each of R^1 and R^2 is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;
- 15 wherein each of R^1 and R^2 is optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;
 wherein R^1 optionally bonds with R^3 , and R^2 optionally bonds with R^5 , in each case to independently form a five-, six- or seven-membered ring;
 R^7 is a C_1 - C_{20} alkyl;
- 20 each of R^3 , R^4 , R^5 , R^8 , R^9 , R^{10} , R^{15} , R^{16} , and R^{17} is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{11}_2$, $-OR^{11}$, halogen, $-SiR^{12}_3$ or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;
- 25 wherein R^3 , R^4 , R^5 , R^7 , R^8 , R^9 , R^{10} , R^{15} , R^{16} , and R^{17} are optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;
 wherein R^3 optionally bonds with R^4 , R^4 optionally bonds with R^5 , R^7 optionally

bonds with R^{10} , R^{10} optionally bonds with R^9 , R^9 optionally bonds with R^8 , R^{17} optionally bonds with R^{16} , and R^{16} optionally bonds with R^{15} , in each case to independently form a five-, six- or seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom from the group consisting of N, P, O and S;

5 R^{13} is C_1 - C_{20} -alkyl bonded with the aryl ring via a primary or secondary carbon atom, R^{14} is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$, or C_1 - C_{20} -alkyl bonded with the aryl ring;

each R^{11} is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, 10 or $-SiR^{12}_3$, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;

each R^{12} is independently hydrogen, C_1 - C_{22} -alkyl, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring,

15 each of E^1 , E^2 , and E^3 is independently carbon, nitrogen or phosphorus;

each u is independently 0 if E^1 , E^2 , and E^3 is nitrogen or phosphorus and is 1 if E^1 , E^2 , and E^3 is carbon,

each X is independently fluorine, chlorine, bromine, iodine, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{10} -alkenyl, C_6 - C_{20} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has 20 from 6 to 20 carbon atoms, $-NR^{18}_2$, $-OR^{18}$, $-SR^{18}$, $-SO_3R^{18}$, $-OC(O)R^{18}$, $-CN$, $-SCN$, β -diketonate, $-CO$, $-BF_4^-$, $-PF_6^-$ or bulky non-coordinating anions, and the radicals X can be bonded with one another;

each R^{18} is independently hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, 25 or $-SiR^{19}_3$, wherein R^{18} can be substituted by halogen or nitrogen- or oxygen-containing groups and two R^{18} radicals optionally bond to form a five- or six-membered ring;

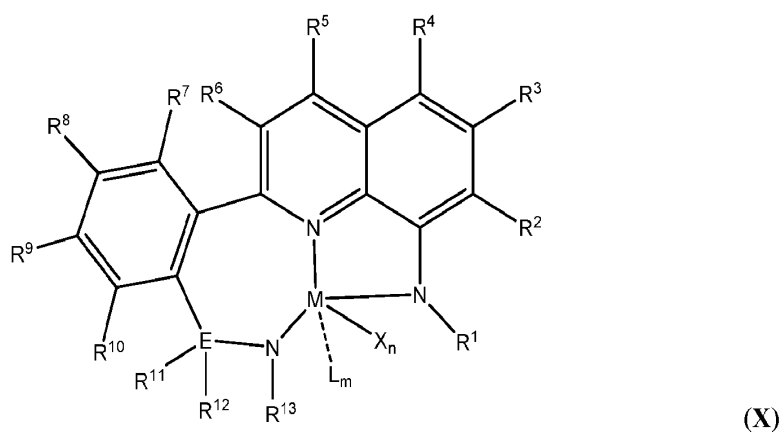
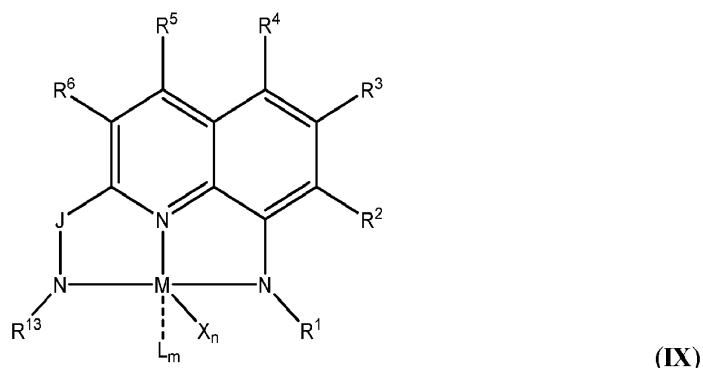
each R^{19} is independently hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, wherein R^{19} can be substituted by halogen or nitrogen- or oxygen-containing groups or two 30 R^{19} radicals optionally bond to form a five- or six-membered ring;

s is 1, 2, or 3,

D is a neutral donor, and

t is 0 to 2.

[0082] In at least one embodiment, the catalyst is a quinolinyldiamido transition metal complex represented by Formulas (IX) and (X):



5 wherein:

M is a Group 3-12 metal;

J is a three-atom-length bridge between the quinoline and the amido nitrogen;

E is selected from carbon, silicon, or germanium;

X is an anionic leaving group;

10 L is a neutral Lewis base;

R¹ and R¹³ are independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups;

R² through R¹² are independently selected from the group consisting of hydrogen, hydrocarbyls, alkoxy, silyl, amino, aryloxy, substituted hydrocarbyls, halogen, and phosphino;

15 n is 1 or 2;

m is 0, 1, or 2

n+m is not greater than 4; and

any two adjacent R groups (e.g. R¹ & R², R² & R³, etc.) may be joined to form a

substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

any two X groups may be joined together to form a dianionic group;

any two L groups may be joined together to form a bidentate Lewis base;

5 any X group may be joined to an L group to form a monoanionic bidentate group.

In a preferred embodiment M is a Group 4 metal, zirconium or hafnium;

In a preferred embodiment J is an arylmethyl, dihydro-1H-indenyl, or tetrahydronaphthalenyl group;

In a preferred embodiment E is carbon;

10 In a preferred embodiment X is alkyl, aryl, hydride, alkylsilane, fluoride, chloride, bromide, iodide, triflate, carboxylate, or alkylsulfonate;

In a preferred embodiment L is an ether, amine or thioether;

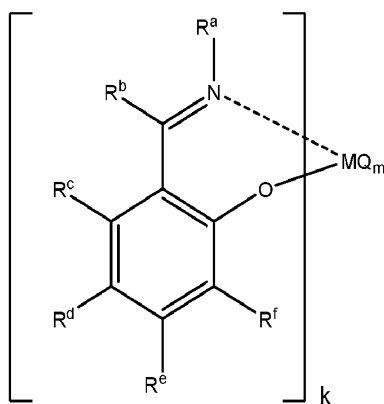
In a preferred embodiment, R^7 and R^8 are joined to form a six membered aromatic ring with the joined R^7 and R^8 group being $-\text{CH}=\text{CHCH}=\text{CH}-$;

15 In a preferred embodiment R^{10} and R^{11} are joined to form a five membered ring with the joined R^{10} and R^{11} groups being $-\text{CH}_2\text{CH}_2-$;

In a preferred embodiment R^{10} and R^{11} are joined to form a six membered ring with the joined R^{10} and R^{11} groups being $-\text{CH}_2\text{CH}_2\text{CH}_2-$;

20 In a preferred embodiment, R^1 and R^{13} may be independently selected from phenyl groups that are variously substituted with between zero to five substituents that include F, Cl, Br, I, CF_3 , NO_2 , alkoxy, dialkylamino, aryl, and alkyl groups having 1 to 10 carbons, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof.

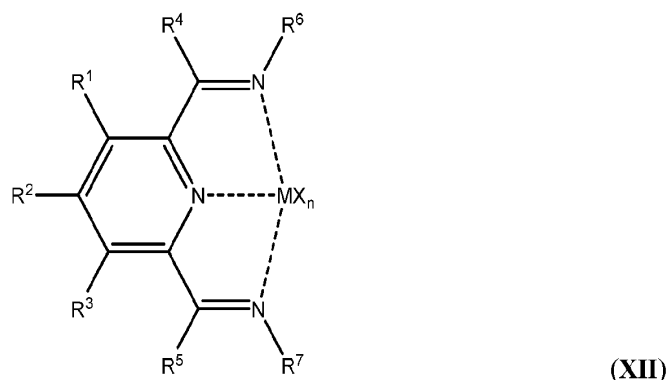
[0083] In another embodiment, the catalyst is a phenoxyimine compound represented by the Formula (XI):



(XI)

wherein M represents a transition metal atom selected from the groups 3 to 11 metals in the periodic table; k is an integer of 1 to 6; m is an integer of 1 to 6; R^a to R^f may be the same or different from one another and each represent a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residue, an oxygen-containing group, a nitrogen-containing group, a boron-containing group, a sulfur-containing group, a phosphorus-containing group, a silicon-containing group, a germanium-containing group or a tin-containing group, among which 2 or more groups may be bound to each other to form a ring; when k is 2 or more, R^a groups, R^b groups, R^c groups, R^d groups, R^e groups, or R^f groups may be the same or different from one another, one group of R^a to R^f contained in one ligand and one group of R^a to R^f contained in another ligand may form a linking group or a single bond, and a heteroatom contained in R^a to R^f may coordinate with or bind to M; m is a number satisfying the valence of M; Q represents a hydrogen atom, a halogen atom, an oxygen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group; when m is 2 or more, a plurality of groups represented by Q may be the same or different from one another, and a plurality of groups represented by Q may be mutually bound to form a ring.

[0084] In another embodiment, the catalyst is a bis(imino)pyridyl of the Formula (XII):



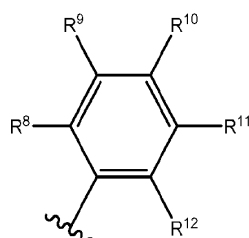
wherein M is Co or Fe; each X is an anion; n is 1, 2 or 3, so that the total number of negative charges on said anion or anions is equal to the oxidation state of a Fe or Co atom present in (XII);

R¹, R² and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, an inert functional group or

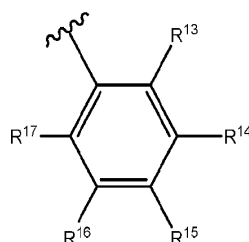
substituted hydrocarbyl;

R⁶ is Formula (XIII):



(XIII)

and R⁷ is Formula (XIV):



(XIV)

R⁸ and R¹³ are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

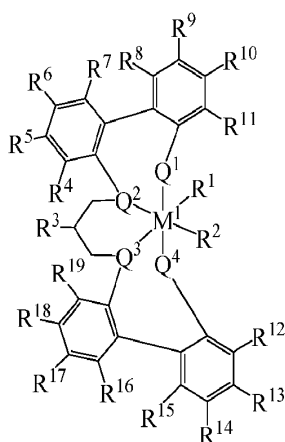
R⁹, R¹⁰, R¹¹, R¹⁴, R¹⁵ and R¹⁶ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R¹² and R¹⁷ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶ and R¹⁷ that are adjacent to one another, together may form a ring.

[0085] In at least one embodiment, the catalyst compound is represented by the

Formula (XV):



(XV)

M¹ is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten. In at least one embodiment, M¹ is zirconium.

[0086] Each of Q¹, Q², Q³, and Q⁴ is independently oxygen or sulfur. In at least one embodiment, at least one of Q¹, Q², Q³, and Q⁴ is oxygen, alternately all of Q¹, Q², Q³, and Q⁴ are oxygen.

[0087] R¹ and R² are independently hydrogen, halogen, hydroxyl, hydrocarbyl, or substituted hydrocarbyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). R¹ and R² can be a halogen selected from fluorine, chlorine, bromine, or iodine. Preferably, R¹ and R² are chlorine.

[0088] Alternatively, R¹ and R² may also be joined together to form an alkanediyl group or a conjugated C₄-C₄₀ diene ligand which is coordinated to M¹. R¹ and R² may also be identical or different conjugated dienes, optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the dienes having up to 30 atoms not counting hydrogen and/or forming a π -complex with M¹.

[0089] Exemplary groups suitable for R¹ and or R² can include 1,4-diphenyl, 1,3-butadiene, 1,3-pentadiene, 2-methyl 1,3-pentadiene, 2,4-hexadiene, 1-phenyl, 1,3-pentadiene, 1,4-dibenzyl, 1,3-butadiene, 1,4-ditolyl-1,3-butadiene, 1,4-bis(trimethylsilyl)-1,3-butadiene, and 1,4-dinaphthyl-1,3-butadiene. R¹ and R² can be identical and are C₁-C₃ alkyl or alkoxy, C₆-C₁₀ aryl or aryloxy, C₂-C₄ alkenyl, C₇-C₁₀ arylalkyl, C₇-C₁₂ alkylaryl, or halogen.

[0090] Each of R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, and R¹⁹ is independently hydrogen, halogen, C₁-C₄₀ hydrocarbyl or C₁-C₄₀ substituted hydrocarbyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen), -NR'₂, -SR', -OR, -OSiR'₃, -PR'₂, where each R' is hydrogen, halogen, C₁-C₁₀ alkyl, or C₆-C₁₀ aryl, or one or more of R⁴ and R⁵, R⁵ and R⁶, R⁶ and R⁷, R⁸ and R⁹, R⁹ and R¹⁰, R¹⁰ and R¹¹, R¹² and R¹³, R¹³ and R¹⁴, R¹⁴ and R¹⁵, R¹⁶ and R¹⁷, R¹⁷ and R¹⁸, and R¹⁸ and R¹⁹ are joined to form a

saturated ring, unsaturated ring, substituted saturated ring, or substituted unsaturated ring. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl. Preferably, R¹¹ and R¹² are C₆-C₁₀ aryl such as phenyl or naphthyl optionally substituted with C₁-C₄₀ hydrocarbyl, such as C₁-C₁₀ hydrocarbyl. Preferably, R⁶ and R¹⁷ are C₁-C₄₀ alkyl, such as C₁-C₁₀ alkyl.

[0091] In at least one embodiment, each of R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, and R¹⁹ is independently hydrogen or C₁-C₄₀ hydrocarbyl. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl. Preferably, each of R⁶ and R¹⁷ is C₁-C₄₀ hydrocarbyl and R⁴, R⁵, R⁷, R⁸, R⁹, R¹⁰, R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁸, and R¹⁹ is hydrogen. In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl.

[0092] R³ is a C₁-C₄₀ unsaturated alkyl or substituted C₁-C₄₀ unsaturated alkyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen).

[0093] Preferably, R³ is a hydrocarbyl comprising a vinyl moiety. As used herein, “vinyl” and “vinyl moiety” are used interchangeably and include a terminal alkene, e.g. represented

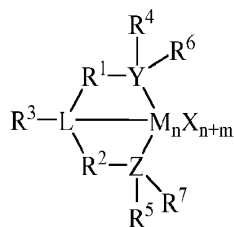


Hydrocarbyl of R³ may be further substituted (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). Preferably, R³ is C₁-C₄₀ unsaturated alkyl that is vinyl or substituted C₁-C₄₀ unsaturated alkyl that is vinyl. R³ can be represented by the structure -R'CH=CH₂ where R' is C₁-C₄₀ hydrocarbyl or C₁-C₄₀

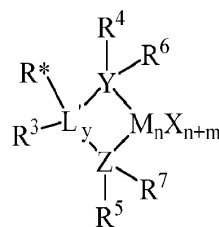
substituted hydrocarbyl (such as C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, C₆-C₂₀ aryl, C₆-C₁₀ aryloxy, C₂-C₁₀ alkenyl, C₂-C₄₀ alkenyl, C₇-C₄₀ arylalkyl, C₇-C₄₀ alkylaryl, C₈-C₄₀ arylalkenyl, or conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl) silyl or tri(hydrocarbyl) silylhydrocarbyl, the diene having up to 30 atoms other than hydrogen). In at least one embodiment, C₁-C₄₀ hydrocarbyl is selected from methyl, ethyl, propyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, sec-pentyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, isooctyl, sec-octyl, n-nonyl, isononyl, sec-nonyl, n-decyl, isodecyl, and sec-decyl.

[0094] In at least one embodiment, R³ is 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl, 1-nonenyl, or 1-decenyl.

[0095] In at least one embodiment, the catalyst is a Group 15-containing metal compound represented by Formulas (XVI) or (XVII):



(XVI)



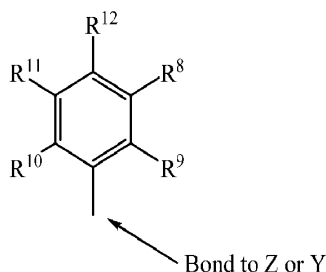
(XVII)

wherein M is a Group 3 to 12 transition metal or a Group 13 or 14 main group metal, a Group 4, 5, or 6 metal. In many embodiments, M is a Group 4 metal, such as zirconium, titanium, or hafnium. Each X is independently a leaving group, such as an anionic leaving group. The leaving group may include a hydrogen, a hydrocarbyl group, a heteroatom, a halogen, or an alkyl; y is 0 or 1 (when y is 0 group L' is absent). The term 'n' is the oxidation state of M. In various embodiments, n is +3, +4, or +5. In many embodiments, n is +4. The term 'm' represents the formal charge of the YZL or the YZL' ligand, and is 0, -1, -2 or -3 in various embodiments. In many embodiments, m is -2. L is a Group 15 or 16 element, such as nitrogen or oxygen; L' is a Group 15 or 16 element or Group 14 containing group, such as carbon, silicon or germanium. Y is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Y is nitrogen. Z is a Group 15 element, such as nitrogen or phosphorus. In many embodiments, Z is nitrogen. R¹ and R² are, independently, a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus. In many embodiments, R¹ and R² are a C₂ to C₂₀ alkyl, aryl or aralkyl group, such as a C₂ to C₂₀ linear, branched or cyclic alkyl group, or a C₂ to C₂₀ hydrocarbon group. R¹ and R² may also be interconnected to each other. R³ may be absent or

may be a hydrocarbon group, a hydrogen, a halogen, a heteroatom containing group. In many embodiments, R^3 is absent, for example, if L is an oxygen, or a hydrogen, or a linear, cyclic, or branched alkyl group having 1 to 20 carbon atoms. R^4 and R^5 are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic aralkyl group, a substituted cyclic aralkyl group, or multiple ring system, often having up to 20 carbon atoms. In many embodiments, R^4 and R^5 have between 3 and 10 carbon atoms, or are a C_1 to C_{20} hydrocarbon group, a C_1 to C_{20} aryl group or a C_1 to C_{20} aralkyl group, or a heteroatom containing group. R^4 and R^5 may be interconnected to each other. R^6 and R^7 are independently absent, hydrogen, an alkyl group, halogen, heteroatom, or a hydrocarbyl group, such as a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms. In many embodiments, R^6 and R^7 are absent. R^* may be absent, or may be a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

[0096] By "formal charge of the YZL or YZL' ligand," it is meant the charge of the entire ligand absent the metal and the leaving groups X. By " R^1 and R^2 may also be interconnected" it is meant that R^1 and R^2 may be directly bound to each other or may be bound to each other through other groups. By " R^4 and R^5 may also be interconnected" it is meant that R^4 and R^5 may be directly bound to each other or may be bound to each other through other groups. An alkyl group may be linear, branched alkyl radicals, alkenyl radicals, alkynyl radicals, cycloalkyl radicals, aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbamoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. An aralkyl group is defined to be a substituted aryl group.

[0097] In one or more embodiments, R^4 and R^5 are independently a group represented by structure (XVIII):



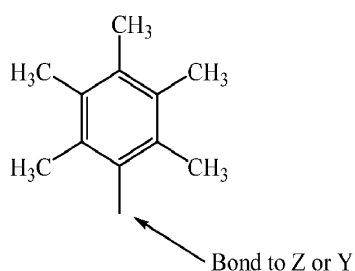
(XVIII)

wherein R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms. In many

embodiments, R^8 to R^{12} are a C_1 to C_{20} linear or branched alkyl group, such as a methyl, ethyl, propyl, or butyl group. Any two of the R groups may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In one embodiment R^9 , R^{10} and R^{12} are independently a methyl, ethyl, propyl, or butyl group (including all isomers). In another

5 embodiment, R^9 , R^{10} and R^{12} are methyl groups, and R^8 and R^{11} are hydrogen.

[0098] In one or more embodiments, R^4 and R^5 are both a group represented by structure (XIX):

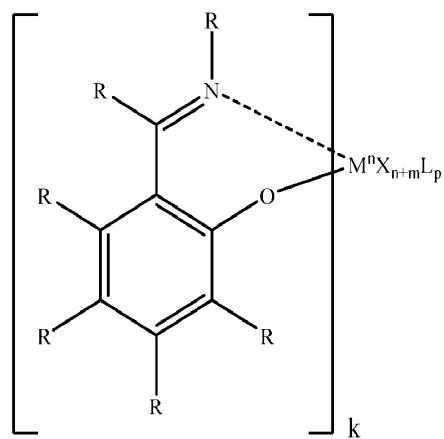
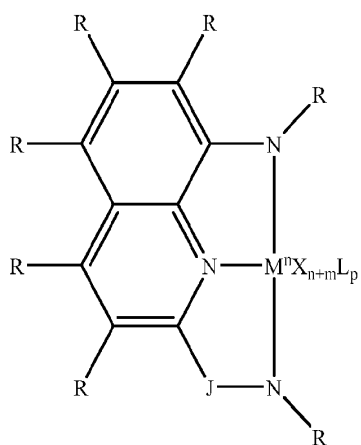
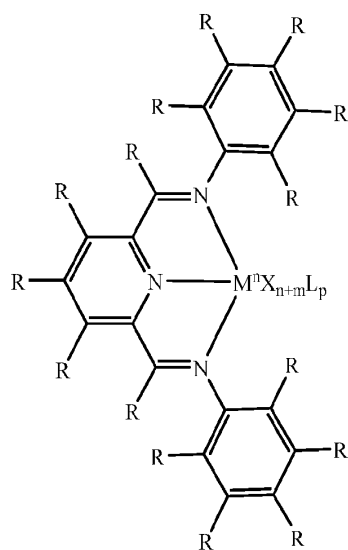
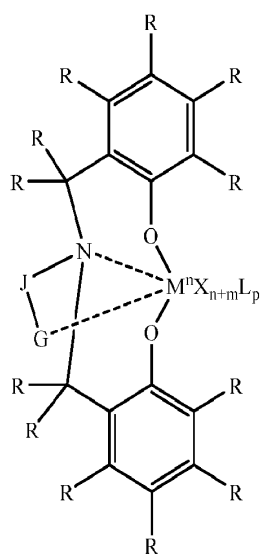
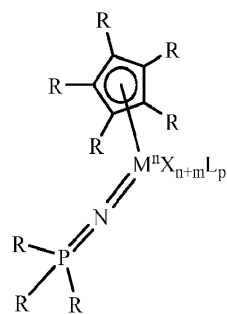
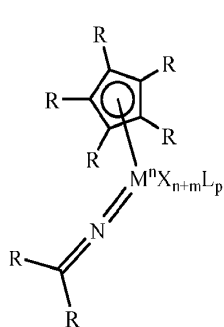
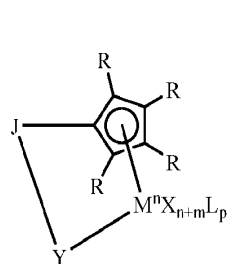


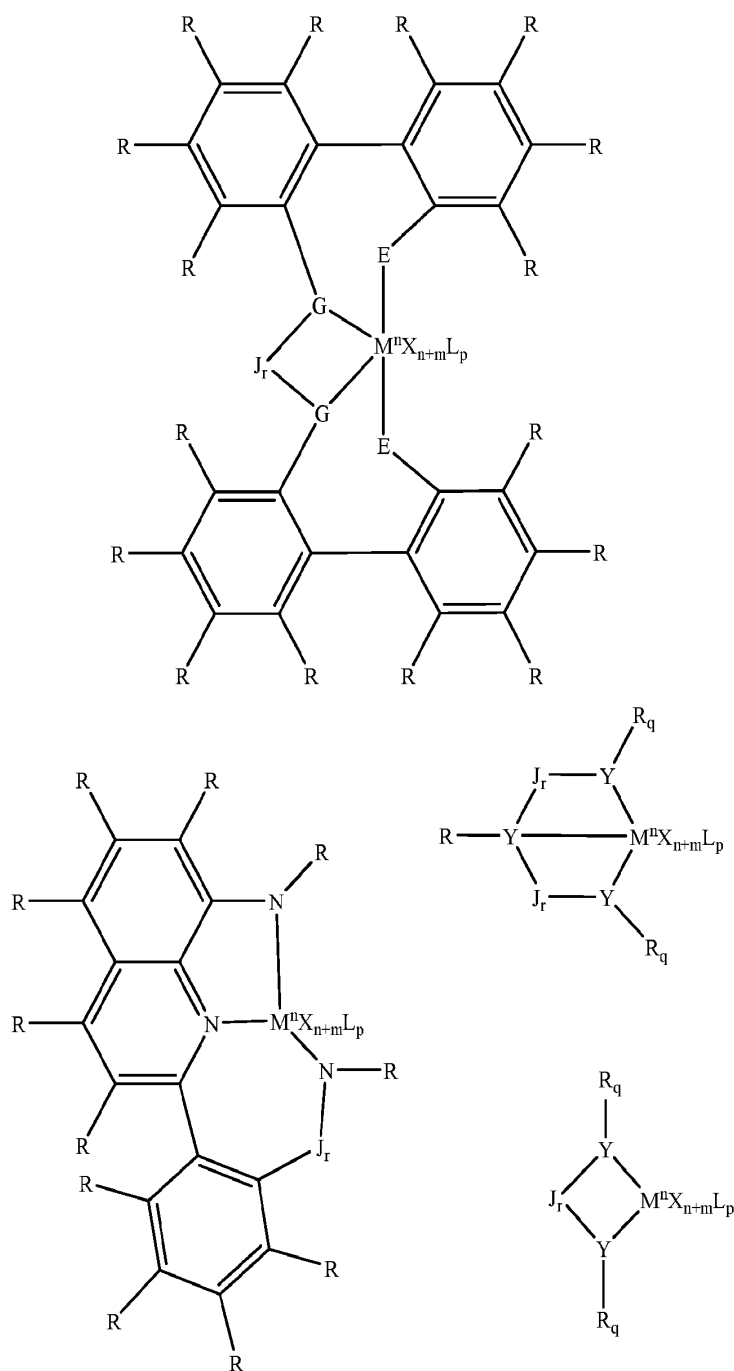
(XIX)

wherein M is a Group 4 metal, such as zirconium, titanium, or hafnium. In at least one

10 embodiment, M is zirconium. Each of L, Y, and Z may be a nitrogen. Each of R^1 and R^2 may be $-CH_2-CH_2-$. R^3 may be hydrogen, and R^6 and R^7 may be absent.

[0099] In certain embodiments, the catalyst may be represented by one of the following formulae:



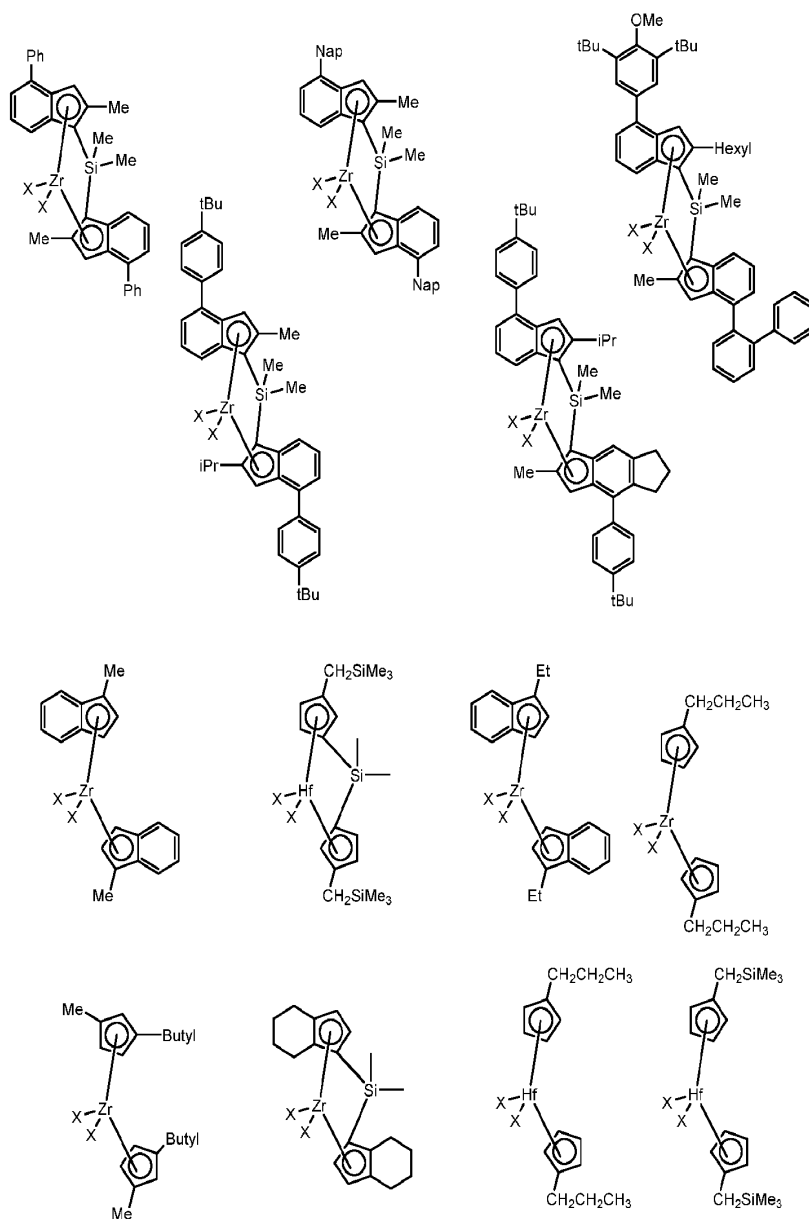


where R is independently H, hydrocarbyl, substituted hydrocarbyl, a halide, a substituted heteroatom group or SiR_3 ; R may be combined together to form a ring; when there is an aromatic ring present, any one or more of the ring C-R may be substituted to form a

5 heterocyclic ring; G is a neutral Lewis Base derived from substituted OR, SR, NR_2 , or PR_2 groups; E is O, S, NR, or PR; Y is either G or E; J is independently a formal diradical O, S,

NR, PR, CR₂, SiR₂; L is a formally neutral ligand or Lewis acid; X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion into a metal hydrocarbyl group; M is a group 3-12 metal; n is the formal oxidation state of the metal between 0 and 6; m is the sum of the formal anionic charges on the non-X ligands, between -1 and -6; p = 0 to 4; r = 1 to 20; k = 1 to 4.

[0100] In certain aspects, the catalyst compound comprises one or more of the following metallocenes or their isomers:



wherein X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion

into a metal hydrocarbyl group.

[0101] In at least one embodiment, the maximum amount of alumoxane is up to a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum alumoxane-to-catalyst-compound is a 1:1 molar ratio. Alternate preferred ranges include from 1:1 to 500:1, alternately from 1:1 to 200:1, alternately from 1:1 to 100:1, or alternately from 1:1 to 50:1.

Catalyst System

[0102] Embodiments of the present disclosure include methods for preparing a catalyst system including contacting in an aliphatic solvent the supported alumoxane with at least one catalyst compound having a Group 3 through Group 12 metal atom or lanthanide metal atom. The catalyst compound having a Group 3 through Group 12 metal atom or lanthanide metal atom can be a metallocene catalyst compound comprising a Group 4 metal.

[0103] In at least one embodiment, the supported alumoxane is heated prior to contact with the catalyst compound.

[0104] The supported alumoxane can be slurried in an aliphatic solvent and the resulting slurry is contacted with a solution of at least one catalyst compound. The catalyst compound can also be added as a solid to the slurry of the aliphatic solvent and the SMAO. In at least one embodiment, the slurry of the supported alumoxane is contacted with the catalyst compound for a period of time from about 0.02 hours to about 24 hours, such as from about 0.1 hours to about 1 hour, 0.2 hours to 0.6 hours, 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

[0105] In at least one embodiment of the present disclosure, one or more catalyst compounds have a loading of between 1 and 1,000 micromoles of precatalyst per gram of supported catalyst. In preferred embodiment, one or more catalyst compounds have a loading of between 1 and 100 micromoles of precatalyst per gram of supported alumoxane. In an even more preferred embodiment, one or more catalyst compounds have a loading of between 1 and 50 micromoles of precatalyst per gram of supported alumoxane.

[0106] In at least one embodiment of the present disclosure, the catalyst system used in the polymerization comprises alumoxane at a molar ratio of aluminum to transition metal of a catalyst compound of less than 2000:1, preferably 50:1 to 1000:1, preferably 75:1 to 500:1, preferably 85:1 to 250:1; preferably 95:1 to 175:1, such as 85:1 to 125:1.

[0107] The mixture of the catalyst compound and the supported alumoxane may be heated to from about 0 degrees Celsius to about 70 degrees Celsius, such as from about 23

degrees Celsius to about 60 degrees Celsius, for example room temperature. Contact times may be from about 0.02 hours to about 24 hours, such as from about 0.1 hours to 1 hour, 0.2 hours to 0.6 hours, 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

[0108] As set forth above, suitable aliphatic solvents are materials in which all of the reactants used herein, e.g., the supported alumoxane and the catalyst compound, are at least partially soluble and which are liquid at reaction temperatures. Non-limiting example solvents are non-cyclic alkanes with formula $C_nH_{(n+2)}$ where $n = 4-30$, such as isobutane, butane, isopentane, hexane, n-heptane, octane, nonane, decane and the like, and cycloalkanes with formula C_nH_n where $n = 5-30$, such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane and the like. Suitable aliphatic solvents also include mixtures of any of the above.

[0109] The solvent can be charged into a reactor, followed by a supported alumoxane. Catalyst can then be charged into the reactor, such as a solution of catalyst in an aliphatic solvent or as a solid. The mixture can be stirred at a temperature, such as room temperature. Additional solvent may be added to the mixture to form a slurry having a desired consistency, such as from about 2 cc/g of silica to about 20 cc/g silica, such as about 4 cc/g. The solvent is then removed. Removing solvent dries the mixture and may be performed under a vacuum atmosphere, purged with inert atmosphere, heating of the mixture, or combinations thereof. For heating of the mixture, any suitable temperature can be used that evaporates the aliphatic solvent. It is to be understood that reduced pressure under vacuum will lower the boiling point of the aliphatic solvent depending on the pressure of the reactor. Solvent removal temperatures can be from about 10 degrees Celsius to about 200 degrees Celsius, such as from about 60 degrees Celsius to about 140 degrees Celsius, such as from about 60 degrees Celsius to about 120 degrees Celsius, for example about 80 degrees Celsius or less, such as about 70 degrees Celsius or less. In at least one embodiment, removing solvent includes applying heat, applying vacuum, and applying nitrogen purged from bottom of the vessel by bubbling nitrogen through the mixture. The mixture is dried.

Polymerization Processes

[0110] Embodiments of the present disclosure include polymerization processes where monomer (such as ethylene, or propylene), and optionally comonomer (such as ethylene, propylene, 1-butene, 1-hexene, 1-octene) are contacted with a catalyst system comprising at least one catalyst compound and a supported alumoxane. At least one catalyst compound and supported alumoxane may be combined in any order, and are combined typically prior to

contact with the monomer. In at least one embodiment of the present disclosure, contact between at least one catalyst compound and a supported alumoxane may occur almost immediately prior to injecting the catalyst in the reactor.

[0111] In at least one embodiment of the present disclosure, a method includes
5 polymerizing olefins to produce a polyolefin composition by contacting at least one olefin with a catalyst system of the present disclosure and obtaining the polyolefin composition. Polymerization processes of the present disclosure can be carried out in any suitable manner. Any suitable solution, slurry or gas phase polymerization process can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Polymerization may be
10 conducted at a temperature of from about 0°C to about 300°C, at a pressure in the range of from about 0.35 MPa to about 10 MPa.

[0112] Monomers useful herein include substituted or unsubstituted C₂ to C₄₀ alpha olefins, preferably C₂ to C₂₀ alpha olefins, preferably C₂ to C₁₂ alpha olefins, preferably ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene,
15 dodecene and isomers thereof. In a preferred embodiment, olefins include a monomer that is propylene and one or more optional comonomers comprising one or more ethylene or C₄ to C₄₀ olefin, preferably C₄ to C₂₀ olefin, or preferably C₆ to C₁₂ olefin. The C₄ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₄ to C₄₀ cyclic olefin may be strained or unstrained, monocyclic or polycyclic, and may include one or more heteroatoms and/or one or
20 more functional groups. In another preferred embodiment, olefins include a monomer that is ethylene and an optional comonomer comprising one or more of C₃ to C₄₀ olefin, preferably C₄ to C₂₀ olefin, or preferably C₆ to C₁₂ olefin. The C₃ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₃ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may include heteroatoms and/or one or more functional groups.

[0113] Exemplary C₂ to C₄₀ olefin monomers and optional comonomers include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted
25 derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and substituted derivatives thereof, preferably norbornene, norbornadiene, and
30 dicyclopentadiene.

[0114] In at least one embodiment, one or more dienes are present in a polymer produced herein at up to about 10 weight %, such as from about 0.00001 to about 1.0 weight %, such as from about 0.002 to about 0.5 weight %, such as from about 0.003 to about 0.2 weight %, based upon the total weight of the composition. In at least one embodiment, about 500 ppm or less of diene is added to the polymerization, such as about 400 ppm or less, such as about 300 ppm or less. In at least one embodiment, at least about 50 ppm of diene is added to the polymerization, or about 100 ppm or more, or 150 ppm or more.

[0115] Diolefin monomers include any hydrocarbon structure, preferably C₄ to C₃₀, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). In at least one embodiment, the diolefin monomers are linear di-vinyl monomers, such as those containing from 4 to 30 carbon atoms. Non-limiting examples of dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than 1,000 g/mol). Non-limiting example cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[0116] In at least one embodiment, where butene is the comonomer, the butene source may be a mixed butene stream comprising various isomers of butene. The 1-butene monomers are expected to be preferentially consumed by the polymerization process as compared to other butene monomers. Use of such mixed butene streams will provide an economic benefit, as these mixed streams are often waste streams from refining processes, for example, C₄ raffinate streams, and can therefore be substantially less expensive than pure 1-butene.

[0117] Hydrogen, may be added to a reactor for molecular weight control of polyolefins. In at least one embodiment, the hydrogen is present in the polymerization reactor between 0

and 30 mol%. In a preferred embodiment, hydrogen is present in the polymerization reactor between 0 and 10 mol%. In a more preferred embodiment, hydrogen is present in the polymerization reactor between 0 and 1 mol%. In an even more preferred embodiment, hydrogen is present in the polymerization reactor between 0 and 0.2 mol%.

5 [0118] In a preferred embodiment, little or no scavenger (e.g., of oxygen, water, and/or carbon dioxide) is used in the process to produce the polyolefin composition. Preferably, scavenger (such as trialkylaluminum or dialkylzinc) is present at zero mol%. Alternatively, the scavenger is present at a molar ratio of scavenger metal to transition metal of the catalyst of less than about 100:1, such as less than about 50:1, such as less than about 15:1, such as
10 less than about 10:1. Such scavengers can also be used as chain transfer agents in amounts > 10:1 scavenger metal: transition metal.

[0119] In at least one embodiment of the present disclosure, a method includes polymerizing olefins in the presence of hydrocarbons. Useful hydrocarbons include C₂-C₂₀ hydrocarbons. Preferred hydrocarbons are contain between three and twelve carbons. Even
15 more preferred hydrocarbons contain between three and six carbons. Examples of preferred hydrocarbons include, but are not limited to propane, butane, isobutane, isopentane, pentane, cyclopentane, isohexane, and hexane.

[0120] Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired polyolefins. Typical temperatures and/or pressures include a
20 temperature from about 0°C to about 300°C, such as from about 20°C to about 200°C, such as from about 35°C to about 150°C, such as from about 40°C to about 120°C, such as from about 65°C to about 95°C; and at a pressure from about 0.35 MPa to about 10 MPa, such as from about 0.45 MPa to about 6 MPa, or preferably from about 0.5 MPa to about 4 MPa.

[0121] In at least one embodiment of the present disclosure, the polymerization takes
25 place in one or more "reaction zones." A "reaction zone", also referred to as a "polymerization zone", is a vessel where polymerization takes place, for example a batch or continuous reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is
30 considered as a separate polymerization zone. In another embodiment, a series of polymerization zones encompass a gradient of temperature, solvent, or monomer concentration within one reactor body.

[0122] Gas phase polymerization: Generally, in a fluidized gas bed process used for

producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. In some embodiments, the reaction medium includes condensing agents, which are typically non-coordinating inert liquids that are converted to gas in the polymerization processes, such as isopentane, isohexane, or isobutane. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See, for example, US Patents 4,543,399; 4,588,790; 5,028,670; 5,317,036; 5,352,749; 5,405,922; 5,436,304; 5,453,471; 5,462,999; 5,616,661; and 5,668,228; all of which are fully incorporated herein by reference.)

[0123] Slurry phase polymerization: A slurry polymerization process generally operates between 1 to about 50 atmosphere pressure range (15 psi to 735 psi, 103 kPa to 5,068 kPa) or even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which monomer and comonomers, along with catalysts, are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used, the process should be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

Polymer Products

[0124] The present disclosure also relates to polymer products, e.g., polyolefin compositions, such as resins, produced by the catalyst systems of the present disclosure. Polymer products of the present disclosure can have no detectable aromatic solvent. Alternatively, the polymer products of the present disclosure may be substantially free of aromatic solvent, e.g., less than about 0.1 wt% of solvent based on the weight of the polymer product, such as less than about 1 ppm.

[0125] In at least one embodiment, a process includes utilizing a catalyst system of the present disclosure to produce propylene homopolymers or propylene copolymers, such as propylene-ethylene and/or propylene-alphaolefin (preferably C₃ to C₂₀) copolymers (such as

propylene-hexene copolymers or propylene-octene copolymers) having an Mw/Mn of greater than about 2, such as greater than about 3, such as greater than about 4, such as greater than about 5.

[0126] In at least one embodiment, a process includes utilizing a catalyst system of the present disclosure to produce olefin polymers, preferably polyethylene and polypropylene homopolymers and copolymers. In at least one embodiment, the polymers produced herein are homopolymers of ethylene or copolymers of ethylene preferably having from about 0 and 25 mol% of one or more C₃ to C₂₀ olefin comonomer (such as from about 0.5 and 20 mol%, such as from about 1 to about 15 mol%, such as from about 3 to about 10 mol%). Olefin comonomers may be C₃ to C₁₂ alpha-olefins, such as one or more of propylene, butene, hexene, octene, decene, or dodecene, preferably propylene, butene, hexene, or octene. Olefin monomers may be one or more of ethylene or C₄ to C₁₂ alpha-olefin, preferably ethylene, butene, hexene, octene, decene, or dodecene, preferably ethylene, butene, hexene, or octene.

[0127] Polymers produced herein may have an Mw of from about 5,000 to about 10,000,000 g/mol (such as from about 25,000 to about 750,000 g/mol, such as from about 50,000 to about 500,000 g/mol), and/or an Mw/Mn of from about 2 to about 50 (such as from about 2.5 to about 20, such as from about 3 to about 10, such as from about 4 to about 5).

[0128] Polymers produced herein may have a melt index (MI) (I₂) of less than about 400 g/10 min., such as less than about 100. Additionally or alternatively, polymers produced herein may have a high load melt index to melt index (HLMI/MI) ratio of from about 12 to about 100, such as about 15 to about 50.

[0129] Polymers produced herein may have a (g'vis) of greater than about 0.900, such as greater than 0.955, such as greater than 0.995.

[0130] Polymers produced herein may have a density of about 0.920 g/cm³, about 0.918 g/cm³, about 0.880 g/cm³, or ≥ about 0.910 g/cm³, e.g., ≥ about 0.919 g/cm³, ≥ about 0.92 g/cm³, ≥ about 0.930 g/cm³, ≥ about 0.932 g/cm³. Additionally, the polyethylene composition may have a density ≤ about 0.965 g/cm³, e.g., ≤ about 0.945 g/cm³, ≤ about 0.940 g/cm³, ≤ about 0.937 g/cm³, ≤ about 0.935 g/cm³, ≤ about 0.933 g/cm³, or ≤ about 0.930 g/cm³. Ranges expressly disclosed include, but are not limited to, ranges formed by combinations any of the above-enumerated values, e.g., about 0.880 to about 0.965 g/cm³, 0.920 to 0.930 g/cm³, 0.925 to 0.935 g/cm³, 0.920 to 0.940 g/cm³, etc.

Blends

[0131] In at least one embodiment, the polymer (such as polyethylene or polypropylene)

produced herein and having no detectable aromatic solvent is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers, which may or may not contain a detectable amount of aromatic solvent, include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic
5 polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM,
10 block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

[0132] In at least one embodiment, the polymer (such as polyethylene or polypropylene)
15 is present in the above blends, at from about 10 to about 99 wt%, based upon the weight of total polymers in the blend, such as from about 20 to about 95 wt%, such as from about 30 to about 90 wt%, such as from about 40 to about 90 wt%, such as from about 50 to about 90 wt%, such as from about 60 to about 90 wt%, such as from about 70 to about 90 wt%.

[0133] Blends of the present disclosure may be produced by mixing the polymers of the
20 present disclosure with one or more polymers (as described above), by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

[0134] Blends of the present disclosure may be formed using conventional equipment and
25 methods, such as by dry blending the individual components, such as polymers, and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending
30 powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™

1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; mixtures thereof, and the like.

[0135] In at least one embodiment, a polyolefin composition, such as a resin, that is a multi-modal polyolefin composition comprises a low molecular weight fraction and/or a high molecular weight fraction. In at least one embodiment, the polyolefin composition produced by a catalyst system of the present disclosure has a comonomer content from about 3 wt% to about 15 wt%, such as from about 4 wt% and about 10 wt%, such as from about 5 wt% to about 8 wt%. In at least one embodiment, the polyolefin composition produced by a catalyst system of the present disclosure has a polydispersity index of from about 2 to about 6, such as from about 2 to about 5.

Films

[0136] Any of the foregoing polymers, such as the foregoing polyethylenes or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any suitable extrusion or coextrusion techniques, such as a blown bubble film processing technique, where the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or a double bubble process and may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene then optionally the combination could be oriented even further. Typically the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio

of up to 15, preferably 7 to 9. However, in another embodiment, the film is oriented to the same extent in both the MD and TD directions.

[0137] The films may vary in thickness depending on the intended application; however, films of a thickness from 1 μm to 50 μm may be suitable. Films intended for packaging are usually from 10 μm to 50 μm thick. The thickness of the sealing layer is typically 0.2 μm to 50 μm . There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

[0138] In another embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In a preferred embodiment, one or both of the surface layers is modified by corona treatment.

[0139] The polymer produced herein may be combined with one or more additional polymers prior to being formed into a film, molded part, or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired.

[0140] Overall, it has been discovered that an alumoxane precursor, which is easy to store and ship, can be used to form supported alumoxane precursor and supported alumoxane. The shelf lives of the alumoxane precursor and the supported alumoxane precursor are longer than that of MAO, which is an intermediate product in conventional methods for forming supported alumoxane.

30

Experimental Section

GPC 4D Procedure: Molecular Weight, Comonomer Composition and Long Chain Branching Determination by GPC-IR Hyphenated with Multiple Detectors

[0141] The distribution and the moments of molecular weight (M_w , M_n , M_w/M_n , etc.), the comonomer content (C_2 , C_3 , C_6 , etc.) and the long chain branching (g'_{vis}) are determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10 μ m Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1 μ m Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min and the nominal injection volume is 200 μ L. The whole system including transfer lines, columns, detectors are contained in an oven maintained at 145°C. Given amount of polymer sample is weighed and sealed in a standard vial with 80 μ L flow marker (Heptane) added to it. After loading the vial in the autosampler, polymer is automatically dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for most PE samples or 2 hour for PP samples. The TCB densities used in concentration calculation are 1.463 g/ml at room temperature and 1.284 g/ml at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples.

[0142] The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation: $c = \beta I$ where β is the mass constant determined with PE or PP standards. The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

[0143] The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M. The MW at each elution volume is calculated with following equation.

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1} \log M_{PS}$$

where the variables with subscript “PS” stands for polystyrene while those without a subscript are for the test samples. In this method, $a_{PS} = 0.67$ and $K_{PS} = 0.000175$ while a and K are calculated from a series of empirical formula established in ExxonMobil and published in literature (T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001)). Specifically, $a/K = 0.695/0.000579$ for PE and 0.705/0.0002288 for PP.

[0144] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR.

10 **[0145]** The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (M) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, *LIGHT SCATTERING FROM POLYMER SOLUTIONS*, Academic Press, 1971):

$$\frac{K_0 c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c$$

15 Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the IR5 analysis, A_2 is the second virial coefficient. $P(\theta)$ is the form factor for a monodisperse random coil, and K_0 is the optical constant for the system:

$$K_0 = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

20 where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 665$ nm.

[0146] A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$[\eta] = \eta_s / c$$

30 where c is concentration and was determined from the IR5 broadband channel output. The viscosity MW at each point is calculated from the below equation:

$$M = K_{PS} M^{\alpha_{PS}+1} / [\eta].$$

[0147] The branching index (g'_{vis}) is calculated using the output of the GPC-IR5-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

- 5 where the summations are over the chromatographic slices, i , between the integration limits. The branching index g'_{vis} is defined as:

$$g'_{vis} = \frac{[\eta]_{avg}}{k M_v^\alpha}$$

- where M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis and the K and α are for the reference linear polymer which is usually PE with
 10 certain amount of short chain branching. For GPC analyses, the concentration is expressed in g/cm^3 , molecular weight is expressed in $g/mole$, and intrinsic viscosity is expressed in dL/g unless otherwise noted.

- [0148] Composition distribution breadth index (CDBI) is defined as the weight percent of the ethylene interpolymer molecules having a comonomer content within 50 percent of the
 15 median total comonomer content.”). For details of determining the CDBI or solubility distribution branch index (SDBI) of a copolymer, see, for example, PCT Patent Publication WO 1993/003093, published Feb. 18, 1993.

[0149] Three co-monomer distribution ratios are also defined on the basis of the % weight co-monomer, denoted as CDR-1,w, CDR-2,w, CDR-3,w, as follows:

$$CDR-1,w = \frac{w2(Mz)}{w2(Mw)}$$

20

$$CDR-2,w = \frac{w2(Mz)}{w2\left(\frac{Mw + Mn}{2}\right)}$$

$$CDR-3,w = \frac{w2\left(\frac{Mz + Mw}{2}\right)}{w2\left(\frac{Mw + Mn}{2}\right)}$$

- where $w2(Mz)$ is the % weight co-monomer signal corresponding to a molecular weight of Mz , $w2[(Mw+Mn)/2]$ is the % weight co-monomer signal corresponding to a molecular
 25 weight of $(Mw+Mn)/2$, where Mw is the weight average molecular weight and Mn the

number average molecular weight and $w2[(Mz+Mw)/2]$ is the % weight co-monomer signal corresponding to a molecular weight of $Mz+Mw/2$.

[0150] Accordingly, the co-monomer distribution ratios can be also defined utilizing the % mole co-monomer signal, CDR-1,m, CDR-2,m, CDR-3,m, as

$$CDR-1,m = \frac{x2(Mz)}{x2(Mw)}$$

5

$$CDR-2,m = \frac{x2(Mz)}{x2\left(\frac{Mw + Mn}{2}\right)}$$

$$CDR-3,m = \frac{x2\left(\frac{Mz + Mw}{2}\right)}{x2\left(\frac{Mw + Mn}{2}\right)}$$

[0151] The reversed-co-monomer index (RCI,m) may also be computed from $x2$ (mol% co-monomer C_3 , C_4 , C_6 , C_8 , etc.), as a function of molecular weight, where $x2$ is obtained from the following expression in which n is the number of carbon atoms in the comonomer (3 for C_3 , 4 for C_4 , 6 for C_6 , etc.):

$$x2 = -\frac{200 w2}{-100 n - 2 w2 + n w2}$$

[0152] Then the molecular-weight distribution, $W(z)$ where $z = \log_{10} M$, is modified to $W'(z)$ by setting to 0 the points in W that are less than 5% of the maximum of W ; this is to effectively remove points for which the S/N in the composition signal is low. Also, points of W' for molecular weights below 2000 gm/mole are set to 0. Then W' is renormalized so that

15

$$1 = \int_{-\infty}^{\infty} W' dz$$

and a modified weight-average molecular weight (M_w') is calculated over the effectively reduced range of molecular weights as follows:

20

$$M_w' = \int_{-\infty}^{\infty} 10^z * W' dz.$$

The RCI,m is then computed as

$$RCI_m = \int_{-\infty}^{\infty} x^2 (10^z - M_w') W' dz.$$

[0153] A reversed-co-monomer index (RCI_w) is also defined on the basis of the weight fraction co-monomer signal ($w_2/100$) and is computed as follows:

$$RCI_w = \int_{-\infty}^{\infty} \frac{w_2}{100} (10^z - M_w') W' dz.$$

- 5 [0154] Note that in the above definite integrals the limits of integration are the widest possible for the sake of generality; however, in reality the function is only integrated over a finite range for which data is acquired, considering the function in the rest of the non-acquired range to be 0. Also, by the manner in which W' is obtained, it is possible that W' is a discontinuous function, and the above integrations need to be done piecewise.

10 Temperature Rising Elution Fractionation (TREF)

- [0155] Temperature Rising Elution Fractionation (TREF) analysis was done using a Crystallization Elution Fractionation (CEF) instrument from Polymer Char, S.A., Valencia, Spain. The principles of CEF analysis and a general description of the particular apparatus used are given in the article Monrabal, B. et al. (2007) "Crystallization Elution Fractionation. A New Separation Process for Polyolefin Resins," *Macromol. Symp.*, v.257, pg. 71. In particular, a process conforming to the "TREF separation process" shown in Figure 1a of this article, in which $F_c=0$, was used. Pertinent details of the analysis method and features of the apparatus used are as follows.

- [0156] The solvent used for preparing the sample solution and for elution was 20 1,2-Dichlorobenzene (ODCB) filtered using a 0.1- μ m Teflon filter (Millipore). The sample (6–16 mg) to be analyzed was dissolved in 8 ml of ODCB metered at ambient temperature by stirring (Medium setting) at 150°C for 90 minutes. A small volume of the polymer solution was first filtered by an inline filter (stainless steel, 10 μ m), which is back-flushed after every filtration. The filtrate was then used to completely fill a 200- μ l injection-valve loop. The 25 volume in the loop was then introduced near the center of the CEF column (15-cm long SS tubing, 3/8" o.d., 7.8 mm i.d.) packed with an inert support (SS balls) at 140°C, and the column temperature was stabilized at 125°C for 20 minutes.

- [0157] The sample volume was then allowed to crystallize in the column by reducing the temperature to 0°C at a cooling rate of 1°C/min. The column was kept at 0°C for 10 minutes 30 before injecting the ODCB flow (1 ml/min) into the column for 10 minutes to elute and measure the polymer that did not crystallize (soluble fraction). The wide-band channel of the

infrared detector used (Polymer Char IR5) generates an absorbance signal that is proportional to the concentration of polymer in the eluting flow. A complete TREF curve was then generated by increasing the temperature of the column from 0 to 140°C at a rate of 2°C/min while maintaining the ODCB flow at 1 ml/min to elute and measure the concentration of the dissolving polymer.

¹H NMR

[0158] ¹H NMR data of the polymers were collected at 120°C using a 10 mm cryoprobe on a 600 MHz Bruker spectrometer with 1,1,2,2-tetrachloroethane-d₂ (tce-d₂). Samples were prepped with a concentration of 30mg/mL at 140°C. Data was recorded with a 30° pulse, 5 second delay, 512 transients. Signals were integrated and the numbers of unsaturation types per 1,000 carbons and methyl branches per 1,000 carbons were reported. The shift regions for unsaturations and methyl branching were in the following table.

Species	Shift Region (ppm)	Number of hydrogens per structure	Calculation
Vinyl	4.95-5.10	2	(Vinyl/2)*1000/(total)
Vinylidene	4.70-4.84	2	(Vinylidene/2)*1000/(total)
Vinylene	5.31-5.55	2	(Vinylene/2)*1000/(total)
Trisubstituted	5.11-5.30	1	(trisub/1)*1000/(total)
Aliphatic	0-2.1	2	
Methyl	0.85-1.05	3	(Methyl/3)*1000/(aliphatic/2)
Total			Vinyl+vinylidene+vinylene+trisub*2+aliphatic/2

Additional Test Methods

[0159] Dynamic shear melt rheological data were measured with an Advanced Rheometrics Expansion System (ARES-G2) from TA Instruments using parallel plates (diameter = 25 mm) in a dynamic mode under nitrogen atmosphere. For all experiments, the rheometer was thermally stable at 190°C for at least 30 minutes before inserting compression-molded sample of resin onto the parallel plates. To determine the samples viscoelastic behavior, frequency sweeps in the range from 0.1 to 250 rad/s were carried out at a temperature of 190°C under constant strain. Depending on the molecular weight and temperature, strains in the linear deformation range verified by strain sweep test were used. A nitrogen stream was circulated through the sample oven to minimize chain extension or cross-linking during the experiments. All the samples were compression molded at 190°C. A sinusoidal shear strain is applied to the material if the strain amplitude is sufficiently small

the material behaves linearly. It can be shown that the resulting steady-state stress will also oscillate sinusoidally at the same frequency but will be shifted by a phase angle δ with respect to the strain wave. The stress leads the strain by δ . For purely elastic materials $\delta=0^\circ$ (stress is in phase with strain) and for purely viscous materials, $\delta=90^\circ$ (stress leads the strain by 90° although the stress is in phase with the strain rate). For viscoelastic materials, $0 < \delta < 90$.

5 [0160] MI, also referred to as I2, reported in g/10 min, was determined according to ASTM D1238, 190°C, 2.16 kg load. HLMI, also referred to as I21, reported in g/10 min was determined according to ASTM D1238, 190°C, 21.6 kg load. Density was determined in tables 4 and 6 accordance with ASTM D-792. Bulk density was measured in accordance with
10 ASTM D-1895 method B, of from 0.25 g/cm³ to 0.5 g/cm³.

[0161] Gel and defect analysis by OCS: The homogeneity of PE materials is characterized by an Optical Control System (OCS), from Southern Analytical, Inc (Houston, Texas 77073), according to an ExxonMobil internal method. The OCS consists of a small extruder, a cast film die, a chill roll unit, a winding system with good film tension control,
15 and an on-line camera system to examine the cast film generated for optical defects. For LLDPE, the typical extruder barrel temperature settings are between 190 to 215°C and the extruder speed was 50 RPM. The resulting melt temperatures are around 220°C. The winding roll speed was adjusted to obtain an average film thickness of 50 micron for defect analysis, and a total of 6 square meter of films was inspected to generated inspection report.
20 Key parameters include Total Defect Area in mm² and normalized Total Defect Area in PPM (mm²/m²), the number of defects per square meter (#/m²). To alleviate the impact of very small defects, especially on number of defects, only defects above a pre-set size limit, such as 200 microns for LLDPE, were reported. Such a TDA is denoted as TDA₂₀₀, typically in normalized form (PPM or mm²/m²). Similarly, the number of defects above 200 microns is
25 denoted as N₂₀₀ (1/m²).

[0162] Gauge, reported in mils, was measured using a HEIDENHAN Gauge Micrometer following ASTM D6988-13, apparatus C, method C. Film specimens are conditioned at 23°C +/- 2°C and 50 +/- 10% relative humidity in accordance with Procedure A of ASTM D618 (40 hour minimum) unless otherwise specified. For average gauge of a film roll,
30 twenty (20) readings were taken, with the location for each reading evenly distributed on the sample. For each film sample, ten film thickness data points were measured per inch of film as the film was passed through the gauge in a transverse direction. From these measurements, an average gauge measurement was determined and reported.

[0163] 1% Secant Modulus (M), reported in pounds per square inch (lb/in² or psi), was measured as specified by ASTM D-882-10.

[0164] Tensile Strength at Yield, Tensile Strength at Break, Ultimate Tensile Strength, Tensile Strength, and Tensile Strength at 50%, 100%, and/or 200% elongation as well as
5 Tensile Peak Load, Elongation at Yield and Elongation at Break (reported as %) are measured as specified by ASTM D-882.

[0165] Elmendorf Tear, reported in grams (g) or grams per mil (g/mil), was determined according to ASTM D-1922.

[0166] Dart Drop Impact or Dart Drop Impact Strength (DIS), reported in grams (g)
10 and/or grams per mil (g/mil), was measured as specified by ASTM D-1709, method A, unless otherwise specified.

[0167] Haze, reported as a percentage (%), was measured as specified by ASTM D-1003. Internal Haze, reported as a percentage (%), is the haze excluding any film surface contribution. The film surfaces are coated with ASTM approved inert liquids to eliminate
15 any haze contribution from the film surface topology. The internal haze measurement procedure is per ASTM D 1003.

[0168] Clarity is measured using Haze-Gard I haze meter (BYK-Gardner GmbH, Geretsried, Germany). It quantifies a film sample's narrow-angle scattering characteristics and is defined as the percentage of transmitted light passing through a film specimen that is
20 deflected at angles of less than 2.5 degree. Three specimen of 3"by 3" size were taken from different sections of the blown film, and the average values were reported. The film samples were conditioned at 23 ± 2°C and 50 ± 10% relative humidity for at least 40 hours prior to testing.

[0169] Seal Properties (Temperature) Procedure: Two layers of films of the polyolefin
25 composition, 1 mil gauge, were sealed on HSX-1 Heat Sealer in the TD direction at various temperatures under 73 psi (0.5 MPa or N/mm²) for 1 second. Once sealed film samples have cooled to room temp, test strips of 1 inch wide were cut then conditioned at 23° ± 2°C and 50±10% Relative Humidity for approximately 24 hours prior to testing on a United 6 Station. The testing is done in T-peel mode at 20 inch/min tensile speed. Three to five test specimens
30 were tested for each sealed specimen and the average seal force was recorded and used to generate a seal force vs. temperature curve. From the curve, the temperatures to reach 1N and 5N seal forces were determined as seal temperatures (also referred to as seal initiation temperatures), and the maximum seal force is also recorded as seal strength.

[0170] Peel-Break Transition Temperature Procedure: The peel-break transition temperature values of the polyolefin compositions were determined by the following procedure. In sealed sample testing, the failure modes of the specimens of the polyolefin compositions can be either peel or break, and generally, peel mode occurs when the sealing temperatures are low, and break mode occurs when the seal temperature reaches a sufficiently high level. Because sealed specimens were prepared at discrete temperatures, normally at 5°C step, several scenarios could happen. When all specimens fail in peel mode at one temperature but in break mode at the next higher temperature, peel-break transition temperature is defined as the average of the two temperatures. When the failure mode is mixed at a sealing temperature, and all specimens fail in peel mode at the temperature below it but in break mode at the temperature above it, the mixed failure mode temperature is taken as the peel-break temperature. When mixed mode failure occurs at two or more adjacent temperatures, the average of them is taken as the peel-break temperature.

[0171] Hot-Tack Test Procedures: After conditioning the film samples of the polyolefin compositions for 40 hours (minimum) at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $50 \pm 10\%$ relative humidity, 2.5 mil 3M/854 polyester film tape is applied to the back (or outside) of the film specimen as a backing, to test the "Inside to Inside" tack. The film sample with tape backing is cut into 1 inch wide and at least 16 inches long specimens, then sealed on J&B Hot Tack Testers 4000 under the standard conditions of 73 psi (0.5 MPa) Seal Pressure for 0.5 seconds, followed by a 0.4 second delay, then the sealed specimens were pulled at 200 mm/speed in T-joint peel mode. Four test specimens are measured at each temperature point and the average hot tack strength is recorded for each temperature point to generate a hot tack strength curve. From that curve, the temperatures to reach 1 N and 5 N tack forces are determined, as well as the maximum hot tack force. Hot tack window is defined as the temperature range where the hot tack is at or above 5 N, from the temperature at which the hot-tack first reaches 5 N to the temperature it eventually drops down to 5 N again.

[0172] Because of blown film samples are non-isotropic, some of the properties and descriptions encompass measurements in both the machine and transverse directions. Such measurements are reported separately, with the designation "MD" indicating a measurement in the machine direction, and "TD" indicating a measurement in the transverse direction.

[0173] Polymer properties reported in Table 9 were determined as reported above and summarized in the following table:

Test Name	Method
Melt Index (MI)	ASTM D-1238 2.16 kg (190°C) (I2) or (I2.16)
High Load Melt Index (HLMI)	ASTM D-1238 21.6 kg (190°C) (I21) or (I21.6)
Melt Index Ratio (MIR)	I ₂₁ /I ₂
Density	ASTM D1505, column density. Samples were molded under ASTM D4703-10a, Procedure C, then conditioned under ASTM D618-08 (23° ± 2°C and 50±10% Relative Humidity) for 40 Hours before testing
1% Secant Modulus; Tensile, and Elongation Properties	Modified ASTM D-882, sample conditioning*, 1" strip. * Samples conditioned according to ASTM D-882 for 40 hours at 23°±2°C and 50±10% Relative Humidity
Elmendorf Tear	ASTM D1922 with ASTM Conditioning for 40 Hours at 23° ± 2°C and 50±10% Relative Humidity
Dart Drop	Modified ASTM D-1709, Phenolic, Method A. Sample conditioning in the lab, calculation uses last 10 passes and 10 fails
Heat Seal	1 inch film strip of 1 mil gauge, sealed at various temperatures under 73 psi (0.5 N/mm ²) for 1 second. Following ASTM Conditioning for 40 Hours at 23° ± 2°C and 50±10% Relative Humidity, the sealed specimen were tested in T-joint peel mode at 20 inch/min pulling speed.
Hot tack	1 inch film strip of 1 mil gauge, sealed at various temperatures under either 1 or 5 N/mm ² for 0.5 second. After a 0.4 second delay, the sealed specimen were pulled at 200 mm/speed in T-joint peel mode.
Haze	ASTM D1003
Blocking	ASTM D3354

Examples

- [0174] Unless specified otherwise, all reagents were obtained from Aldrich Chemical Company. Methacrylic acid (MAA) was sparged with N₂ immediately prior to use. Anhydrous alkanes and toluene were sparged with N₂ then stored over dry 3 Å molecular sieves. ES70 Silica were obtained from PQ Corporation and dehydrated in a tube furnace under a stream of flowing N₂; the temperature of dehydration in degrees Celsius is indicated in brackets within the text. (1,3-Me, BuCp)₂ZrCl₂ (PreCat 1) was obtained from Grace Chemical and purified by crystallization from hexanes. Rac-Me₂Si(tetrahydroindenyl)₂ZrCl₂ was obtained from Grace Chemical and methylated with Grignard reagent to obtain rac-Me₂Si(tetrahydroindenyl)₂ZrMe₂ (PreCat 2). (PrCp)₂HfMe₂ (PreCat 3) was obtained from Boulder Scientific. MAO solution in toluene (30 wt%) was obtained from Grace Chemical.

XCATTM HP100 Catalyst is available from Univation Technologies.

Comparative 1. Reaction in Heptane.

[0175] A 500 mL 3-neck flask, equipped with a condenser and stirbar, was charged with heptane (35 mL) and trimethylaluminum (TMA) (5.0570 g, 70 mmol). A solution of methacrylic acid (MAA) (6.0341 g, 70 mmol) and heptane (50 mL) was added dropwise into the stirred TMA solution. After completion, the TMA/MAA solution turned cloudy.

[0176] A 1 L 3-neck flask, equipped with mechanical stirrer, condenser and a heating mantle, was charged with heptane (100 mL) and then stirred. ES70(200) (35.07 g) was added, followed by addition of the above TMA/MAA solution to the silica slurry. TMA/MAA flask was rinsed with heptane (10 mL) onto slurry and the mixture was stirred for 5 minutes. The mixture was stirred for approximately 16 hours. Next, TMA (10.0952 g, 140 mmol) was added to the mixture via pipette. The slurry was heated to reflux for 1 hour then allowed to cool to room temperature. The solids filtered then dried *in-vacuo* at 50°C for 3 hours to afford 57.74 g of comparative SMAO.

Comparative 1a. Catalyst from Comparative 1.

[0177] To an overhead stirred slurry of SMAO from Comparative 1 (2.04 g) and pentane (20 mL) was drop-wise added a solution of PreCat 1 (43.1 mg, 0.1 mmol) and pentane (5 mL) dropwise over the course of 5 minutes then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 1.5 g.

Comparative 2. Reaction in Toluene.

[0178] A 500 mL 3-neck flask, equipped with a condenser and stirbar, was charged with toluene (35 mL) and TMA (5.0595 g, 70 mmol). A solution of MAA (6.0339 g, 70 mmol) and toluene (50 mL) was added dropwise into the stirred TMA solution. After completion, the TMA/MAA solution turned cloudy.

[0179] A 1 L 3-neck flask, equipped with mechanical stirrer, condenser and a heating mantle, was charged with toluene (100 mL) and then stirred. ES70(200) (35.0191 g) was added, followed by addition of above TMA/MAA solution to the silica slurry. TMA/MAA flask was rinsed with toluene (10 mL) onto slurry and the mixture was stirred for 5 minutes. The mixture was stirred for approximately 16 hours. Next, TMA (10.0989 g, 140 mmol) was added to the mixture via pipette. The slurry was heated to 100°C for 1 hour then allowed to cool to room temperature. The solids filtered then dried *in-vacuo* at 70-80°C afford 59.72 g of comparative SMAO.

Comparative 2a. Catalyst from Comparative 2.

[0180] To an overhead stirred slurry of SMAO from Comparative Example 2 (2.04 g) and pentane (20 mL), a solution of PreCat 1 (43.7 mg, 0.1 mmol) and pentane (5 mL) was added dropwise over the course of 5 minutes then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 1.3 g.

Comparative 3. SMAO Preparation

[0181] ES70(875) (741 g) was added to a stirred solution of 30 wt% MAO in toluene (894 g) and toluene (1,800 g). The mixture was heated to 80°C for 3 hours then cooled to 25°C and dried for 60 hours. Yield was 1,012 g.

10 Comparative 3a. Catalyst from Comparative 3.

[0182] To an overhead stirred slurry of SMAO from Comparative Example 3 (50.0 g) and pentane (200 mL), a solution of PreCat 1 (0.865 g, 2.0 mmol) and pentane (5 mL) was added dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was about 50 g.

15 Comparative 3b. Catalyst from Comparative 3.

[0183] To an overhead stirred slurry of SMAO from Comparative Example 3 (50.0 g) and pentane (200 mL), a solution of PreCat 2 (0.914 g, 2.2 mmol) and pentane (10 mL) was added dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was about 50 g.

20 Comparative 3c. Catalyst from Comparative 3.

[0184] To an overhead stirred slurry of SMAO from Comparative 3 (50.0 g) and pentane (200 mL), a solution of PreCat 3 (0.845 g, 2 mmol) and pentane (5 mL) was added dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was about 50 g.

25 Comparative 4. SMAO Preparation

[0185] A 250 mL 3-neck flask equipped with a mechanical stirrer was placed in a cold bath at 0°C. To the flask, neat TMA (7.5055 g, 104 mmol) and pentane (48 mL) were added to make TMA solution. To the cold stirred solution of TMA, neat MAA (2.9895 g, 34.6 mmol) was added slowly at the rate of 0.3 mL / 12 s. After completion, the mixture was stirred for 20 minutes at cold temperature then warm to room temperature and stirred for further 20 minutes. An aliquot was removed, with the vinyl region of an ¹H NMR(C₆D₆) spectrum of the aliquot shown in Figure 1. ES70(875) 16.0147 g was added to the flask, then more pentane (10 mL) and the slurry was stirred for 20 minutes. The pentane was removed

under vacuum for 3 hours to afford the precursor to SMAO (yield 24.02 g). An aliquot of the precursor (3.5514 g) was placed inside a stainless-steel bomb, and heated at 120°C for 3 hours.

Comparative 4a. Catalyst from Comparative 4.

- 5 [0186] A supported catalyst was prepared from the SMAO from Comparative 4 in accordance with the procedure of Comparative 2a.

Example 1a. Representative Preparation of Precursor.

- [0187] A 3 L three-neck flask equipped with mechanical stirrer, addition funnel, and a very efficient condenser (similar to a dry-ice condenser – cooled with a cold-finger and
10 heptane to – 55°C) with takeoff adapter was charged with TMA (116.3 g, 1.61 mol) and pentane (700 mL) and stirred at 120 RPM. Next a solution of MAA (36.35 g, 0.42 mol) and pentane (300 mL) was added at a rate to maintain a controlled reflux. After addition, the reflux was maintained by gentle heating for 1 hour.

Example 1b. Representative SMAO Prep from Precursor.

- 15 [0188] To the precursor solution was added portion-wise ES70(200) silica (210.6 g). The slurry was stirred for 30 minutes. Then the pentane was removed by simple distillation. The flask was then equipped with a vacuum-jacketed Vigreux column and distillation head that exited to a cold trap. The flask was heated to an internal wall temperature of approximately 120°C and stirred for 5 hours and the volatiles were allowed to distill out into the cold trap.
20 Then, the solids were dried under vacuum at temperature for 3 hours. Yield was 293.2 g SMAO.

Example 1c. Representative Large Scale Catalyst Preparation.

- [0189] A 3 L three-neck flask equipped with mechanical stirrer was charged with Pentane (900 mL) and SMAO obtained from Ex. 1b (260.34 g) and stirred at 120 RPM. Then, a
25 solution of Precat 1 (4.4818 g, 10.6 mmol) and pentane (100 mL) was added via addition funnel over the course of 1 hour. After stirring an additional 2 hours, the slurry was filtered, returned to the stirrer equipped flask and the solid dried at 40°C with gentle stirring for 2 hours. Yield was 261.4 g white catalyst.

Examples 2 – 4.

- 30 [0190] For each of Examples 2 and 4, precursor, SMAO, and catalyst were prepared in accordance with the procedure of Ex. 1a, 1b, and 1c. For Ex. 3, precursor and SMAO were prepared in accordance with the procedure of Ex. 1a and 1b, and catalyst was prepared from the SMAO in accordance with the procedure of Example 5c except that the SMAO was

Soxhlet extracted with hexane for 6 hours then dried beforehand. Additional details of the catalysts prepared in Examples 2-4 are depicted in Table 2.

Example 5a. Representative Preparation of Concentrated Precursor.

[0191] A 3 L three-neck flask equipped with mechanical stirrer, addition funnel, and a very efficient condenser (similar to a dry-ice condenser – cooled with a cold-finger and heptane to – 55°C) with takeoff adapter was charged with TMA (90.85 g, 1.26 mol) and pentane (700 mL) and stirred for 15 minutes. Next a solution of MAA (36.17 g, 0.42 mol) and pentane (300 mL) was added at a rate to maintain a controlled reflux over the course of 60 minutes. After addition, the reflux was maintained by gentle heating for 1 hour. The pentane was removed by simple distillation to afford the MAO precursor as a colorless oil. The oil was stored at -45°C until use. Yield was 151 g. NMR analysis showed the oil contained 17.6 wt% pentane, and 2.88 equivalents MAA/g of oil. ¹H NMR(C₆D₆) of the concentrated precursor is shown in Figures 2 and 3. ¹H NMR(C₆D₆) of the concentrated precursor both before and after the addition of hemialkoxide Me₂Al(μ-Me)(μ-OCMe₂CMe=CH₂)AlMe₂ is shown in Figure 4.

Example 5b. Representative SMAO Prep from Concentrated Precursor.

[0192] A 250 mL 3-neck flask was equipped with mechanical stirrer, vacuum-jacketed Vigreux column and a distillation head connected to an efficient cold trap. The flask was charged with pentane (100 mL), TMA (1.611 mL, 16.8 mmol) and concentrated precursor oil (6.9784 g, 20.1 mmol equiv. of MAA) and stirred for 5 minutes. ES70(200) (10.03 g) was added to the stirred solution, then the slurry was stirred at room temperature for 30 minutes. The pentane was distilled from the slurry. The temperature was then raised such that the internal wall temperature of the flask was ca. 120°C. Heating was continued for 3 hours while the volatiles were allowed to distill away from the reaction then vacuum was applied for 2 hours. Yield was 13.9 g SMAO as a white solid.

Example 5c. Representative Small Scale Catalyst Preparation.

[0193] A solution of PreCat 3 (36.1 mg, 0.085 mmol) in pentane (5 mL) was added to an overhead stirred slurry of SMAO (2.0309 g) and pentane (25 mL). After 30 minutes, the slurry was filtered and the solid dried under vacuum for 1 hour. Yield was 1.82 g of white solid.

Example 6 – 12.

[0194] For each of Examples 6-10, precursor, SMAO, and catalyst were prepared in accordance with the procedure of Ex. 5a, 5b, and 5c. For Ex. 11, precursor and SMAO were

prepared in accordance with the procedure of Ex. 5a and 5b, and catalyst was prepared from the SMAO in accordance with the procedure of Example 5c except that the SMAO was Soxhlet extracted with hexane then dried beforehand. For Ex. 12, precursor and SMAO were prepared in accordance with the procedure of Ex. 5a and 5b, and catalyst was prepared from the SMAO in accordance with the procedure of Example 5c except that the SMAO was Soxhlet extracted with hexane then dried beforehand and the catalyst was prepared with approximately twice the amount of PreCat 3 used in Ex. 5c.

Example 13.

[0195] For Example 13, precursor, SMAO, and catalyst were prepared in accordance with the procedure of Ex. 5, except that the catalyst was isolated from the slurry by removing the solvent *in-vacuo* instead of by filtration.

Example 14a. Fluorided Alumina Silica (FAS) Preparation

[0196] A mixture of 6 wt% (NH₄)₂SiF₆ and 94 wt% of 5% Al on ES70 was fluidized with a stream of dry air and heated at 30 – 50°C/h up to 650°C, held for 3 hours, then cooled to ambient temperature then the air was removed with a N₂ purge.

Examples 14b.

[0197] FAS-SMAO was prepared in accordance with the procedure of Ex. 5b except substituting the FAS prepared in Ex. 14a in place of ES70, with additional details shown in Table 2.

Example 14c.

[0198] Catalyst was prepared from the FAS-SMAO of Ex. 14b in accordance with the procedure of Ex. 5c. Additional details of the catalyst prepared in Example 14c are depicted in Table 2.

Example 15a. Preparation and Characterization of [Me₂Al(μ-O₂CCMe=CH₂)]₂.

[0199] TMA (10.8 g; 150 mmol) in iso-hexane (50 mL) was cooled to -47°C with stirring. MAA (13.0 g; 150 mmol) was dissolved in isohexane (ca. 30 ml) and kept cold, just above the temperature that the MAA would begin to crystallize out. It was added dropwise in about 1 mL portions over about 30 minutes. A colorless precipitate formed. After the addition was finished the reaction was stirred 10 minutes at -47°C then warmed up. The precipitate redissolved except for some solid stuck to the side of the flask. About 25 mL of the solvent was evaporated off and the solution was decanted into a 100 mL flask and cooled to -47°C for about half an hour. A colorless crystalline solid formed and was isolated by decanting and dried under vacuum, probably about half the expected product. The

supernatant was dried down to a clear colorless liquid; iso-hexane (ca. 25 mL) was added and the mixture cooled to -24°C. A solid product (ca. 11 g) was obtained. A portion of the solid (0.662 g) was dissolved in isohexane (ca. 10 mL) and cooled to -24°C. The solution was concentrated to about 7 mL and cooled to -24°C. Most of the iso-hexane was removed and the sample redissolved in about 2 mL pentane and cooled to -24°C. Some crystals grew. One crystal was mounted on the crystal holder in the drybox by putting it in a small plastic straw filled with silicone grease, one end of the straw was attached to the crystal holder. This gave good diffraction. Crystallographic data for $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$ is shown in Table 1. An Ortep drawing for $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$ is shown in Figure 5. The ^1H NMR(C_6D_6) spectrum of the precursor solution is shown in Figure 6.

Table 1. Crystallographic data for $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$

Space Group	P-1
a (Å)	7.5427(15)
b (Å)	9.0267(18)
c (Å)	12.669(3)
α (deg)	84.28(3)
β (deg)	76.37(3)
γ (deg)	72.41(3)
Volume (Å ³)	798.7(3)
Cell Formula Units (Z)	2
Goodness of Fit on F ²	1.163

Example 15b. SMAO Preparation from $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$.

[0200] A 250 mL 3-neck flask was equipped with mechanical stirrer, and a vacuum-jacketed Vigreux column. The flask was charged with pentane (100 mL), a solution of $[\text{Me}_2\text{Al}(\mu\text{-O}_2\text{CCMe=CH}_2)]_2$ (2.8497 g, 10.0 mmol) and pentane (5 mL) then TMA (4.0955 g, 56.8 mmol). The mixture was heated to gentle reflux for 2 hours (stopper at top of column) then stirred overnight without heating. The mixture was slightly hazy. ES70(200) (10.04 g) was added, then the slurry was stirred at room temperature for 5 minutes. The pentane was distilled from the slurry. The temperature was then raised such that the internal wall temperature of the flask was ca. 120°C. Heating was continued for 3 hours while the volatiles were allowed to distill away from the reaction then vacuum was applied for 2 hours. Yield was 14.0 g SMAO in the form of a white solid.

Example 15c.

[0201] Catalyst was prepared from the SMAO of Ex. 15b in accordance with the procedure of Ex. 5c.

Example 16a. SMAO Preparation

- 5 [0202] A 2 L round bottom 3-neck flask equipped with mechanical stirrer, condenser and addition funnel was charged with pentane (135 mL) and TMA (19.3875 g, 268.8 mmol). A solution of methacrylic acid (6.0431 g, 70 mmol) and pentane (50 mL) was added dropwise over the course of 15 minutes. The reaction was heated to reflux for 1 hour then cooled to RT. ES70X(200) (35.05 g) was added to the stirred solution. Pentane was removed by
10 distillation through a jacketed Vigreux column. The flask was heated to 120°C. After 3 hours, vacuum was applied for 1 hour then the contents cooled to RT. Yield of SMAO was 49.8 g.

Example 16b. Catalyst Preparation

- [0203] To an overhead stirred slurry of SMAO from Example 16a (45.06 g) and pentane
15 (350 mL) was drop-wise added a solution of PreCat 3 (0.775 g, 1.83 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 41.8 g.

Example 17. Preparation of MAO Precursor

- [0204] A 2 L three-neck flask equipped with mechanical stirrer, addition funnel, and a
20 very efficient condenser (similar to a dry-ice condenser – cooled with a cold-finger and heptane to – 50°C) with takeoff adapter was charged with TMA (75.6978 g, 1.05 mol) and pentane (500 mL) then stirred for 10 minutes. Next a solution of MAA (30.1398 g, 0.35 mol) and pentane (250 mL) was added at a rate to maintain a controlled reflux. After addition, the reflux was maintained by gentle heating for 1 hour then the pentane was removed by simple
25 distillation yielding 113.6 g of a colorless oil. After accounting for CH₄ loss, and pentane residuals, the oil was calculated to be 3.16 mmol equivalents of MAA/g of oil.

Example 18a. SMAO Preparation

- [0205] A 2 L three-neck flask equipped with mechanical stirrer was charged with pentane
(200 mL) and TMA (4.244 g, 58.8 mmol), then Ex. 17 MAO Precursor (16.61 g, 58.8 mmol
30 equivalents of MAA). ES70X(200) silica (35.19 g) was added to the stirred solution. A vacuum jacketed Vigreux column was installed and connected with a solvent transfer manifold to a cold trap. Pentane was removed by distillation then the flask interior wall temperature raised to 120°C. After 3 hours, the volatiles were removed under vacuum for 1

hour then the heat was removed yielding 46.37 g of SMAO.

Example 18b. Catalyst Preparation

[0206] To an overhead stirred slurry of SMAO from Example 18 (43.18 g) and pentane (350 mL) was drop-wise added a solution of PreCat 3 (0.746 g, 1.75 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 41.3 g.

Example 19a. SMAO-ES70(550) Preparation

[0207] A 2 L round bottom 3-neck flask equipped with mechanical stirrer, condenser and addition funnel was charged with pentane (235 mL) and TMA (4.29 g, 58.8 mmol). ES70X(200) (35.14 g) was added to the stirred solution. A solution of MAA (0.609 g, 7 mmol) and pentane (50 mL) was added dropwise then the slurry stirred for 30 minutes. Next, a solution prepared from Example 2 MAO precursor (19.94 g, 63 mmol equiv. MAA), TMA (1.51 g, 21 mmol), and pentane (45 mL) was added to the stirred solution. Pentane was removed by distillation then the flask interior wall temperature raised to 120°C. After 3 hours, the volatiles were removed under vacuum for 1 hour then the heat was removed yielding 46.8 g of SMAO.

Example 19b. Catalyst Preparation

[0208] To an overhead stirred slurry of SMAO from Ex. 19a (43.07 g) and pentane (350 mL) was drop-wise added a solution of PreCat 3 (0.742 g, 1.75 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 40.03 g.

Example 20. Preparation of MAO Precursor

[0209] The procedure of Example 17 was followed employing TMA (75.71 g, 1.05 mol), MAA (30.13 g, 0.35 mol), yielding 115.5 g oil with 3.01 mmol equivalents of MAA/g of oil.

Example 21. SMAO Preparation

[0210] The procedure of Ex. 18a was followed employing TMA (4.25 g, 58.8 mmol), Ex. 5a MAO Precursor (23.31 g, 70 mmol equiv. of MAA), D948(600) (35.09 g). Yield was 49.1 g.

Example 21b. Catalyst Preparation

[0211] To an overhead stirred slurry of SMAO from Ex. 21a (45.12 g) and pentane (350 mL) was drop-wise added a solution of PreCat 1 (0.793 g, 1.83 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 42.0 g.

Example 22a. SMAO Preparation

[0212] The procedure of Ex. 18a was followed employing TMA (4.25 g, 58.8 mmol), Ex. 5a MAO Precursor (22.2 g, 70 mmol equiv. of MAA), ES70X(200) (35.06 g). Yield was 49.5 g.

5 Example 22b. Catalyst Preparation

[0213] To an overhead stirred slurry of SMAO from Ex. 22a (43.11 g) and pentane (350 mL) was drop-wise added a solution of PreCat 2 (0.717 g, 1.72 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 40.0 g.

10 Example 23a. SMAO Preparation

[0214] The procedure of Ex. 18a was followed employing TMA (2.6 g, 36.05 mmol), Ex. 2 MAO Precursor (22.21 g, 70 mmol equiv. of MAA), ES70(875) (35.17 g). Yield was 48.87 g.

Example 23b. Catalyst Preparation

15 [0215] To an overhead stirred slurry of SMAO from Ex. 23a (43.07 g) and pentane (350 mL) was drop-wise added a solution of PreCat 3 (0.746 g, 1.75 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 40.94 g.

Example 24a. SMAO Preparation

20 [0216] The procedure of Ex. 18a was followed employing TMA (4.25 g, 58.8 mmol), Ex. 5a MAO Precursor (23.3 g, 70 mmol equiv. of MAA), ES757(200) (35.17 g). Yield was 49.9 g.

Example 24b Catalyst Preparation

25 [0217] To an overhead stirred slurry of SMAO from Ex. 24a (45.12 g) and pentane (350 mL) was drop-wise added a solution of PreCat 3 (0.747 g, 1.75 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 38.7 g.

Example 25a. SMAO Preparation

30 [0218] The procedure of Ex. 18a was followed employing TMA (4.25 g, 58.8 mmol), Ex. 5a MAO Precursor (23.3 g, 70 mmol equiv. of MAA), ES70(200) (35.13 g). Yield was 50.09 g.

Example 25b. Catalyst Preparation

[0219] To an overhead stirred slurry of SMAO from Ex. 25a (45.02 g) and pentane

(350 mL) was drop-wise added a solution of PreCat 3 (0.769 g, 1.81 mmol) and pentane (50 mL) dropwise over the course of 1 hour then stirred for an additional hour then filtered and dried *in-vacuo*. Yield was 42.0 g.

Example 26. Catalyst Preparation

- 5 [0220] The procedure in Ex. 1a, 1b, and 1c was repeated twice to prepare 500 g of combined catalyst. This catalyst was blended with Aluminumdistearate (15.46 g) to make a 3 wt% mixture.

Salt Bed Gas-Phase Polymerization Screening.

- 10 [0221] A 2 L autoclave was charged, under N₂, with NaCl (350 g), TIBAL-SiO₂ scavenger (4 to 6 g of 1.9 mmol TIBAL / g ES70(100)) and heated for 30 min at ≥ 85°C. The reactor was cooled to ~81°C. 1-Hexene (1.5 mL) and 10% H₂ in N₂ (85 sccm) were added then the stirring was commenced (450 RPM). Solid catalyst (~ 10 mg) was injected into the reactor with ethylene (+1570 KPa). After the injection, the reactor temperature was controlled at 85°C and ethylene allowed to flow into the reactor to maintain pressure. Both
- 15 H₂ in N₂, and hexene were fed in ratio to the ethylene flow. The polymerization was halted after 60 minutes by venting the reactor. The polymer was washed with water to remove salt then dried. Data are reported in Tables 2 and 3.

Fluidized Bed Gas-Phase Polymerization Screening: 1.2 M Tall Reactor.

- 20 [0222] Polymerization was performed in a gas-phase fluidized bed reactor with straight (1.2 M, 0.1524 M diameter) and expanded (0.914 M, 0.0254 M diameter) sections. Feed and cycle gas were fed into the reactor body through a perforated distributor plate. Temperature was controlled by heating the cycle gas. Table 2 reports average process conditions, monomer and H₂ concentrations and product properties. The remainder of gas composition was isopentane (~ 2 mol %) and nitrogen.

- 25 [0223] Supported catalyst was dry blended with aluminumdistearate (3 wt%) and fed as a 10 wt% slurry in Sono Jell ® from Sonneborn (Parsippany, NJ). The slurry was delivered to the reactor by nitrogen and isopentane feeds in a 1/8" diameter catalyst probe. Polymer was collected from the reactor as necessary to maintain the desired bed weight. Data are reported in Tables 4 and 5.

- 30 Fluidized Bed Gas-Phase Polymerization Screening: 6.7 M Tall Reactor.

[0224] Polymerization was performed in a gas-phase fluidized bed reactor with straight (6.7 M, 0.3302 M diameter) and a wider conical expanded section. Feed and cycle gas were fed into the reactor body through a perforated distributor plate, and the reactor was controlled

at 290 psig and 64 mol% ethylene. Temperature was controlled by heating the cycle gas. Catalyst was fed as a 10 wt% slurry in Sono Jell with isopentane and nitrogen carrier flows to provide adequate dispersion in the reactor ed. Continuity additive (CA-300 from Univation Technologies) was co-fed into the reactor by a second carrier nozzle to the reactor bed, and
5 the feed rate of continuity additive was adjusted to maintain a weight concentration in the bed of between 20 and 40 ppm. Polymer comonomer composition was controlled by adjustment of the mass feed ratio of comonomer to ethylene, and MW of the polymer was controlled by adjustment of hydrogen concentration. CPol-10 was carried out with 3 wt% aluminumdistearate blended with the catalyst while CPol-11 was carried out with no
10 aluminumdistearate blended with the catalyst. Table 6. reports average process conditions, monomer and H₂ concentrations and product properties. Tables 7-9 report polymer characterization and film properties.

Compounding, Blending and Film Fabrication.

[0225] Polymer granules from the 6.7 M continuous reactor testing were first dry blended
15 in a tumble mixer with 500 ppm of Irganox™-1076, 1,000 ppm of Irgafos™ 168, and 600 ppm of Dynamar™ FX5920A. Then the mixture was compounded into pellet resins through simple melt mixing in a Coperion W&P 57 twin-screw extruder. The pellets were next fed into a 2.5" Gloucester film line equipped with a general purpose screw of 30:1 L:D (length to diameter ratio), a 6" oscillating die and a Saturn II air ring. The blown film die was set at
20 390°F and the target melt temperature was 410°F. Chilled air was used to cool the film bubble. A 23 inch frost-line height (FLH) was typical. The extruder speed was adjusted to deliver a target rate of 188 lb/hr, which is equivalent to an output rate of 10 lb/hr/in. The die gap employed was 60 mil and the blow-up ratio was 2.5, resulting in an approximate 23.5 inch film layflat. The line speed was adjusted to make film of 1 and 2 mil thickness. Details
25 on the extrusion process are given in Table 8 and film properties in Table 9.

Table 2. Lab gas-phase polymerization testing

Polymerization Example	Catalyst Example	Support	Equiv. MAA Loading (mmol/g)	Total TMA/MAA (mol/mol)	Prep from Concentrate	Support Mass (g)	Heating Time (h) at 120°C Open/Vac	SMAO Yield (g)	Average Productivity	Note
SPol-1	Comp 4a	ES70(875)	2	3	No	16.0147	NA	24.02	2,532*	Comparative heated in bomb
SPol-2	1c	ES70(200)	2	3.83	No	210.6	5/3	293.2	7,523	Large Scale Prep 1
SPol-3	2	ES70(200)	2	3.83	No	210.1	5/3	296.7	6,894	Large Scale Prep 2
SPol-4	3	ES70(200)	2	3.85	No	210	5/3	307.3	9,399	Extracted SMAO with Hexane
SPol-5	4	ES70X(200)	2	3.84	No	35.1	3/1	49.8	5,996	Larger Particle Size (50 μ m)
SPol-6	5c	ES70(200)	2	3.76	Yes	10.0	3/2	13.9	6,503	High TMA/MAA
SPol-7	6	ES70(200)	2	3.37	Yes	10.1	3/2	13.93	6,043	Medium TMA/MAA
SPol-8	7	ES70(200)	2	3	Yes	10.1	3/2	13.85	1,476	Low TMA/MAA
SPol-9	8	ES70(200)	2	3.82	Yes	10.0	0/6	13.21	2,897*	Vacuum during heating
SPol-10	9	ES70(200)	1.5	4.12	Yes	35.2	3/1	46.37	3,437	Lower MAA loading
SPol-11	10	ES70(875)	2	3.51	Yes	35.2	3/1	48.87	6,753	High Silica Dehydration Temp
SPol-12	11	PD14024	4	4	Yes	28.5	3/2	37.15	10,024*	High Surface Area
SPol-13	12	PD14024	4	4	Yes	28.5	3/2	37.15	9,942*	High Surface Area and Loading
SPol-14	13c	ES70(200)	2	3.83	Yes	10.0	3/2	13.9	7,936*	Catalyst Dried In-vacuo
SPol-15	14c	FAI-ES70(650)	2	3.22	Yes	10.0	3/2	13.71	11,016	Fluorided Silica Alumina
SPol-16	15c	ES70(200)	2	3.84	Yes	10	3/2	14.02	7,423*	[Me ₂ AlO ₂ C(Me)=CH ₂] ₂

1-Hexene (2.5 mL) and 10 mol % H₂ in N₂ (120 SCCM) were added then H₂ in N₂, and hexene were fed in at 0.5 mg/g and 0.1 g/g ratio to the ethylene flow respectively. Productivity is the average of two runs except where indicated. *Polymerizations were carried out once.

Table 3. Semi-batch polymerization testing in salt-bed reactor.

Ex	Catalyst	Precatalyst Mass (mg)	C ₆ Charge (mL)	10% H ₂ in N ₂ Charge (sccm)	H ₂ /C ₂ Feed Ratio (mg/g)	C ₆ /C ₂ Feed Ratio (g/g)	Yield (g)	Productivity (g Pol/g cat h)
SPol-C1	Comp-1a	23.9	1.5	85	0.25	0.06	3.2	134
SPol-C2	Comp-2a	23.8	1.5	85	0.25	0.06	7.9	332
SPol-17	16b	12.8	2.5	120	0.5	0.1	100.1	7820
SPol-18	18b	12.2	2.5	120	0.5	0.1	55.3	4533
SPol-19	19b	12.9	2.5	120	0.5	0.1	65.1	5047
SPol-20	21b	13.3	1.5	85	0.25	0.06	57.5	4323
SPol-21	22b	12.4	1.5	85	0.25	0.06	193.7	15621
SPol-22	23b	12	2.5	120	0.5	0.1	89.7	7475
SPol-23	24b	13.3	2.5	120	0.5	0.1	83.5	6278

Table 4 part 1. 1.2M Continuous Reactor Testing.

Example	CPol-C1	CPol-1	CPol-2	CPol-3
Catalyst	Comp 3c	16b	18b	19b
Reactor Temp (°C)	79.4	79.4	79.4	79.4
Rx. Pressure (KPa)	2,170	2,170	2,170	2,170
Avg Velocity (m/s)	0.46	0.44	0.44	0.46
C ₂ conc. (mol%)	70.8	70.1	69.9	70
C ₆ /C ₂ Ratio (mol/mol)	0.018	0.015	0.016	0.016
H ₂ /C ₂ Ratio (ppm/mol)	4.9	5.3	5.3	5.7
C ₂ flow (g/hr)	2,041	1,918	1,850	1,890
C ₆ /C ₂ Flow Ratio (g/g)	0.055	0.04	0.04	0.043
Hydrogen flow (sccm)	14.25	15.04	14.69	15.69
Avg. Bedweight (g)	2,352	2,349	2,316	2,414
Production (g/hr)	615	407	313	372
Residence Time (hr)	3.8	5.8	7.4	6.5
Catalyst Slurry Feed (ml/hr)	2.4	2.2	2.6	2.2
Cat productivity (g poly/g cat)	2,739	2,097	1,386	1,892
MI (g/10 min)	0.75	1.05	1.42	1.17
HLMI (g/10min)	18.74	23.97	30.71	24.95
HLMI/MI Ratio	24.89	22.85	21.63	21.42
Gradient Density (g/cm ³)	0.9192	0.9216	0.9217	0.9185
Bulk Density (g/cm ³)	0.3828	0.3682	0.3734	0.3646

Table 4 part 2. 1.2M Continuous Reactor Testing.

Example	CPol-4	CPol-5	CPol-6	CPol-7
Catalyst	19b	24b	25b	25b
Reactor Temp (°C)	73.9	79.4	87.8	73.9
Rx. Pressure (KPa)	2,170	2,170	2,170	2,170
Avg Velocity (m/s)	0.46	0.46	0.47	0.48
C ₂ conc. (mol%)	70.1	70	69.9	69.7
C ₆ /C ₂ Ratio (mol/mol)	0.018	0.016	0.014	0.018
H ₂ /C ₂ Ratio (ppm/mol)	5.7	5.7	6	6
C ₂ flow (g/hr)	1,946	1,970	1,941	1,980
C ₆ /C ₂ Flow Ratio (g/g)	0.048	0.045	0.039	0.055
Hydrogen flow (sccm)	16.95	16.66	16.95	17.5
Avg. Bedweight (g)	2,407	2,417	2,382	2,383
Production (g/hr)	408	443	465	459
Residence Time (hr)	5.9	5.5	5.1	5.2
Catalyst Slurry Feed (ml/hr)	2.6	2	2	2.3
Cat productivity (g poly/g cat)	1,777	2,492	2,591	2,240
MI (g/10 min)	1.6	0.98	0.93	0.91
HLMI (g/10 min)	42.78	20.55	16.16	20.19
HLMI/MI Ratio	26.74	21.07	17.34	22.07
Gradient Density	0.9212	0.9185	0.9181	0.9162
Bulk Density (g/cm ³)	0.3713	0.3838	0.3744	0.3765

Table 4 part 3. 1.2M Continuous Reactor Testing.

Example	CPol-C2	CPol-8	CPol-C3	CPol-9
Catalyst	Comp 3c	21b	Comp 3b	22b
Reactor Temp (°C)	85	85	85	85
Rx. Pressure (KPa)	2,170	2,170	2,170	2,170
Avg Velocity (m/s)	0.46	0.45	0.45	0.45
C ₂ conc. (mol%)	70.0	70.1	70.1	70
C ₆ /C ₂ Ratio (mol/mol)	0.026	0.021	0.012	0.009
H ₂ /C ₂ Ratio (ppm/mol)	2.9	2.9	11.4	10
C ₂ flow (g/hr)	2,031	2,086	1,891	1,999
C ₆ /C ₂ Flow Ratio (g/g)	0.067	0.055	0.046	0.036
Hydrogen flow (sccm)	9.01	8.18	28.82	24.15
Avg. Bedweight (g)	2,388	2,379	2,363	2,379
Production (g/hr)	484	550	448	512
Residence Time (hr)	4.9	4.3	5.3	4.6
Catalyst Slurry Feed (ml/hr)	2.5	2.1	1.7	2
Cat productivity (g poly/g cat)	2,232	2,965	3,017	2,897
MI (g/10 min)	0.98	0.99	0.86	0.72
HLMI (g/10 min)	17.90	16.57	36.76	34.25
HLMI/MI Ratio	18.32	16.75	42.89	47.5
Gradient Density (g/cm ³)	0.9189	0.9175	0.9183	0.9193
Bulk Density (g/cm ³)	0.2869	0.3888	0.3325	0.354

Table 5. Characterization Data for 1.2 M Continuous Reactor Testing

Example	CPol-C1	CPol-1	CPol-2	CPol-3	CPol-4	CPol-5	CPol-6	CPol-7	CPol-C2	CPol-8	CPol-C3	CPol-9
Mn – IR (g/mol)	35,756	35,748	33,359	34,230	23,350	36,063	38,011	33,240	33,461	40,505	23,061	27,073
Mw – IR (g/mol)	127,175	110,002	109,635	113,133	80,067	117,718	114,400	117,360	120,134	118,544	95,949	91,000
Mz IR (g/mol)	336,481	239,990	291,609	294,966	253,462	266,488	378,222	287,792	509,172	346,360	290,707	249,991
Mw – LS (g/mol)	137,535						122,622		130,211		108,166	100,605
Mz – LS (g/mol)	345,111						221,768		426,666		244,872	339,716
Mw/Mn (IR)	3.56	3.08	3.29	3.31	3.43	3.26	3.01	3.53	3.59	2.93	4.16	3.36
Mw(LS)/Mn(IR)	3.85						3.23		3.89		4.69	3.72
(g _{vis})	0.983						0.99		0.985		0.964	0.941
Wt% C ₆	7.41	9.2	6.18	7.02	6.44	7.4	6.46	8.58	6.62	6.56	8.44	7.66
CDR-1,m	1.41	1.32	1.41	1.32	1.74	1.26	1.23	1.33	1.14	1.03	1.05	1.03
CDR-2,m	1.79	1.57	1.65	1.54	2.15	1.48	1.32	1.72	1.17	1.02	1.16	1.01
CDR-3,m	1.53	1.38	1.41	1.36	1.69	1.32	1.20	1.51	1.10	1.01	1.14	0.99
Tw (°C)	80.16	82.14	82.74	80.59	80.99	79.64	82.06	74.16	81.85	81.55	76.21	77.68
stdev T (°C)	11.57	10.1	9.94	10.47	12.02	11.05	8.77	15.28	9.6	10.07	9.98	10.06
Tmedian (°C)	82.85	84.61	85.7	82.34	85.13	81.03	83	76.75	83.99	84.79	76.27	79.86
T75-T25 (°C)	18.41	13.9	13.8	15.16	16.63	15.65	10.36	23.55	9.87	9.37	7.87	7.64
SDBI (°C)	15.52	17.78	16.7	16.87	18.86	18.28	16.95	23.47	19.05	18.7	18.25	18.94

Table 6. 6.7 M Continuous Reactor Process Conditions

Example	CPol-C4	CPol-10	CPol-11
Catalyst	HP100	26	1c
Reactor Temp (°C)	84.9	85.0	87.8
Rx. Pressure (KPa)	2095	2101	2099
Avg Velocity (m/s)	0.823	0.823	0.823
C ₂ conc. (mol%)	65.2	65.0	65.2
iC ₃ conc. (mol%)	6.8	8.7	8.6
C ₆ /C ₂ Ratio (mol/mol)	0.015	0.010	0.013
H ₂ /C ₂ Ratio (ppm/mol)	2.7	6.8	7.1
C ₂ flow (Kg/h)	31.8	37.0	40.1
C ₆ /C ₂ Flow Ratio (g/g)	0.1000	0.0685	0.0650
H ₂ /C ₂ Flow Ratio (mg/g)	0.0242	0.0458	0.0478
Avg. Bedweight (Kg)	92.1	85.0	85.3
Production (Kg/hr)	24.4	20.1	15.3
Residence Time (hr)	3	4.25	4.05
Catalyst Slurry Feed (mL/h)	20	42	46
Cat productivity (g poly/g cat)	4104	7710	7327
MI (g/10 min)	0.96	0.86	0.88
HLMI (g/10 min)	15.5	16.1	16.2
HLMI/MI Ratio	16.1	18.6	18.4
Gradient Density (g/cm ³)	0.9165	0.9171	0.9179
Settled Bulk Density (g/cm ³)	0.430	0.410	0.423

Table 7. Polymer Characterization Data for 6.7 M Continuous Reactor Testing

Example	CPol-C4	CPol-10	CPol-11
MI (comp) (g/10 min)	0.94	0.82	0.9
Density (comp) (g/cm ³)	0.9165	0.9171	0.9179
MIR (comp)	15.8	17.9	17.6
Mn – IR (g/mol)	39,702	38,845	38,640
Mw – IR (g/mol)	107,740	117,379	113,458
Mz IR (g/mol)	197,676	241,982	226,980
Mw – LS (g/mol)	118,054	125,296	121,357
Mz – LS (g/mol)	188,727	226,052	216,793
Mw/Mn (IR)	2.7	3	2.9
Mw(LS)/Mn(IR)	3	3.2	3.1
(g' _{vis})	0.997	0.991	0.997
Wt% C ₆ (GPC-4D)	6.8	7	6.1
Me/1000C	12.7	13.2	12.2
mol% C ₆ (nmr)	2.6	2.7	2.5
wt% C ₆ (nmr)	7.4	7.7	7.1
vinylenes/1000C	0.03	0.02	0.02
trisub/1000C	0.11	0.05	0.04
vinyls/1000C	0.07	0.01	0.01
vinylidene/1000C	0.04	0.01	0
TREF peak 1 (°C)	83.2	81	82.1
TREF peak 1 (wt%)	99.38	85.81	87.39
TREF peak 2 (°C)		91.7	91.4
TREF peak 2 (wt%)		13.47	12.09
Cw (mol%)	3.28	3.36	3.07
Cmed (mol%)	3.18	3.48	3.16
CDBI (%)	62.18	64.65	66.68
Tw (°C)	79.3	78.6	80.1
stdev T (°C)	10.3	10.5	9.6
Tmed (°C)	81	79.6	81.1
T75-T25 (°C)	11.7	11.6	9.8
SDBI (°C)	19.8	20.7	20.1
η ⁰ (Pa.s)	8,352	9,490	8,508
EXI [log(η ¹ /η ¹⁰⁰)]	0.464	0.556	0.512

Table 8. Average Film Extrusion Process Data for 6.7 M Continuous Reactor Testing

Example	CPol-C4-1,2	CPol-10-1,2	CPol-11-1,2
Nominal Gauge (mil)	1 & 2	1 & 2	1 & 2
Die Gap (mil)	60	60	60
Speed (RPM)	63.2	67.1	64.1
Rate (lb/hr)	186.5	190.0	189.5
% motor load	58.9	55.8	58.5
Head Pressure (psi)	4,675	4,860	4,645
Head Pressure 2 (psi)	3,095	3,335	3,210
Melt (°F)	410.5	412.5	409.5
Horsepower	20	20	20
Torque (HP/RPM)	0.312	0.295	0.310
lb/hr/RPM	2.95	2.82	2.94
Energy Specific Output (lb/HP-hr)	9.47	9.57	9.54
lb/in die	9.90	10.06	10.05
Line Speed 1 mil film (fpm)	166.6	166.6	166.6
Line Speed 2 mil film (fpm)	83.1	83.1	83.1
% air	67.7	73.1	65.0
Press. (in H ₂ O)	3.9	4.6	3.8
T air (°F)	50.0	50.0	50.0
Frost Line Height (in)	24.0	24.0	25.5
Blow Up Ratio	2.5	2.5	2.5
Lay Flat (in)	23.5	23.5	23.5

Table 9 part 1. Film Properties from 6.7 M Continuous Reactor Testing

Example	CPol-C4-1	CPol-10-1	CPol-11-1	CPol-C4-2	CPol-10-2	CPol-11-2
Compounded I2 (g/10min)	0.94	0.82	0.90	0.94	0.82	0.90
Compounded I21 (g/10min)	14.8	14.7	15.9	14.8	14.7	15.9
MIR (I21/I2)	15.8	17.9	17.6	15.8	17.9	17.6
Compound density (g/cm ³)	0.9172	0.9172	0.9186	0.9172	0.9172	0.9186
Number of gels, 1/m ²	2,317	3,257	1,583			
TDA (ppm)	17.3	54.4	16.4			
Number of gels > 200 micron, 1/m ²	93	380	125			
TDA (ppm) > 200 micron	6.0	37.7	10.5			
Average Gauge (mil)	1.02	1.034	1.023	1.983	1.996	2.022
Low Gauge (mil)	0.946	0.926	0.94	1.828	1.614	1.864
High Gauge (mil)	1.1	1.348	1.1	2.21	2.206	2.162
Std Dev Gauge (mil)	0.043	0.093	0.051	0.094	0.152	0.071
RSD% Gauge	4.2%	9.0%	5.0%	4.7%	7.6%	3.5%
MD - 1% Secant Modulus (psi)	24,116	24,725	26,063			
TD - 1% Secant Modulus (psi)	26,946	28,281	29,518			
AVG - 1% Secant Modulus (psi)	25,531	26,503	27,791			
MD - Tensile Yield Strength (psi)	1,209	1,263	1,258			
TD - Tensile Yield Strength (psi)	1,228	1,273	1,307			
MD - Elongation @ Yield (%)	7.0	7.4	6.5			
TD - Elongation @ Yield (%)	6.3	6.4	6.2			
MD - Tensile Strength (psi)	8,611	8,539	8,014			
TD - Tensile Strength (psi)	8,783	8,440	8,516			
MD - Elongation @ Break (%)	500	436	493			
TD - Elongation @ Break (%)	673	644	675			

Table 9 part 2. Film Properties from 6.7 M Continuous Reactor Testing

Example	CPol- C4-1	CPol- 10-1	CPol- 11-1	CPol- C4-2	CPol- 10-2	CPol- 11-2
MD - Elmendorf Tear (g)	233.0	233.7	253.5	514.4	503.8	620.5
TD - Elmendorf Tear (g)	412.5	382.6	388.5	807.2	724.3	713.0
Elmendorf Tear MD (g/mil)	222	219	237	254	255	299
Elmendorf Tear TD (g/mil)	412	378	382	406	345	361
Dart Drop, Phenolic (g)	805	889	721			
Dart Drop, Phenolic (g/mil)	789	860	705			
Puncture - Peak Force (lbs)	13.3	12.3	12.4			
Puncture - Peak Force (lbs/mil)	13.0	11.9	12.1			
Puncture - Break Energy (in-lbs)	49.8	45.2	47.4			
Puncture - Break Energy (in-lbs/mil)	48.8	43.7	46.4			
Haze (%)	13.1	10.6	10.7			
Haze- internal (%)	2.3	2.3	2.7			
Clarity (%)	97.6	97.9	97.8			
Blocking (I/I), g	32.5	33	18.2			
Seal Initiation Temperature at 1N force (°C)	95.3	100.3	100.2			
Seal Temperature at 5N force (°C)	98.3	102.9	104.0			
Maximum Seal force (N)	11.0	10.2	10.5			
Peal-Break transition temperature (°C)	112.5	110.0	112.5			
Hot Tack Initiation Temperature at 1N force (°C)	97.4	96.1	104.0	97.0	100.2	101.8
Hot Tack Temp up to 5N force (°C)	103.0	105.3	110.8	104.8	104.0	107.0
Hot Tack Temp down to 5N force (°C)	150.9	155.3	166.7	156.9	151.7	152.6
HotTackWindow@5N (°C)	48.0	50.0	55.9	52.1	47.6	45.5
Maximum Hot Tack force (N)	10.1	10.3	9.5	10.1	13.3	9.8

[0226] Overall, processes of the present disclosure provide supported alumoxane precursors having improved stability and shelf life, as compared to supported methylalumoxane in toluene. The supported alumoxane precursors can be formed *in-situ*, e.g. the precursor is obtained while in the presence of the support material. In addition, supported alumoxane precursors of the present disclosure can be optionally heat treated to form supported alumoxanes without compromising catalyst activity when the supported alumoxanes are used in catalyst systems for olefin polymerizations. Supported alumoxane precursors can be formed without the use of toluene, which can provide polyolefins that are substantially free of toluene and suitable for use in packaging applications, such as food packaging.

[0227] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0228] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while some embodiments have been illustrated and described, various modifications can be made without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0229] While the present disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will

appreciate that other embodiments can be devised which do not depart from the scope and spirit of the present disclosure.

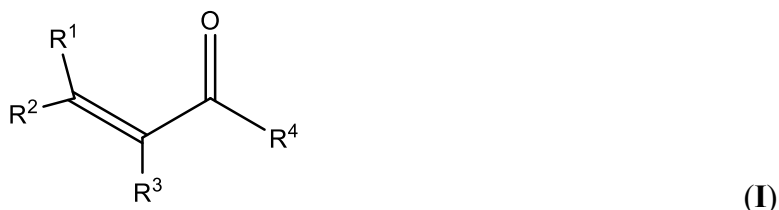
Claims:

We claim:

1. A process to prepare a supported alumoxane, comprising:

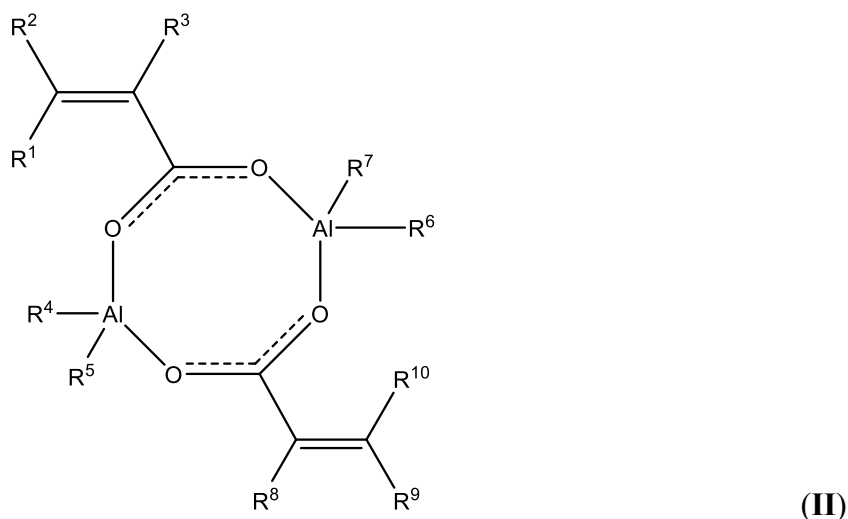
(a) forming a solution by, in an aliphatic hydrocarbon fluid, which is a C₃ to C₁₂ alkane, combining at least one hydrocarbyl aluminum with at least one non-hydrolytic oxygen-containing compound and a support material, wherein the molar ratio of aluminum to non-hydrolytic oxygen in the solution is greater than or equal to 1.5, wherein the aliphatic hydrocarbon fluid has a boiling point of less than 70 degrees Celsius, and wherein the combining is conducted at a temperature of less than 70 degrees Celsius and at the reflux temperature of the aliphatic hydrocarbon fluid; and wherein

(A) the at least one non-hydrolytic oxygen-containing compound comprises one or more compounds represented by the Formula (I):



wherein R¹ and R² independently are hydrogen or a hydrocarbyl group; R³ is a hydrocarbyl group; optionally R¹, R², or R³ may be joined together to form a ring; and R⁴ is –OH, –OC(O)CR³=CR¹R², OCR³, –F, or –Cl; or

(B) the at least one non-hydrolytic oxygen-containing compound comprises one or more compounds represented by the Formula (II):



where R¹, R², R⁹, and R¹⁰ independently are hydrogen or a hydrocarbyl group; R³ and R⁸ is a hydrocarbyl group; optionally R¹, R², or R³ may be joined together to form a ring; optionally

R⁸, R⁹, or R¹⁰ may be joined together to form a ring; and each of R⁴, R⁵, R⁶, and R⁷ is independently a C₂-C₂₀ hydrocarbyl group, a methyl group, hydrogen, or a heteroatom containing group;

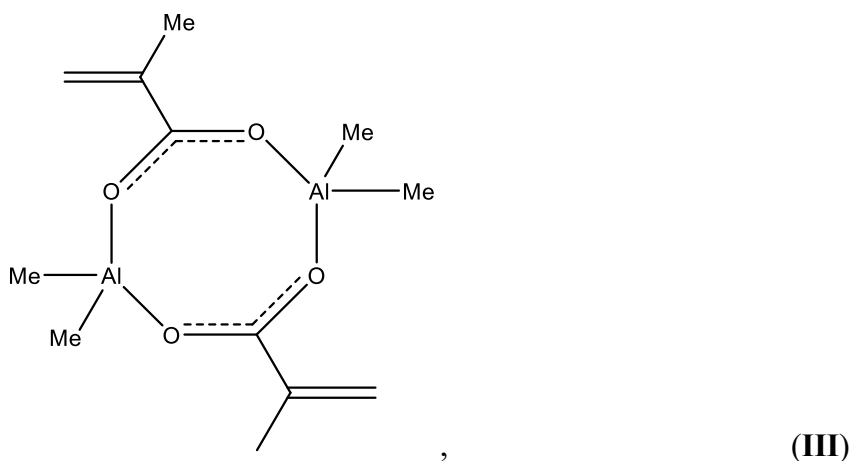
(b) distilling the solution at a pressure of greater than 50.7 kPa (0.5 atm) to form a supported alumoxane precursor, wherein the precursor comprises from 0 wt% to 50 wt%, preferably from 1 wt% to 20 wt%, of the aliphatic hydrocarbon fluid based on the total weight of the precursor; and

(c) heating the precursor to a temperature greater than the boiling point of the aliphatic hydrocarbon fluid and less than 160 degrees Celsius to form a supported alumoxane, wherein heating the precursor produces volatile compounds; and

(d) removing at least a portion of the volatile compounds.

2. The process of claim 1, wherein the non-hydrolytic oxygen-containing compound comprises a plurality of compounds represented by the Formula (II), and further wherein R⁴, R⁵, R⁶, and R⁷ is at least 85% methyl, up to 15% C₂-C₂₀ hydrocarbyl group or a heteroatom containing group, and up to 10 mol% hydrogen based on the total amount of moles of R⁴, R⁵, R⁶, and R⁷ in the plurality of compounds.

3. The process of any of claims 1 or 2, wherein the at least one non-hydrolytic oxygen containing compound is selected from the group consisting of methacrylic acid, a compound represented by the Formula (III):



or combinations thereof.

4. The process of claim 3, wherein the at least one non-hydrolytic oxygen containing compound comprises methacrylic acid.

5. The process of any of the preceding claims, wherein the aliphatic hydrocarbon fluid has a boiling point of at least 40 degrees Celsius less than the boiling point of the hydrocarbyl aluminum.
6. The process of any of the preceding claims, wherein the aliphatic hydrocarbon fluid is selected from the group consisting of propane, butane, 2-methylpropane, pentane, cyclopentane, 2-methylbutane, 2-methylpentane, hexane, cyclohexane, methylcyclopentane, 2,4-dimethylpentane, heptane, 2,2,4-trimethylpentane, methylcyclohexane, octane, nonane, decane, dodecane and combination(s) thereof.
7. The process of any of the preceding claims, wherein the at least one hydrocarbyl aluminum comprises one or more compounds represented by the formula $R_1R_2R_3Al$, wherein each of R_1 , R_2 , and R_3 is independently a C_1 to C_{20} alkyl group, hydrogen, or a heteroatom containing group.
8. The process of claim 7, wherein the at least one hydrocarbyl aluminum comprises a plurality of compounds represented by the formula $R_1R_2R_3Al$, wherein R_1 , R_2 , and R_3 is at least 85% methyl, up to 15 mol% C_1 - C_{20} hydrocarbyl group or a heteroatom containing group, and from 0 to 10 mol% hydrogen based on the total amount of moles of R_1 , R_2 , and R_3 in the plurality of compounds.
9. The process of any of the preceding claims, wherein the at least one hydrocarbyl aluminum comprises trimethyl aluminum.
10. The process of any of the preceding claims, wherein the support material and/or the solution is free of absorbed water.
11. The process of any of the preceding claims, wherein the support material is silica, alumina, alumina-silica or a derivative thereof, wherein the support material has an average particle size between 1 and 200 microns, an average pore volume of between 0.05 and 5 mL/g, and a surface area between 50 and 800 m^2/g .
12. The process of any of the preceding claims, wherein the support material has been treated with one or more of a Bronsted acid, a Lewis acid, a salt, and a Lewis base.

13. The process of any of the preceding claims, wherein the support material comprises a silylating agent and/or a hydrocarbyl aluminum compound, optionally wherein the support material and/or the hydrocarbyl aluminum compound comprises an electron withdrawing anion, wherein the electron withdrawing anion is selected from sulfate, bisulfate, fluordie, chloride, bromide, iodide fluorsulfate, fluoroborate, phosphate fluorophosphate, trifluoroacetate, triflate, fluoroaluminum, fluoroaluminum, phosphotungstate, or mixtures thereof, or combination thereof.

14. The process of any of claims 1 or 5-9, wherein the molar ratio of the at least one hydrocarbyl aluminum to the at least one non-hydrolytic oxygen containing compound is greater than or equal to $[A*B + 0.5(C*D)]/B$, wherein;

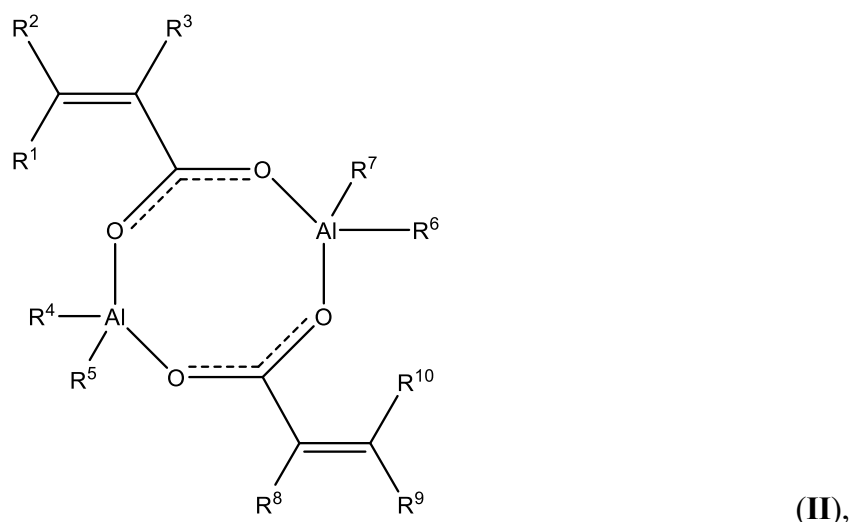
A is 2 or 3;

B is the moles of the non-hydrolytic oxygen containing compound;

C is the moles of hydrocarbyl aluminum chemisorbed to the surface of the support material in the absence of the non-hydrolytic oxygen containing compound per gram of the support material;

D is the grams of the support material; and

wherein A is 2 if the non-hydrolytic oxygen containing compound comprises a compound represented by the Formula (II):



where R^1 , R^2 , R^9 , and R^{10} independently are hydrogen or a hydrocarbyl group; R^3 and R^8 is a hydrocarbyl group; optionally R^1 , R^2 , or R^3 may be joined together to form a ring; optionally R^8 , R^9 , or R^{10} may be joined together to form a ring; and each of R^4 , R^5 , R^6 , and R^7 is independently a C_2 - C_{20} hydrocarbyl group, a methyl group, hydrogen, or a heteroatom

containing group,

wherein A is 3 if the non-hydrolytic oxygen-containing compound comprises a compound represented by the Formula (I):



wherein R^1 and R^2 independently are hydrogen or a hydrocarbyl group; R^3 is a hydrocarbyl group; optionally R^1 , R^2 , or R^3 may be joined together to form a ring; and R^4 is $-\text{OH}$, $-\text{OC}(\text{O})\text{CR}^3=\text{CR}^1\text{R}^2$, OCR^3 , $-\text{F}$, or $-\text{Cl}$,

and wherein B/D is greater than or equal to 1.5 mmol/g.

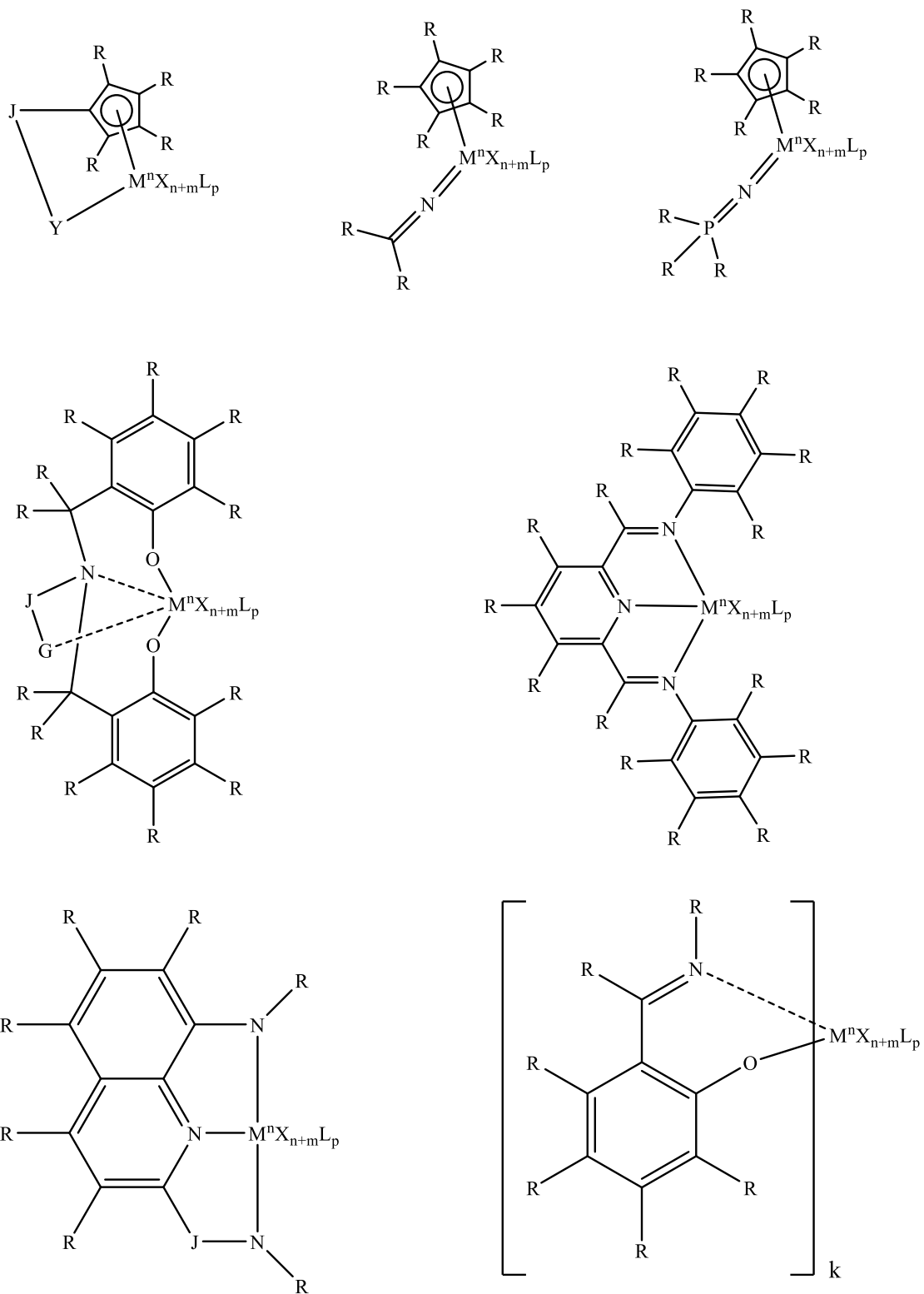
15. The process of any of the preceding claims, further comprising (e) introducing at least one catalyst compound, and optionally a continuity additive, to the supported alumoxane to form a catalyst system.

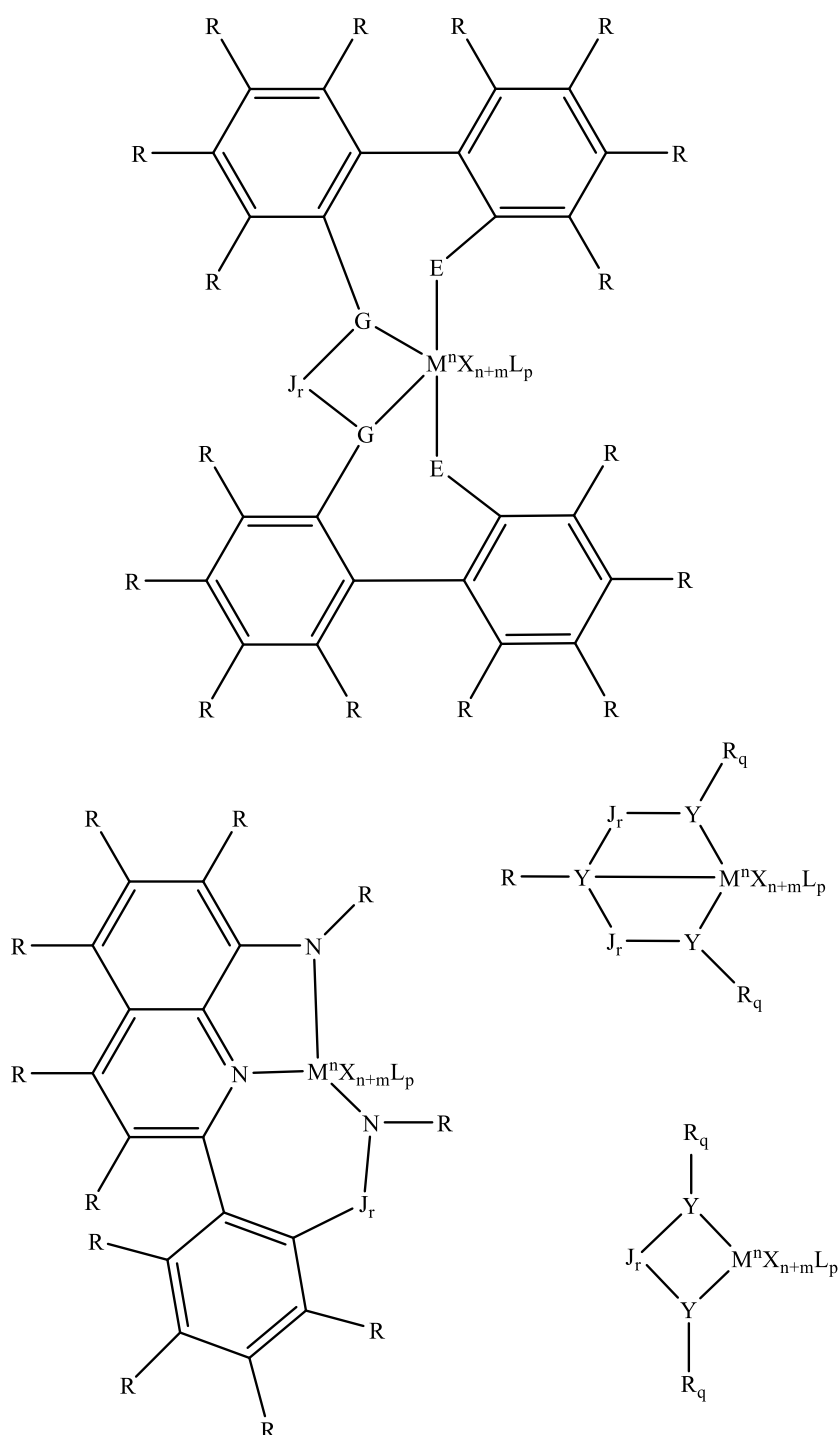
16. The process of claim 15, wherein the catalyst compound is an unbridged metallocene catalyst compound represented by the formula: $\text{Cp}^{\text{A}}\text{Cp}^{\text{B}}\text{M}'\text{X}'_n$, wherein each of Cp^{A} and Cp^{B} is independently selected from the group consisting of cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, one or both of Cp^{A} and Cp^{B} may contain heteroatoms, and one or both of Cp^{A} and Cp^{B} may be substituted by one or more R'' groups, wherein M' is an element selected from the group consisting of Groups 3 through 12 and lanthanide Group, wherein X' is an anionic ligand, wherein n is 0 or an integer from 1 to 4, wherein R'' is selected from the group consisting of alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, lower alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.

17. The process of claim 15, wherein the metallocene catalyst compound is a bridged metallocene catalyst compound represented by the formula: $\text{Cp}^{\text{A}}(\text{A})\text{Cp}^{\text{B}}\text{M}'\text{X}'_n$, wherein each of Cp^{A} and Cp^{B} is independently selected from the group consisting of cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, one or both of Cp^{A} and Cp^{B} may contain

heteroatoms, and one or both of Cp^{A} and Cp^{B} may be substituted by one or more R'' groups, wherein M' is an element selected from the group consisting of Groups 3 through 12 and lanthanide Group, wherein X' is an anionic ligand, wherein n is 0 or an integer from 1 to 4, wherein (A) is selected from the group consisting of divalent alkyl, divalent substituted alkyl, divalent heteroalkyl, divalent alkenyl, divalent substituted alkenyl, divalent heteroalkenyl, divalent alkynyl, divalent substituted alkynyl, divalent heteroalkynyl, divalent alkoxy, divalent aryloxy, divalent alkylthio, divalent arylthio, divalent aryl, divalent substituted aryl, divalent heteroaryl, divalent aralkyl, divalent aralkylene, divalent alkaryl, divalent alkarylene, divalent haloalkyl, divalent haloalkenyl, divalent haloalkynyl, divalent heteroalkyl, divalent heterocycle, divalent heteroaryl, a divalent heteroatom-containing group, divalent hydrocarbyl, divalent substituted hydrocarbyl, divalent heterohydrocarbyl, divalent silyl, divalent boryl, divalent phosphino, divalent phosphine, divalent amino, divalent amine, divalent ether, divalent thioether; wherein R'' is selected from the group consisting of alkyl, lower alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.

18. The process of claim 15, wherein the catalyst compound is represented by the formulae:

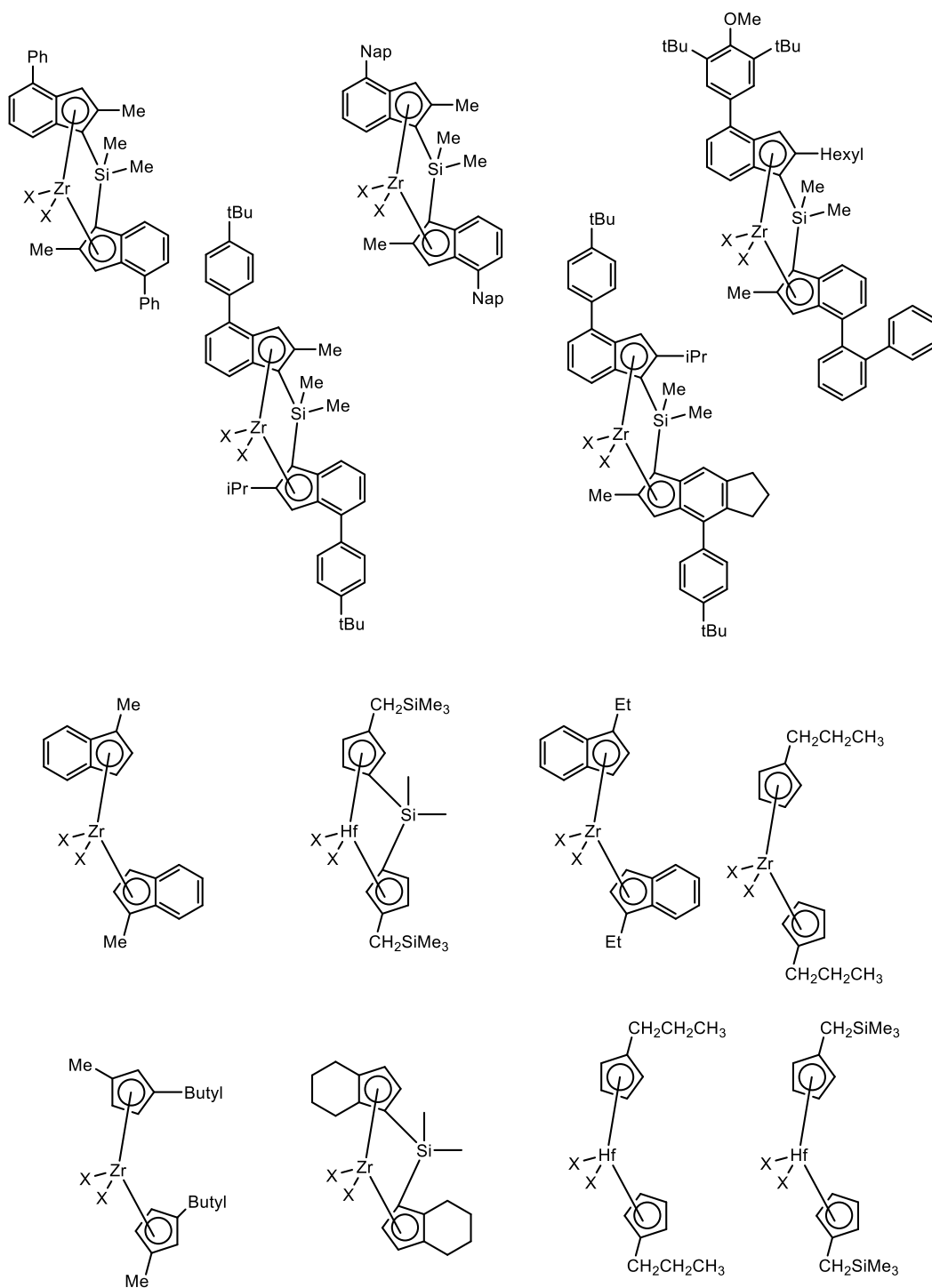




where R is independently H , hydrocarbyl, substituted hydrocarbyl, a halide, a substituted heteroatom group or SiR_3 ; R may be combined together to form a ring; when there is an aromatic ring present, any one or more of the ring $C-R$ may be substituted to form a heterocyclic ring; G is a neutral Lewis Base derived from substituted OR , SR , NR_2 , or PR_2 groups; E is O , S , NR , or PR ; Y is either G or E ; J is independently a formal diradical O , S , NR , PR , CR_2 , SiR_2 ; L is a formally neutral ligand or Lewis acid; X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion into a metal hydrocarbyl group;

M is a group 3-12 metal; n is the formal oxidation state of the metal between 0 and 6; m is the sum of the formal anionic charges on the non-X ligands, between -1 and -6; p = 0 to 4; r = 1 to 20; k = 1 to 4.

19. The process of claim 15, wherein the catalyst compound comprises one or more of the following metallocenes or their isomers:



wherein X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion into a metal hydrocarbyl group.

20. The process of any of claims 15-19, further comprising (f) contacting the catalyst system with one or more monomers to produce a polymer product.

21. The process of claim 20, wherein the contacting of step (f) is carried out in a gas phase fluidized bed, solution phase, and/or a slurry phase.

22. The process of claim 20 or 21, wherein the contacting of step (f) is conducted at a temperature of from 0°C to 300°C and a pressure in the range of from 0.35 MPa to 10 MPa.

23. The process of any of claims 20-22, wherein the contacting of step (f) is carried out in the presence of a scavenger and/or a chain transfer agent.

24. The process of any of claims 20-23, wherein the contacting of step (f) is carried out in the presence of a continuity additive and/or a static control agent.

25. The process of any of claims 20-24, wherein the monomer(s) include at least one of ethylene and propylene, optionally with at least one C₃-C₂₀ olefin comonomer.

26. The process of any of claims 20-24, wherein the monomer(s) are selected from the group consisting of ethylene, propylene, butene, hexene, octene, and a diene.

27. The process of any of claims 20-26, wherein the polymer product has one or more of the following properties:

- (i) a density of from 0.880 g/cm³ to 0.965 g/cm³;
- (ii) an M_w/M_n of from 2 to 50;
- (iii) an M_w of from 5,000 to 10,000,000 g/mol;
- (iv) an MI (I₂) of less than 400 g/10 min; and
- (v) an HLMI/MI ratio of from 12 to 100.