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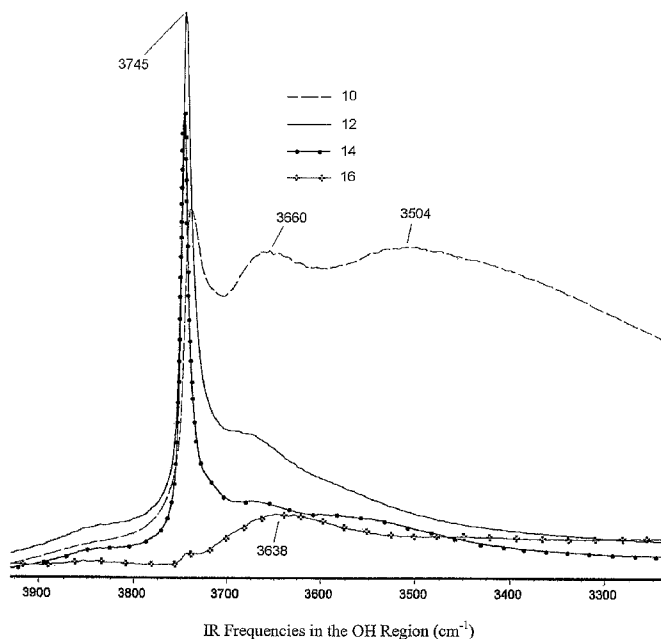
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(54) Title: ACTIVATOR COMPOSITIONS AND THEIR USE IN CATALYSTS AND OLEFIN POLYMERIZATION



(57) Abstract: This invention relates to compounds and catalyst compositions useful for olefin polymerization. In one aspect, this invention encompasses metal oxide-supported, Brønsted acidic, bulky aluminate activators and their utility for forming catalyst compositions comprising cationic d- block or f-block compounds ionically bonded with the supported aluminate activators. The catalysts of this invention are useful in olefin polymerization processes such as slurry or gas phase polymerization of ethylene or propylene which utilize supported catalysts.

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ACTIVATOR COMPOSITIONS AND THEIR USE IN CATALYSTS AND OLEFIN POLYMERIZATION

[0001] The work leading to the invention described in this patent application was performed pursuant to a contract with an agency of the United States Government. The contract is Cooperative Agreement No. 70NANBOH3049 between Albemarle Corporation and the National Institute of Standards and Technology of the United States Department of Commerce (Advanced Technology Program).

BACKGROUND

[0002] The development of metallocene catalysts for olefin polymerization has provided abundant opportunities for designing the active catalytic sites, in an effort to tailor the properties of the resulting polyolefin. Conventional metallocene catalysts typically employ an early transition metal compound, particularly of titanium, zirconium, or hafnium (Group 4), comprising one or two η^5 -cycloalkadienyl groups, such as cyclopentadienyl, indenyl, or fluorenyl ligands. Generally, it is necessary to activate metallocenes to convert them into effective olefin polymerization catalysts, a step that is often achieved using organoaluminum cocatalysts, such as methylaluminoxane (MAO). This resulting catalyst is generally considered homogenous, because at least a portion of the metallocene-organaluminum catalyst system is soluble in the olefin polymerization media. While some advantages are associated with homogeneous systems, several disadvantages also surround their use, such as the small particle size and low bulk density of the resulting polymer, processing problems under slurry polymerization conditions, and the large excess of expensive MAO that is typically required to form the active metallocene catalyst.

[0003] Supported or heterogeneous catalysts feature several advantages over an analogous homogenous catalyst system and are typically required for most modern commercial polymerization processes. For example, heterogeneous catalysts often promote the formation of substantially uniform polymer particles with a high bulk density, features that are desirable for efficient polymer production. Such catalysts may also be more suited for use in a slurry type polymerization process. Supported metallocene compounds also usually require reaction with an activator compound or composition to convert them into effective olefin polymerization catalysts.

[0004] Recent catalyst design efforts toward producing practical heterogeneous metallocene catalysts have centered largely around altering the metallocene precursor. Just as metallocene design can alter the nature of an active catalytic site, design changes of the activator may also profoundly influence the steric and electronic features of the active site. Therefore, there exists a need for new activator compounds, compositions, and methods directed to providing low-cost, supported metallocene-type polymerization catalysts that still exhibit the desired level of activity for

polymerizing olefins. To be of the greatest utility, such activator compounds and compositions would also be suitable for activating a range of transition metal based catalyst precursors other than metallocenes.

THE INVENTION

[0005] The present invention meets the above-described needs by providing activator compositions comprising a metal oxide support, an aluminate anion, and a Brønsted acidic cation. The aluminum atom of the aluminate anion is covalently bonded to the support through two chelating oxygen atoms on the support, and is also coordinated with at least one bulky functional ligand (as defined herein). The activator aluminate anion is also ionically bonded to an acidic proton. The description of the interaction between the activator anion and Brønsted acidic cation (having at least one active proton) as ionically bonded is not intended to be limiting, but rather is intended to provide one formal description of the interaction between a proton and an oxygen atom or atoms bonded to an aluminate anion, in which the proton of this moiety exhibits Brønsted acidity. Although this terminology is used generally throughout, this interaction can similarly be termed coordination of a proton to the aluminate anion, hydrogen-bonding between the proton and the aluminate, and the like.

[0006] The present invention further provides activator compositions derived from at least: a) metal oxide support having at least one surface hydrogen-bonded hydroxyl group; and b) organoaluminum compound comprising an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate; wherein the metal oxide support and the organoaluminum compound are combined in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion that is covalently bonded to the metal oxide support through two chelating oxygen atoms and ionically bonded to a H^+ .

[0007] The present invention further provides activator compositions comprising $[(\text{support})(-O-)_2\text{Al}(\text{ER}^3)_n(\text{R}^2)_{2-n}][\text{H}]^+$ or $[(\text{support})(-O-)_2\text{Al}(\text{ER}^3)_n(\text{R}^2)_{2-n}][\text{QH}]^+$, wherein the support comprises silica, n is 1 or 2, R^2 is hydrogen or a hydrocarbyl ligand having up to about 20 carbon atoms, R^3 is a hydrocarbyl group or a silyl group, each said group having up to about 20 carbon atoms, E is O, S, or NR^4 , wherein (i) R^4 is (a) hydrogen or (b) a hydrocarbyl group or a silyl group, each said group having up to about 10 carbon atoms, or (ii) R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms, and Q is a Lewis base. Such activator compositions can also comprise $[(\text{support})(-O-)\text{Al}(\text{ER}^3)_n(\text{R}^2)_{3-n}][\text{H}]^+$ or $[(\text{support})(-O-)\text{Al}(\text{ER}^3)_n(\text{R}^2)_{3-n}][\text{QH}]^+$

[0008] These and other features, aspects, embodiments, and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed features, and an examination of the Examples provide herein.

[0009] FIG. 1 illustrates the infrared (IR) spectra of the OH stretching region of Silica I after (a) calcining at 150°C (spectrum 10), (b) calcining at 600°C (spectrum 12), (c) calcining at 800°C (spectrum 14), and (d) calcining at 600°C followed by treatment of the silica with an excess of PhCH₂MgCl (spectrum 16).

[0010] FIG. 2 illustrates the infrared (IR) spectra of the OH stretching region of Silica I (a) calcined at 600°C (spectrum 20) (b) calcined at 600°C and then reacted with 10 mol% DBAB based on the OH concentration on the silica (spectrum 22), (c) calcined at 600°C and then reacted with 50 mol% DBAB based on the OH concentration on the silica (spectrum 24), and (d) calcined at 600°C and then reacted with 95 mol% DBAB based on the OH concentration on the silica (spectrum 26).

[0011] FIG. 3 illustrates the infrared (IR) spectra of the OH stretching region of Silica I calcined at 600°C after the following different treatments: (a) treatment with DBAB based on a molar ratio of Al:OH of 1:0.95 (spectrum 30); (b) treatment with DBAB followed by treatment with *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl) zirconium dimethyl (**M1**) with a Zr:OH molar ratio of 220 mol% based on the mmole OH after DBAB treatment (spectrum 32); and (c) treatment with excess BzMgCl (benzyl magnesium chloride) (spectrum 34).

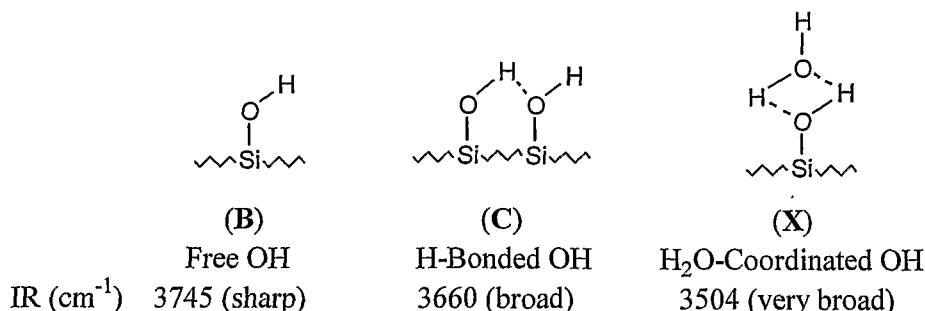
[0012] FIG. 4 compares the infrared (IR) spectra of the OH stretching regions of Silica I calcined at 800°C: (a) before BAM treatment (spectrum 40); (b) after BAM treatment (spectrum 42); and (c) after treatment with excess BzMgCl (benzyl magnesium chloride) (spectrum 44).

Metal Oxide Support

[0013] In one aspect, the activators and catalysts of this invention comprise compositions that are supported on a metal oxide support that comprises at least one surface hydrogen-bonded hydroxyl group. The reactivity of these surface hydrogen-bonded hydroxyl groups is used to form the chelated bulky aluminate activators on the support. In one aspect, this metal oxide support comprises silica, alumina, silica-alumina, or one or more clays. Typically, this metal oxide support comprises silica.

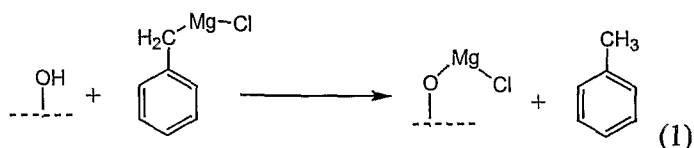
[0014] When the metal oxide support comprises silica, any type silica containing hydrogen-bonded hydroxyl groups can be used, including, but not limited to, the commercial silicas described in the Examples as Silica I, Silica II, or a combination thereof. The uncalcined silica is observed to contain three basic types of “active” OH groups, referred to herein as free OH (**B**), hydrogen-bonded (H-bonded) OH (**C**), and H₂O-coordinated OH (**X**), structures of which are illustrated below along with the fingerprint IR resonances for each type of OH group (in cm⁻¹). Most of these active OH groups react readily with benzylmagnesium chloride Grignard to produce toluene, and this reaction can be used to quantify the concentration of active OH groups on a particular silica. As illustrated by these structures, the H-bonded OH (**C**) (a surface hydrogen-bonded hydroxyl group) can arise when

two silica Si-OH groups are contiguous or neighboring, such that O-(μ -H)-O type H-bonding can form between the two groups.



[0015] In addition, some free and some hydrogen-bonded hydroxyl groups are more inert and do not react with the Grignard reagent C₆H₅CH₂MgCl (also abbreviated PhCH₂MgCl or BzMgCl), aluminum alkyls, or d-block metal or f-block metal dialkyls. While not intending to be bound by theory, it is believed that these inert OH groups are likely either to be hidden under the surface of the silica or in very narrow pore sites and cannot be accessed using any of these aforementioned reagents. Examples of each of these OH groups, both active and inert, are illustrated by the infrared (IR) resonances shown in FIG. 1, where the commercial Silica I has been subjected to various calcining temperatures and conditions (spectra 10, 12, and 14), and subjected to treatment with BzMgCl (spectrum 16). Thus, FIG. 1 illustrates the IR spectra of the OH stretching region of Silica I: (a) after calcining at 150°C (spectrum 10), (b) after calcining at 600°C (spectrum 12), (c) after calcining at 800°C (spectrum 14); and (d) after calcining at 600°C followed by treatment of the silica with an excess of PhCH₂MgCl (spectrum 16).

[0016] If an OH group does not react with a Grignard reagent such as BzMgCl, it usually also does not react with a dialkyl catalyst precursor (such as *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)) either. Thus, the total active OH content in a silica such as Silica I, which includes free OH (**B**), H-bonded OH (**C**), and/or H₂O-coordinated OH (**X**), can be quantified by reacting the silica with a Grignard reagent, as illustrated in Reaction (1).



[0017] Because the reaction of an active OH group with a benzylmagnesium chloride produces toluene, this reaction can be used to quantify the concentration of active OH groups on a particular silica using, for example, NMR spectroscopic techniques. Accordingly, three samples of Silica I

were calcined for four hours at 150°C, 600°C, and 800°C, respectively, each was reacted with excess PhCH_2MgCl , and the amount of toluene produced determined by ^1H NMR, and the OH content for each silica sample was calculated according to Example 3. Silica I was found to have an OH content of 0.78 mmol OH/g after calcining at 600°C for four hours. The 150°C-calcined and 800°C-calcined Silica I were characterized as having more and less mmol OH/g silica, respectively. The results of these tests are provided in Example 3 and Table 3.

[0018] In one aspect of this invention, useful metal oxide supports for the activators and catalysts disclosed herein retain significant concentrations or amounts of adjacent or neighboring, hydrogen-bonded hydroxyl groups on the surface, such as illustrated in structure C above, after any calcining treatment. Such structures are possible in a range of support materials. For example, support materials which are useful in the present invention include silica and silica containing metal oxides which are available, for example, as silica particles, silica gels, glass beads, and the like. Typically, the silica used in this invention is porous and typically has a surface area in the range of from about 10 to about 700 m^2/g , a total pore volume in the range of from about 0.1 to about 4.0 cc/g, and an average particle diameter in the range of from about 10 to about 500 μm . In another aspect, for example, the silica used in this invention has a surface area in the range of from about 50 to about 500 m^2/g , a pore volume in the range of from about 0.5 to about 3.5 cc/g, and an average particle diameter in the range of from about 15 to about 150 μm . In still another aspect, for example, the silica used herein has a surface area in the range of from about 200 to about 350 m^2/g , a pore volume in the range of from about 1.0 to about 2.0 cc/g, and an average particle diameter in the range of from about 10 to about 110 μm .

[0019] In another aspect, an average pore diameter of a typical porous silicon dioxide support materials is in the range of from about 10 Å to about 1000 Å, and in yet another aspect, from about 50 Å to about 500 Å, or from about 175 to about 350 Å. As disclosed throughout and in the Examples provided herein, the most useful activators were prepared and calcined such that the support contained significant concentrations or amounts of adjacent, or hydrogen bonded, hydroxyl groups on the surface in order to form the ion-pairs comprising of a siloxyl group chelated aluminate anion and a proton cation. In this aspect, the typical content of adjacent or hydrogen-bonded hydroxyl groups was from about 0.04 to about 3.0 mmol OH/g silica, with or without the presence of free hydroxyl groups, as determined by the Grignard method disclosed herein. In another aspect, the typical content of adjacent or hydrogen-bonded hydroxyl groups was from about 0.10 to about 2.0 mmol OH/g silica, or from about 0.4 to about 1.5 mmol OH/g silica.

[0020] Alternatively, the support material can also be an inorganic oxide, a covalently bonded metal or metalloid oxide, polymeric support, or any combination thereof. The metal or metalloid oxide supports that can be useful in the present invention typically have surface hydroxyl groups exhibiting

a pK_a equal to or less than that observed for amorphous silica, namely, a pK_a less than or equal to about 11. Any of the conventionally known inorganic oxides, silica, or any other support materials that retain reactive hydroxyl groups, particularly after dehydration treatment, will be suitable as support materials in accordance with this invention. These supporting material should contain adjacent (hydrogen bonded) hydroxyl groups as disclosed herein.

[0021] The metal oxide compositions can additionally contain oxides of other metals such as Al, K, Mg, Na, Si, Ti or Zr, which can be treated by thermal means, chemical means, or both to remove water and free oxygen. Such treatments can be conducted in various ways, for example, in a vacuum, in a heated oven, in a heated fluidized bed, or with dehydrating agents such as organo silanes, siloxanes, alkyl aluminum compounds, and the like. The extent of treatment should be such that as much retained moisture and oxygen as possible is removed, but that a significant amount of hydroxyl functionality is retained such that hydrogen-bonded hydroxyl groups remain in the support material. For example, it is expected that calcining these materials up to 800°C or even higher, up to a point just below the decomposition temperature of the support material, for several hours should be permissible. If higher loading of a supported anionic activator is desired, lower calcining temperatures for shorter times should be suitable. In this aspect, when the metal oxide is silica, loadings to achieve from less than about 0.1 mmol to about 3.0 mmol activator/g SiO₂ are typically suitable and can be achieved, for example, by varying the temperature of calcining from about 200°C to about 1200°C. In this aspect the calcining temperature can also vary from about 400°C to 1000°C, or from about 500°C to 900°C. In another aspect, the support can be calcined at a temperature below about 700°C. After calcination, the most useful support materials will retain significant concentrations or amounts of adjacent, hydrogen-bonded hydroxyl groups on the surface in order to form the ion-pairs consisting of a siloxyl group chelated aluminate anion and a proton cation through the two hydrogen-bonded hydroxyl groups.

Organoaluminum Compounds

[0022] Organoaluminum compounds that are particularly useful in this invention comprise at least one bulky functional ligand (as defined herein).

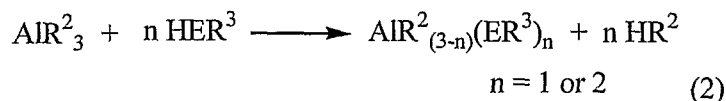
[0023] One example process for preparation of an organoaluminum compound comprising at least one bulky functional ligand is by coordinating one or two bulky functional ligands, such as an aryloxide like 2,6-di-*t*-butyl-4-methylphenoxide, to an organoaluminum compound that also has one or two hydrocarbyl ligands. For example, upon reacting the following components:

- A) AlR^2_3 wherein each R^2 is independently a hydrocarbyl group having up to about 20 carbon atoms or hydrogen; and
- B) HER^3 , wherein:

1) R^3 is a hydrocarbyl group or a silyl group, each said group having up to about 20 carbon atoms; and

2) E is O, S, or NR^4 , wherein (i) R^4 is (a) hydrogen or (b) a hydrocarbyl group or a silyl group, each said group having up to about 10 carbon atoms, or (ii) R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms;

either one or two of the hydrocarbyl groups of AlR^2_3 undergo protonolysis to form the organoaluminum compound $R^{2_{3-n}}Al(ER^3)_n$ wherein n is 1 or 2. The by-product from this reaction is 1 or 2 molar equivalents of the corresponding hydrocarbon by-product HR^2 , as indicated in Reaction (2).



In this aspect, the molar ratio of HER^3 to aluminum that are useful in Reaction (2) can vary to a considerable extent, but it typically spans the range from about 0.5 to about 2.5. The molar ratio of HER^3 to aluminum can also be from about 1 to about 2. Typically, in the usual reaction, a slight molar excess of HER^3 is used to drive the reaction to completion.

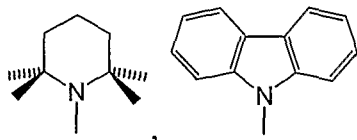
[0024] The organoaluminum compound AlR^2_3 used to form the organoaluminum compound $R^{2_{3-n}}Al(ER^3)_n$ is typically a trialkyl aluminum compound, but can be any suitable organoaluminum compound that reacts according to Reaction (2) that can be supported on a metal oxide as disclosed herein. For example, in one aspect, each hydrocarbyl group R^2 of AlR^2_3 is typically an alkyl or cycloalkyl group and in another aspect, typically has from 1 to about 20 carbon atoms. Each hydrocarbyl group R^2 can also have from 1 to about 12 carbon atoms, from 1 to about 8 carbon atoms, or from about 2 to about 6 carbon atoms. Useful hydrocarbyl groups include, but are not limited to, methyl, ethyl, propyl, butyl, hexyl, heptyl, and octyl. Each hydrocarbyl group can be cyclic (for example, cycloalkyl, alkyl-substituted cycloalkyl, or cycloalkyl-substituted alkyl groups) or acyclic, and each group can be a linear or a branched alkyl group. Typically, though not necessarily, each alkyl group of a trialkylaluminum compound is a primary alkyl group, that is, the alpha-carbon atom of each alkyl group is bonded to two hydrogen atoms.

[0025] Suitable organoaluminum compounds that can be used to form suitable organoaluminum compound reactants of this invention include, but are not limited to, aluminum trialkyls as well as dialkylaluminum hydrides. Examples of trialkylaluminum compounds which can be used in this invention include, but are not limited to, trimethylaluminum, triethylaluminum, tripropylaluminum, tributylaluminum, tripropylaluminum, trihexylaluminum, triheptylaluminum, trioctylaluminum, and their higher straight chain homologs; triisobutylaluminum, tris(2,4,4-trimethylpentyl)aluminum, tri-2-

ethylhexylaluminum, tris(2,4,4,6,6-pentamethylheptyl)aluminum, tris(2-butyloctyl)aluminum, tris(2-hexyldecyl)aluminum, tris(2-heptylundecyl)aluminum, and their higher branched chain homologs; tri(cyclohexyl-carbinyl)aluminum, tri(2-cyclohexylethyl)aluminum and analogous cycloaliphatic aluminum trialkyls. Examples of the dialkylaluminum hydrides that can be used in this invention include, but are not limited to, diethylaluminum hydride, dipropylaluminum hydride, diisobutylaluminum hydride, di(2,4,4-trimethylpentyl)aluminum hydride, di(2-ethylhexyl)aluminum hydride, di(2-butyloctyl)aluminum hydride, di(2,4,4,6,6-pentamethylheptyl)aluminum hydride, di(2-hexyldecyl)aluminum hydride, dicyclopropylcarbinylaluminum hydride, dicyclohexylaluminum hydride, dicyclopentylcarbinylaluminum hydride, and analogous dialkylaluminum hydrides. In one aspect, triisobutylaluminum, triethylaluminum, and trimethylaluminum are useful organoaluminum compounds. In another aspect, the useful organoaluminum compounds include, but are not limited to, AlR^2_3 , wherein R^2 is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, n-hexyl, n-heptyl, and n-octyl. Most of the examples provided herein utilize AlR^2_3 , wherein R^2 is selected from methyl, ethyl, and isobutyl.

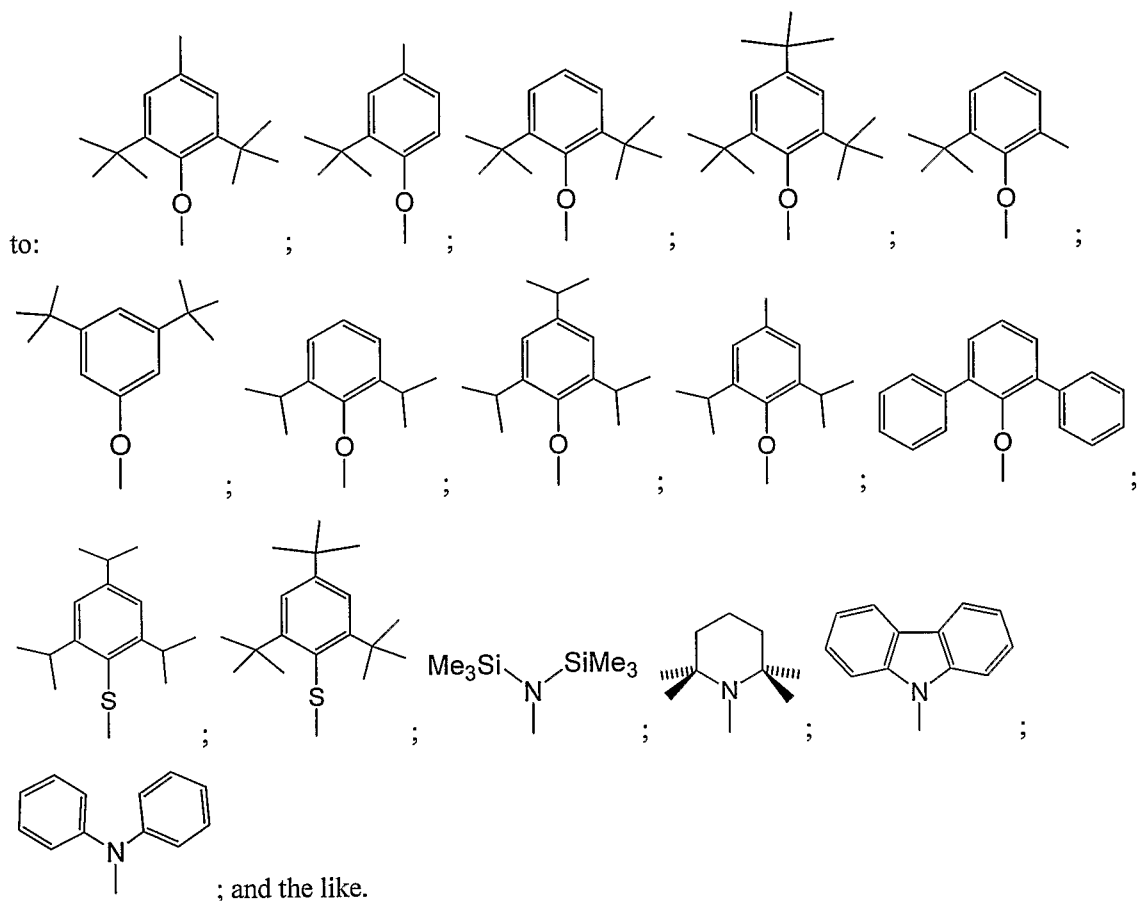
[0026] In one aspect, the organoaluminum compound is reacted with a compound having the formula HER^3 , wherein R^3 is a hydrocarbyl group having up to about 20 carbon atoms, and E is O, S, or NR^4 , as defined herein. One example of a bulky functional ligand ER^3 is derived from 2,6-di-t-butyl-4-methylphenol (BHT), shown schematically in Reaction (2) as forming BHT-modified organoaluminum compounds. The bulky functional ligand is not limited to alkoxide or aryloxy ligands, as this invention also encompasses organoaluminum compounds wherein the aluminum atom is covalently bonded to at least one bulky functional ligand selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate, and typically having up to about 20 carbon atoms.

[0027] While the bulky functional ligand ER^3 can have up to about 20 carbon atoms, bulky functional ligands up to about 30 carbon atoms, or up to about 60 carbon atoms also work well. Moreover, when the moiety E of the bulky functional ligand HER^3 is NR^4 , then R^4 is hydrogen or a hydrocarbyl group having up to about 10 carbon atoms, or R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms. Examples of a suitable heterocyclic group include, but



are not limited to, , and the like. In another aspect, the compound having the formula HER^3 used to form the ER^3 ligand of the organoaluminum compound provides a functional atom E such as O, S, or N and the bulky group R^3 such as 2,6- t Bu₂-4-Me-C₆H₂-. Because the usually synthetic method to prepare an ER^3 ligand on $R^2_{3-n}Al(ER^3)_n$ involves the reaction of HER^3 with AlR^2_3 , the term ligand can be used interchangeably to refer to either HER^3 or ER^3 . The bulky

ER³ ligand is typically selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate, having up to about 20 carbon atoms. Examples of ER³ that are useful in this invention include, but are not limited



[0028] In yet another aspect of the present invention, the bulky HER³ or ER³ ligand can be a halogenated or a non-halogenated ligand. Further, the bulky HER³ or ER³ ligand can be a fluorinated or a non-fluorinated ligand.

[0029] In another aspect, this invention also provides for the preparation of suitable organoaluminum compounds AIR₂(ER³) by means other than the protonolysis reaction of AIR₃ and HER³, for example, from a simple metathesis reaction. One non-limiting example of this type preparative method to form AIR₂(ER³) is illustrated below in Reaction (3), in which AIR₂Cl and M'ER³ are precursors to the desired compound, and where M' can be a metal ion such as Li⁺, Na⁺, K⁺, 0.5 Mg²⁺, and the like.



Preparation of Activator Compositions

Preparation of Activator Compositions - Reaction of Organoaluminum Compound $R^2_{3-n}Al(ER^3)_n$ with Silica

[0030] This invention also encompasses preparation of activator compositions by contacting a suitable organoaluminum compound $R^2_{3-n}Al(ER^3)_n$ with a hydroxylated support such as silica. Again, while not intending to be bound by theory, these reactions appear to involve coordination of the bulky $R^2_{3-n}Al(ER^3)_n$ with a surface hydroxyl group, to afford a moiety of the type $[(\text{support})(-\mu\text{-OH-})Al(ER^3)_n(R^2)_{3-n}]$ or $[(\text{support})(-\text{O-})Al(ER^3)_n(R^2)_{3-n}][H]^+$, in which the organoaluminum moiety $R^2_{3-n}Al(ER^3)_n$ is bonded to the support through one oxygen group, and can be characterized as an aluminate ion to which an active proton is ionically bonded. Based on the reactivity of the organoaluminum compound $R^2_{3-n}Al(ER^3)_n$ to Brønsted acids, a relatively fast ($n = 1$) or relatively slow ($n = 2$) protonolysis of either an R^2 group or an ER^3 group on $R^2_{3-n}Al(ER^3)_n$ by the active proton in $[(\text{support})(-\text{O-})Al(ER^3)_n(R^2)_{3-n}][H]^+$ can occur to afford a neutral aluminum compound of the formula $[(\text{support})(-\text{O-})Al(ER^3)_n(R^2)_{2-n}]$, which is a poor activator. The more stable, active species $[(\text{support})(-\mu\text{-OH-})(-\text{O-})Al(ER^3)_n(R^2)_{2-n}]$, which can be alternatively depicted by the formula $[(\text{support})(-\text{O-})_2Al(ER^3)_n(R^2)_{2-n}][H]^+$, can only form when the neutral aluminum compound has a neighboring OH that can coordinate to the aluminum center thus to form an aluminate covalently bonded to the support through two chelating oxygen atoms on the support and ionically bonded to an active proton.

[0031] It has been observed generally that, for a given alkyl group R, the order of Al-R reactivity with respect to an active proton is that each Al-R in the $-AlR_3$ moiety (primary aluminum alkyl, an Al center contains three Al-C sigma bonds) > each Al-R in the $-AlR_2$ moiety (secondary aluminum alkyl, an Al center contains two Al-C sigma bonds) > Al-R in the $-AlR$ moiety (tertiary aluminum alkyl, an Al center contains one Al-C sigma bond), wherein ">" means "more reactive than." Thus, protonolysis of either an R^2 group or an ER^3 group on $R^2_{3-n}Al(ER^3)_n$ by the active proton in $[(\text{support})(-\text{O-})Al(ER^3)_n(R^2)_{3-n}][H]^+$ is expected to be relatively fast for $n = 1$ and relatively slow for $n = 2$.

Preparation of Activator Compositions - Reaction of a Bulky Secondary Aluminum Alkyl (BHT)Al(i-Bu)₂ (DBAB) with Silica

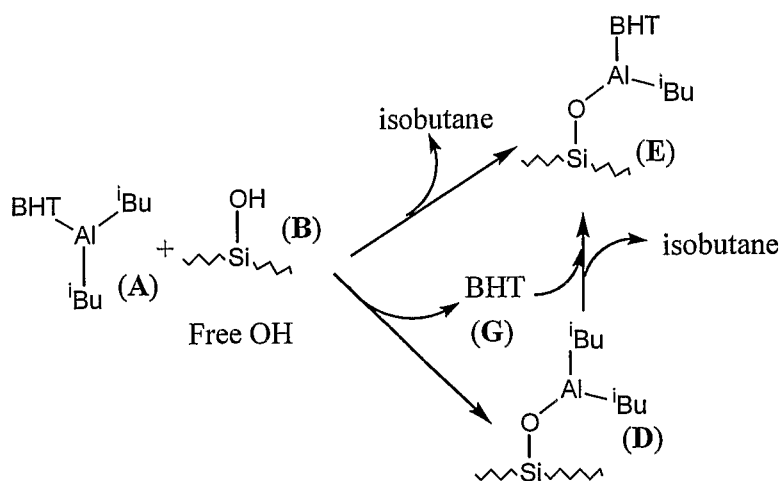
[0032] This invention also encompasses preparation of a supported activator composition by contacting the organoaluminum compound $R^2_{3-n}Al(ER^3)_n$ with a hydroxylated support such as silica. This reaction appears to proceed by protonolysis of either an R^2 group or an ER^3 group (such as BHT) on $R^2_{3-n}Al(ER^3)_n$ with a surface hydroxyl, to form a supported aluminum compound wherein the aluminum atom is bonded to the support through oxygen groups.

[0033] The reaction of (BHT)Al(i-Bu)₂ (DBAB) with Silica I was examined. The experiments and data discussed here and in the Examples provide a detailed disclosure for how to make and use this invention. Most experiments were conducted using Silica I that had been calcined at 600°C as provided herein, although different silicas and other calcining conditions were also examined and provided useful information. Although the total active OH content in uncalcined Silica I was observed to include free OH (B), H-bonded OH (C), and H₂O-coordinated OH (X), upon calcination at 600°C, the H₂O-coordinated or H₂O-“masked” OH (X) sites substantially disappear as water is lost, as illustrated in FIG. 1. Accordingly, the reactions of (BHT)Al(i-Bu)₂ (DBAB) with free OH (B) and H-bonded OH (C) sites of Silica I are specifically considered here.

[0034] Based on the quantitative analytical results, the reaction schemes that illustrate the reactions of DBAB with 600°C calcined Silica I are illustrated in Schemes 1-3. While not intending to be bound by theory, the data on which these schemes are established provide an experimental basis by which the applicable appended claims are fully supported, and by which compounds, compositions, and methods can be examined regarding whether these claims read thereon. Therefore, regardless of whether these schemes are provided as reaction mechanisms or simply reaction schemes, and regardless of how each scheme can be discussed herein, each is fully supported by experimental data that is used to establish a basis for certain claims.

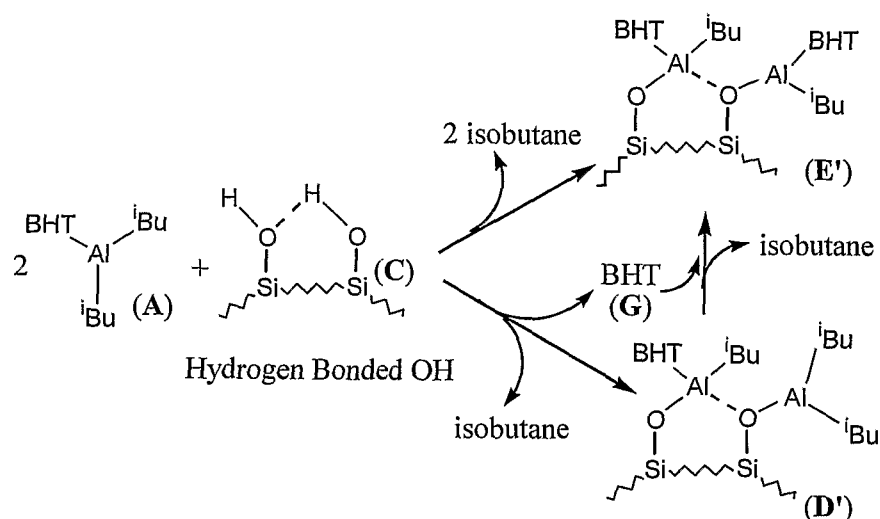
[0035] The reaction of DBAB with free OH (B) proceeds rapidly, to produce the supported but inactive species, D and E, as illustrated in Scheme 1. Thus, either an i-Bu or a BHT ligand of DBAB (A) can be protonated initially upon reacting DBAB (A) with B, but if a BHT ligand is initially protonated to form D, free phenol BHT (G) can react with D to form E, and by-product isobutane.

Scheme 1



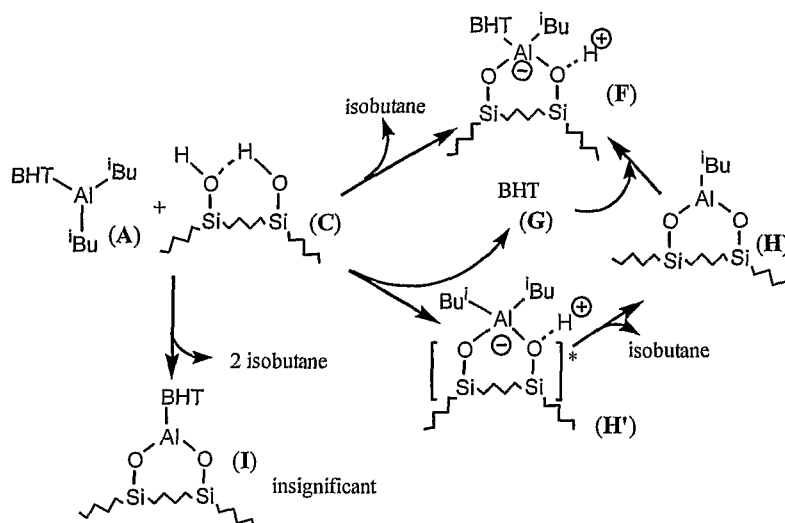
[0036] Similarly, the reaction of DBAB with H-bonded OH (C) of Silica I to produce the supported but inactive species, D' and E', is illustrated in Scheme 2. Parallel to the reactions of Scheme 1, free phenol BHT (G) can react with D' to form E', and by-product isobutane.

Scheme 2



[0037] Both Schemes 1 and 2 illustrate reactions of DBAB with equimolar amounts of surface OH groups, and both schemes produce inactive bound aluminum sites D, E, D' and E', as shown. In order to produce active aluminum sites that are capable of forming catalytic sites upon reaction with a d-block or f-block metal compound, an excess of H-bonded OH (C) groups relative to DBAB (A) are employed, to construct active species F illustrated in Scheme 3. Compound F is illustrated in Scheme 3 as comprising a supported aluminate anion wherein the 4-coordinate aluminum atom is bonded to the support through two chelating oxygen atoms on the support, and an acidic proton that originated from a surface hydroxyl is ionically bonded to the aluminate ion. An alternative to the aluminate-ionically bonded proton depiction for compound F is a silica-O-Al(BHT)(i-Bu) moiety that is coordinated by a neighboring surface hydroxyl group, although the difference between these two alternative descriptions is likely more formal than real, especially because there is likely more than one pathway by which compound F can arise. Computational modeling studies suggest that a proton hydrogen bonded to both bridging oxygen atoms of a structure such as F is not favored.

Scheme 3



[0038] As illustrated in Scheme 3, active species **H'** might exist in low concentrations, but it is likely to be a short-lived species (as indicated by *), because of a secondary alkyl in Al-ⁱBu group adjacent to an active proton that would be expected to readily undergo alkane elimination to produce a more stable species **H**. This possibility appears likely, given the order of Al-R reactivity with respect to an active proton is that each Al-R in the -AlR₃ moiety (primary) > each Al-R in the -AlR₂ moiety (secondary) > each Al-R in the -AlR moiety (tertiary), wherein ">" means "more reactive than." Thus, the tertiary Al-R bond in the -AlR moiety (tertiary) is much less reactive than the corresponding secondary and primary. However, the reaction stoichiometry indicates that even if compound **H** was generated in the reaction of DBAB with silica, it eventually reacted with the previously produced free BHT (**G**) to form **F**. (See Table 2 and Table 7 for reaction stoichiometry). Basically, it indicates that one DBAB reacts with one OH group by losing one ligand to form either isobutane (nearly 100% if allow enough reaction time, e.g., 2 hrs) or a small amount of free BHT). Table 7, Entries 3-5 indicates that BHT was first produced, but eventually reattached to the Al center by losing an isobutane over time.) The reaction stoichiometry also indicates that the amount of species **I**, which requires the loss of two equivalents of isobutane, should be insignificant because of the analytical results indicating the loss of only one equivalent. Thus, examining Schemes 1-3 illustrates that one DBAB reacts with one OH to release one isobutane, if sufficient reaction stoichiometry is employed and sufficient reaction time is allowed.

[0039] The Silica **I** that has been calcined at 600°C is commonly employed in this invention and contains a significant amount of H-bonded OH (**C**) needed for the construction of the active species **F**, as illustrated in Scheme 3. The Silica **I** calcined at 150°C is not as useful because it retains a significant amount of coordinated water in the form of H₂O-coordinated OH (**X**), which complicated

the reaction with DBAB and a metallocene, and reduced the productivity (See Table 4, Entry 1 vs. Entry 2). Silica I calcined at 800°C is also not as useful because the content of the surface hydroxyl groups most utilized for forming the active site with DBAB, H-bonded OH (C), was too low, which also reduced the productivities because H-bonded OH was not enough to construct the active sites (See Table 4, Entry 2 vs. Entry 3 and Table 6). Silica I calcined at 800°C contains mainly isolated OH (Figure 1, Spectrum 14). Although a substoichiometric charge of DBAB to OH allowed excess OH groups, these excess OH groups were mainly isolated and could not form an active species since there was no aluminum compound nearby to construct the active species F. These isolated OH groups may form inactive species with metallocene.

Preparation of Activator Compositions - Experimental Evidence for the Reaction of (BHT)Al(i-Bu)₂ (DBAB) with Silica

1. Higher Reactivity of Free OH (B) than H-bonded OH (C) with DBAB.

[0040] As illustrated in Table 3 (Entry 2) and Example 3, Silica I after calcining at 600°C contains 0.78 mmol OH/g silica. The infrared (IR) spectra of the OH stretching frequency region of a sample of the 600°C calcined Silica I reveals both free OH (structure B, 3745 cm⁻¹, sharp) (FIG. 1, spectrum 12) and H-bonded OH (structure C, 3660 cm⁻¹, broad), FIG. 2, spectrum 20. After the reaction of 10, 50, and 95 mol% DBAB based on the OH concentration on the silica, that is based on a DBAB:OH ratio of 10:100, 50:100, and 95:100 mol:mol, respectively, the sharp peak for free OH sites at 3745 cm⁻¹ reduced more rapidly than the broad peak for H-bonded OH at 3660 cm⁻¹ and almost completely disappeared when DBAB:OH was 95:100, as indicated in FIG. 2, spectrum 22, spectrum 24, and spectrum 26, respectively. This observation indicated that free OH reacted faster with DBAB than H-bonded OH. Thus, FIG. 2 illustrates the infrared (IR) spectra of the OH stretching region of Silica I after calcining at 600°C, that has been reacted with (a) 0 mol%, DBAB (spectrum 20)(b) 10 mol%, DBAB (spectrum 22) (c) 50 mol% DBAB (spectrum 24), and (d) 95 mol% DBAB (spectrum 26), wherein in each case the mol% DBAB is based on the OH concentration on the silica.

2. Stoichiometric Reactions Between DBAB and the OH Groups on Silica.

[0041] Four samples of 600°C calcined Silica I, which afforded an OH content of 0.78 mmol OH/g silica, were treated with differing amounts of DBAB, to provide samples with Al:OH molar ratios of 0.36:0.78, 0.51:0.78, 0.73:0.78, and 0.85:0.78, as provided in Example 2. Thus, the OH content of these four samples was determined by the Grignard titration method as provided herein, the results of which are summarized in Table 2. These titration results clearly show that under well-controlled reaction conditions and with sufficient time, one DBAB consumes one OH on silica to produce one isobutane. Therefore, the OH content on the silica is observed to decrease in an amount

corresponding to the amount of DBAB used to treat the silica. Although free BHT was also observed at the beginning of the reactions, it subsequently reacted with the aluminum alkyl (for example, compound **H'**) on silica to release a stoichiometric amount of isobutane.

[0042] Example 11 and Table 7 also examines the reaction by-products resulting from the treatment of 600°C calcined Silica I with different amounts of DBAB and for different reaction times, in order to determine stoichiometries of the by-products and identify kinetic versus thermodynamic products. These studies showed that given sufficient reaction time, one mole of DBAB reacted with one mole of OH to release one mole of isobutane (abbreviated iC_4), thus, iC_4 can be considered a thermodynamic by-product of this reaction. With shorter reaction times, a mixture of kinetic and thermodynamic products, both isobutane iC_4 and free BHT phenol, were observed. Thus, BHT is produced relatively quickly in these reactions, but further reacts with an aluminum alkyl Al-*i*-Bu to form iC_4 in an equimolar amount, therefore the ratio of (mol iC_4 + mol free BHT) to mol DBAB used in the reaction is very close to 1 in each experiment. These data therefore support the reactions provided in the above schemes, including the formation of transient **H'** and its conversion to the active product **F** in Scheme 3.

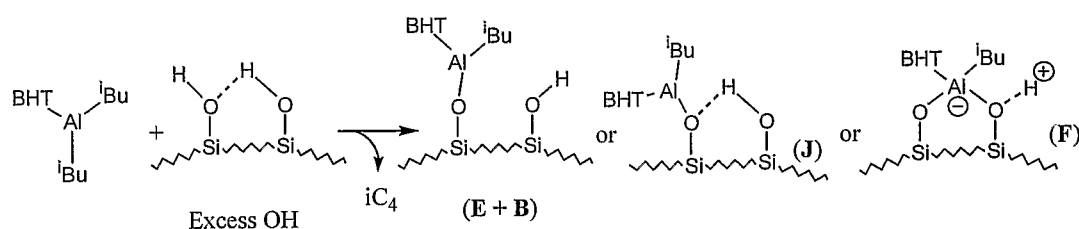
3. Formation of New OH Species with a Sub-Stoichiometric Charge of DBAB (A).

[0043] When a sub-stoichiometric amount of DBAB is used to treat 600°C calcined Silica I, wherein less than one molar equivalent of DBAB for each molar equivalent of silica OH (based on the measured OH concentration) is employed, a new OH species appear to be formed. The presence of a new OH species is indicated by the appearance of a new IR frequency at 3690 cm^{-1} , illustrated in FIG. 2, spectra 22, 24, and 26. The appearance of the new resonance is accompanied by the disappearance of the free OH (**B**) and H-bonded OH (**C**) bands that appeared at 3745 and 3660 cm^{-1} , respectively, that were shown in FIG. 1, spectrum 12, and FIG. 2, spectrum 20, respectively. Because an absolute moisture free environment is typically not possible to achieve, at times the moisture peak at 3600 cm^{-1} became significant if the sample was placed in the drybox for a longer time before an IR test (FIG. 2, spectrum 24). A small amount of BAM-related OH species (at 3490 cm^{-1}) could also be detected if the preparation was rigorously controlled (FIG 2, spectrum 26). This aspect is disclosed in detail below in which the reaction of $(\text{BHT})_2\text{AlMe}$ (BAM) with Silica is discussed.

[0044] Because ^1H NMR studies indicate that one DBAB reacts with one OH to release one isobutane, the final stable structures of the resulting silica supported aluminum compounds, that is, the thermodynamic products, should be **E** (Scheme 1) and **E'** (Scheme 2) when OH is not in excess. However, to construct or assemble the active proton site of this catalyst that retains Brønsted acidity, a slight excess of OH groups on silica is typically required, a feature which is achieved when, for example, 0.95 eq of DBAB are used to treat 1.0 eq of silica OH groups (Table 2, Entry 4). Because a

higher reactivity with DBAB was observed for free OH (**B**) as compared to H-bonded OH (**C**), the new OH species present after reacting a sub-stoichiometric charge of DBAB, should be a H-bonded OH derivative. Thus, the faster reaction of DBAB with free OH (**B**) would be expected to form **E** as illustrated in Scheme 1. The slower reaction of DBAB with H-bonded OH (**C**) sites would produce **E'** as illustrated in Scheme 2. Then the excess OH, which should be on the less reactive H-bonded OH sites, would form the active site **F** as illustrated in Scheme 3.

Scheme 4

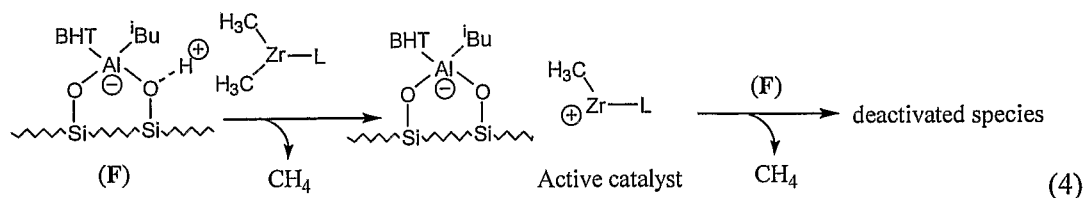


[0045] Scheme 4 considers possible new OH structures formed when H-bonded OH (**C**) sites are in excess over DBAB reactant. Because the IR spectrum (FIG. 2, spectrum 26) does not exhibit a sharp peak related to free OH (**B**), the combination of **E + B** in Scheme 4 can be excluded. In comparing **J** and **F**, it is expected that **F** is much more stable than **J** because, among other reasons: (a) the additional Al-O bond in **F** is much stronger than the H-O bond in **J**; (b) **F** comprises a more stable four-coordinate aluminate species, whereas **J** comprises a less stable three-coordinate Al compound; and (c) the possible ionization energy for **F** can also gain extra stability. Therefore even if **J** forms as a kinetic product in Scheme 4, it should eventually be converted to more stable **F**, therefore **F** is the only favored species formed.

4. Different Reactivities of OH on DBAB-Treated Silica with a Metallocene.

[0046] Based on IR spectroscopy, **F**-type sites appear to have different structures that are observed to exhibit a range of activities toward different d-block and f-block metal alkyl compounds. The OH species (activator **F**) with stretching frequencies at 3690 cm^{-1} (FIG. 3, spectrum 30) was observed to partially react with a metallocene dialkyl compound *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl) zirconium dimethyl (**M1**), even though **M1** was present in 10 mol% excess based on OH (FIG. 3, spectrum 32). In contrast, this OH species (activator **F**) with stretching frequencies at 3690 cm^{-1} was observed to react substantially to completion with benzylmagnesium chloride (FIG. 3, spectrum 34). Therefore, excess OH species with stretching frequency at 3690 cm^{-1} was required to fully activate a catalyst precursor such as **M1**. However, a large excess of OH was found to deactivate the active

catalyst (Table 4, Entry 2 as compared to Entry 4 or 5), likely through Reaction (4). Thus, in one aspect, one aspect of this invention involves matching the OH number with a catalyst precursor to optimize the catalyst activity.



[0047] Based on the polymerization test results (Table 4), amounts up to a four molar excess of moles OH on the DBAB-treated silica to moles catalyst precursor provided a sufficient amount of “active OH” to obtain the most active system (Table 4, Entries 2, 6, 7a, 10, and 11). In one aspect, a typical DBAB:OH molar ratio was from about 90:100 to about 95:100. Thus, for the silica with 0.78 mmol OH/g silica, the charge of DBAB was typically about 0.73-0.74 mmol DBAB/g silica (that is, about 95 mol%). See: Table 2, Entry 4 and Table 4, Entries 2, 6, and 7a.

5. Consistency of the Polymerization Results with the Observed Chemistry.

[0048] Example 7 examines the propylene polymerization results obtained from using *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)-derived, DBAB-treated silica supported catalysts, in which parameters are varied such as the DBAB charge used, and the charges of metallocene **M1**, and the type silica. The results of these tests are provided in Table 4.

[0049] Table 4 (Entries 1, 2 and 3) and Example 7 indicate that, under identical DBAB/OH ratios and metallocene/OH ratios, higher activities were obtained for silica calcined at 600°C. Comparing DBAB/OH ratios used to prepare the activator, the highest activity was obtained at a DBAB/OH molar ratio of about 95 mol% for Silica I containing 0.78 mmol/g OH after calcining at 600°C and 80-95 mol% for Silica II containing 1.1 mmol/g OH after calcining for shorter time at 600°C (Table 4, Entries 2, 6, 7a, 7b, 10, and 11). Reducing the DBAB charge to about 50-60 mol% of the OH concentration caused a significant drop in polymer productivity, even though the Zr loading is significantly higher (Table 4, Entries 4, 5, and 9). When the DBAB charge was 50 mol% of the total active OH on the support, free OH was still observed (FIG 2, spectrum 24). An overcharge of DBAB causes low active proton contents and thus results in low Zr loading, although the Zr efficiency is very high, presumably due to a very low concentration of structure **F** (Scheme 3). This observation supports the structure of structure **F**, comprising a chelated bulky functional aluminate-proton ion-pair, as one aspect of obtaining a highly active catalytic system.

[0050] Table 4 and Example 7 indicate that not all active protons on DBAB-treated silica are equally active as indicated by the facts that the 62 mol% and 110 mol% Zr charges based on the same

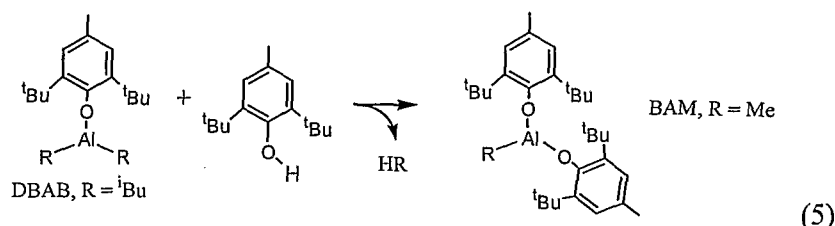
residual OH content on DBAB treated silica show almost the same Zr loadings and productivities (Table 4, Entry 2 vs. Entry 7a), consistent with the IR observation as illustrated in FIG. 3.

[0051] As provided herein, activators of the general formulas provided above can also be generated in the presence of a Lewis base, and either the base-free activators or the activators generated in the presence of a Lewis base can be utilized to prepare the active olefin polymerization catalysts of this invention. The formation of activators in the presence of a Lewis base, and the formation of metallocene-based catalysts are considered below.

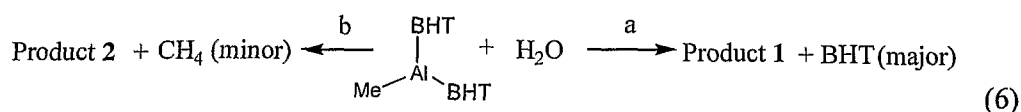
Reaction of a Bulky Tertiary Aluminum Alkyl (BHT)₂AlMe (BAM) with Silica

[0052] This invention encompasses, among other things, the preparation of a supported activator composition by contacting the functionalized bulky organoaluminum compound $R^{2}_{3-n}Al(ER^3)_n$ with a hydroxylated support such as silica. Although this aspect of the invention is not limiting, and while not intending to be bound by theory, the experimental results appear to support the reactions of (BHT)Al(i-Bu)₂ (DBAB) and (BHT)₂AlMe (BAM) with silica as proceeding by slightly different mechanisms. The reaction of (BHT)₂AlMe (BAM) with silica to provide an activator of the present invention is described here. The experiments and data discussed here and in the Examples provide a detailed disclosure for how to make and use this invention. Most experiments were conducted using Silica I that had been calcined at 600°C as provided herein. The reaction schemes that illustrate the reaction of BAM with 600°C calcined Silica I are illustrated in Schemes 5-7. While not intending to be bound by theory, the data on which these schemes are established provide an experimental basis by which the applicable appended claims are fully supported, and by which compounds, compositions, and methods can be examined regarding whether these claims read thereon. Therefore, regardless of whether these schemes are provided as reaction mechanisms or simply reaction schemes, and regardless of how each scheme can be discussed herein, each is fully supported by experimental data that is used to establish a basis for certain claims.

[0053] The functionalized bulky organoaluminum compounds BAM and DBAB exhibit different reactivities toward a given active proton due to their structural differences between these compounds based on their steric and electronic distinctions. For example, the one tertiary Al-R (R = Me) group and the two bulky BHT groups in BAM are expected to impart different properties to the aluminum compound as compared to the two secondary Al-R (R = i-Bu) groups and one bulky BHT group in DBAB, because, among other reasons, a tertiary Al-R is less active than a secondary Al-R toward a particular active proton. For example, DBAB can react with a free BHT to produce a BAM analog under ambient conditions, as illustrated in reaction 5.



[0054] However, the reaction of BAM with even a more active proton source such as H₂O, which has an OH moiety that is much more reactive than the OH in BHT, produces free BHT as the major product instead of methane, as illustrated in reaction 6. (See: Scott Collins *et al*, *JACS* **2003**, *125* (31), 9246-9247). Accordingly, these reactivity observations guide the discussion of the interactions of BAM with silica.



[0055] Although the total active OH content in uncalcined Silica I was observed to include free OH (**B**), H-bonded OH (**C**), and H₂O-coordinated OH (**X**), upon calcination at 600°C, the H₂O-coordinated or H₂O-“masked” OH (**X**) sites substantially disappear as water is lost, as illustrated in FIG. 1. Accordingly, the reactions of reaction of (BHT)₂AlMe (BAM) with free OH (**B**) and H-bonded OH (**C**) sites of Silica I are specifically considered here.

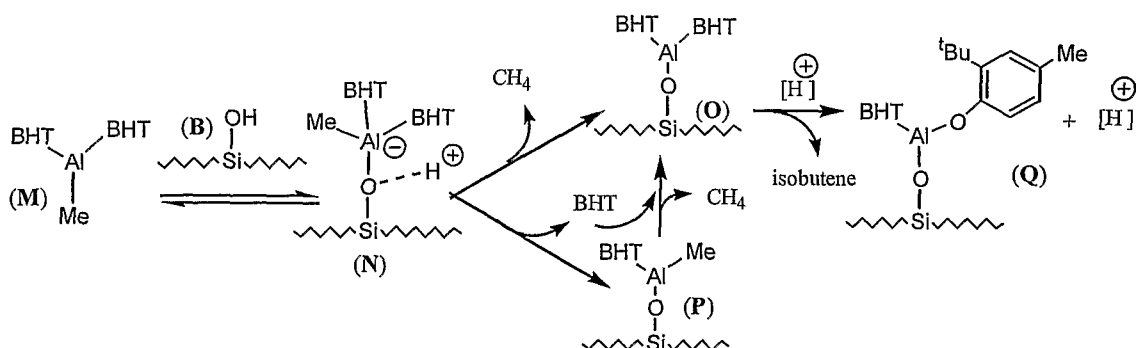
[0056] Because BAM is less reactive to an active proton and structurally has more bulky groups than DBAB, somewhat different reactions occur for BAM with active protons on silica. Generally, the reaction of BAM with OH on silica is slower when comparing to the reaction of DBAB with OH on silica, although similar aluminum structures result, namely, neutral aluminum compounds along with chelated bulky aluminate-proton ion pair structures. Because of the slower reactivity of BAM, the reaction with OH on silica requires an excess of BAM relative to the moles of OH on silica to obtain desired OH residue to construct the active site. Similar to the DBAB-derived catalyst, in one aspect, to maximize catalyst activity the moles of residual active protons (OH groups) on silica after BAM treatment should roughly match the moles of metallocene to minimize deactivation resulting from excess active protons reacting with the second alkyl group on a metallocene dialkyl. Thus, as in the DBAB case, the reaction of a metallocene dialkyl with a first active proton produces a monoalkyl metallocene cation, the active species, and reaction of this species with a second active proton deactivates the catalyst. However, because BAM is more sterically congested than DBAB and hence less reactive, the reaction of even an excess of BAM, that is, more than 1 mol BAM:mol OH on silica, still resulted in higher than desired residual silica OH content. For example, 600°C calcined

Silica I containing 0.78 mmol OH/g silica was treated with excess BAM based on 1.0 mmol BAM/g silica (for a 1.0:0.78 molar ratio of BAM/OH), after which the BAM-treated silica was still found to contain 0.05 to 0.08 mmol OH/g silica.

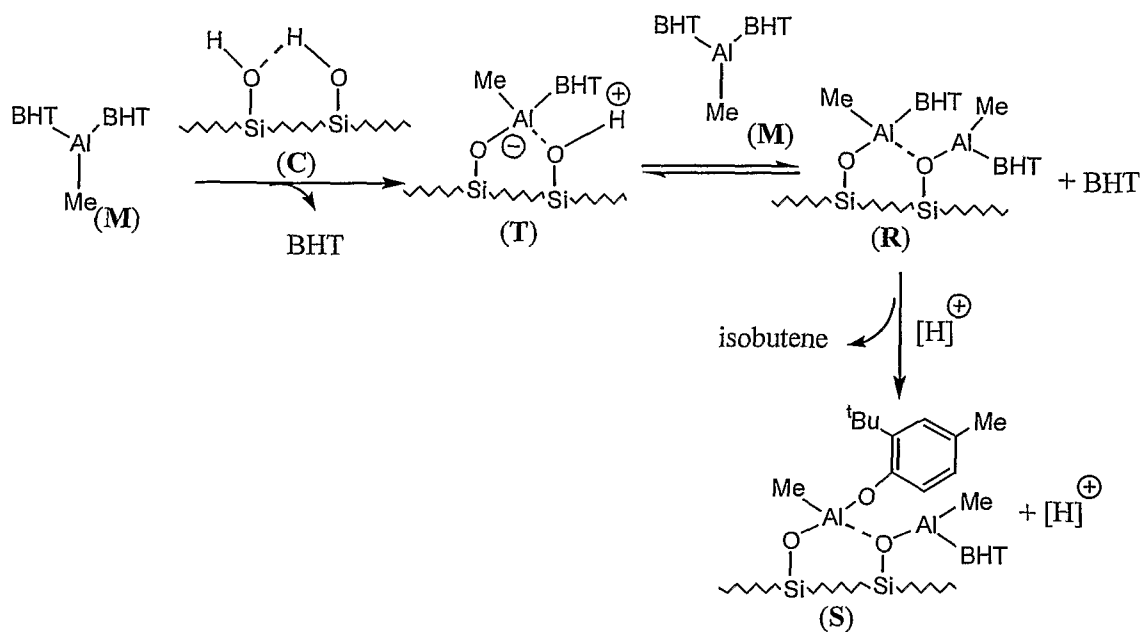
[0057] Based on the observed chemistry as disclosed herein, the reaction mechanisms for contacting BAM with the active OH on silica, are illustrated in four different schemes, as follows: **1)** reaction of BAM with free OH (**B**) is provided in Scheme 5; and **2)** the reaction of BAM with H-bonded OH (**C**) is illustrated in Schemes 6 and 7. One common theme observed in these reaction schemes is the loss of isobutene from one of the t-butyl groups of the BHT ligand, a reaction catalyzed by active protons. Unlike DBAB, catalysts derived from contacting a molar deficiency of BAM with active OH on silica resulted in lower polymer productivities.

[0058] In general, reactions of BAM with silica are similar to DBAB. Their differences are related to the low activity and steric congestion of BAM: 1) because of the low activity of BAM, it can form a complex with a siloxyl group on silica without protonation of its ligands to form an active species **N** (Scheme 5), although this ionic complex eventually decomposes to form neutral compounds (Scheme 5, **O** and **P**), similar to the neutral compounds derived from DBAB (Scheme 1, **D** and **E**); 2) Two BHT groups on one Al center are apparently so congested that one of the BHT group tends to lose a t-Bu group to reduce the system strained energy to become more stable (Scheme 5, **Q** and Scheme 7, **V**); 3) Again, because BAM is unreactive, therefore some reactions are reversible, for example, **M** to **N** in Scheme 5, **T** to **R** in Scheme 6, and **M** to **T** in Scheme 7; that can be the reason why excess BAM has to be used to obtain a highly active system.

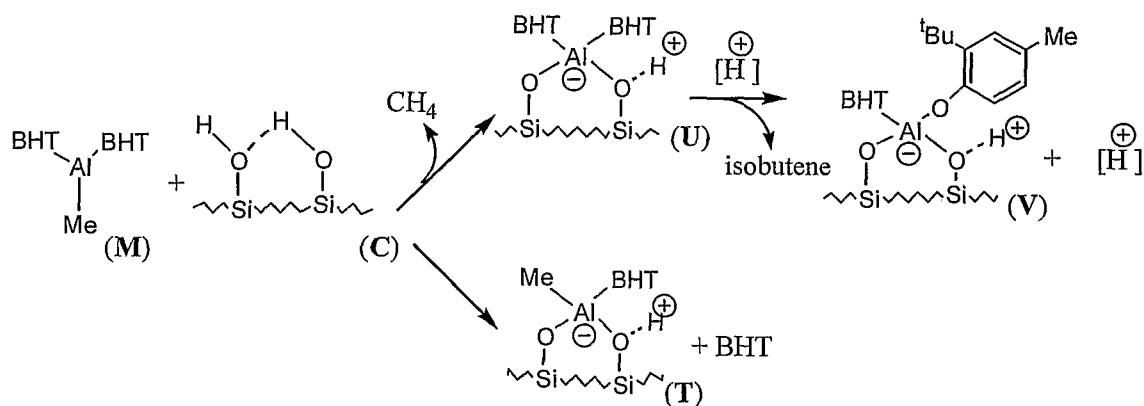
Scheme 5



Scheme 6



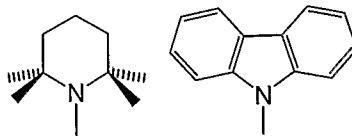
Scheme 7



Supported Aluminate Activators Utilizing Other Bulky Functional Ligands

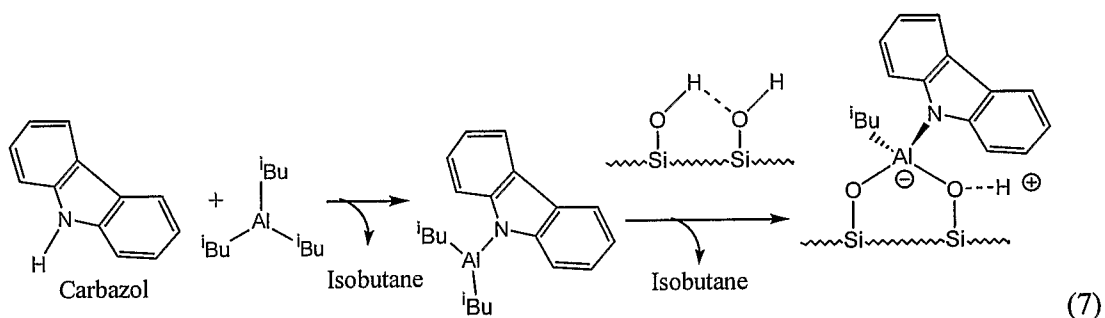
[0059] In another aspect, this invention provides for the preparation and use of silica-supported aluminate activators comprising bulky functional ligands other than DBAB and BAM coordinated to the aluminum atom. For example, in one aspect, the organoaluminum compound is reacted with a bulky compound having the formula HER^3 , wherein R^3 is a hydrocarbyl group or a silyl group, each said group having up to about 20 carbon atoms, and E is O, S, or NR^4 , as defined herein. The bulky functional ligand is selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl

aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate, and typically having up to about 20 carbon atoms. When the moiety E of the bulky functional ligand HER^3 is NR^4 , then R^4 is hydrogen or a hydrocarbyl group having up to about 10 carbon atoms, or R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms. Examples of a suitable



heterocyclic group include, but are not limited to, , , and the like.

[0060] In this aspect, bulky amide groups were found to be suitable for coordination to a supported organoaluminum activators for metallocene-based polymerization catalysts. For example, as illustrated in Reaction (7), the silica-supported aluminate-proton ion-pair can comprise a carbazole amide ligand. Thus, carbazole $C_{12}H_9N$ (9-azafluorene or dibenzopyrrole) was reacted with TIBA to provide an amide compound $(C_{12}H_8N)Al(i-Bu)_2$, which is an amide analog of DBAB. The amide compound $(C_{12}H_8N)Al(i-Bu)_2$ was supported on Silica I in a manner analogous to that disclosed for the DBAB, which was observed to activate the metallocene **M1** toward polymerization of propylene.



Lewis Base Treatment of the Metal Oxide Support or the Supported Activator

[0061] In one aspect, this invention encompasses metal oxide-supported, Brønsted acidic, bulky aluminate activators, in which the aluminate is ionically bonded to a moiety comprising an active proton that imparts the Brønsted acidity to the activator composition. The Brønsted acidic moiety typically is a proton or a Brønsted acidic cation having the formula $[QH]^+$, wherein Q is a Lewis base. In this aspect, $[QH]^+$ can be an ammonium-type ion arising from using an amine as the Lewis Base Q. Thus, the terms ammonium ion or ammonium-type ion are intended to encompass primary, secondary, or tertiary ammonium ions, as the context allows or requires.

[0062] When the activator of this invention comprises an aluminate ion ionically bonded to an ammonium ion, there are three methods by which such a moiety could be prepared: 1) by treatment of the hydroxylated support such as silica with an amine, followed by contacting the amine-treated support with a suitable organoaluminum compound $R^{2-3-n}Al(ER^3)_n$, termed "pre-treatment" of the

support with an amine; 2) by treatment of the already-formed activator, the $R^2_{3-n}Al(ER^3)_n$ -treated hydroxylated support, with an amine, that is contacting the hydroxylated support with at least one suitable organoaluminum compound $R^2_{3-n}Al(ER^3)_n$ to form an activator, followed by contacting the activator with an amine, termed "post-treatment" of the support or activator with an amine; or 3) by the simultaneous treatment of the hydroxylated support with an amine and a suitable organoaluminum compound $R^2_{3-n}Al(ER^3)_n$. It is expected that different methods can work better with some combinations of hydroxylated support, $R^2_{3-n}Al(ER^3)_n$ and amine. Typically the first method works well and has been employed herein across a wide range of components.

[0063] Generally, a wide range of amines can be utilized in the Lewis base treatment of the metal oxide support or the supported activator in this invention. In one aspect, the Lewis base Q can be a primary, secondary, or tertiary amine NR^1_3 , or any combination thereof, wherein R^1 in each occurrence is selected independently from a hydrocarbyl group having up to about 20 carbon atoms, or hydrogen. For example, Q can be selected from a variety of amines, including, but not limited to, NMe_2Ph , $NMe_2(CH_2Ph)$, NEt_2Ph , and $NEt_2(CH_2Ph)$, or Q can be selected from a range of long chain amines having a general formulas such as $NMe(C_nH_{2n+1})(C_mH_{2m+1})$, $NMe_2(C_nH_{2n+1})$, $NEt(C_nH_{2n+1})(C_mH_{2m+1})$, and $NEt_2(C_nH_{2n+1})$, wherein n and m are selected independently from an integer from about 3 to about 20. Examples of long chain amines of the formula $NMe(C_nH_{2n+1})(C_mH_{2m+1})$ include, but are not limited to, compounds such as $NMe(C_{16}H_{33})_2$, $NMe(C_{17}H_{35})_2$, $NMe(C_{18}H_{37})_2$, $NMe(C_{16}H_{33})(C_{17}H_{35})$, $NMe(C_{16}H_{33})(C_{18}H_{37})$, $NMe(C_{17}H_{35})(C_{18}H_{37})$, and the like, including any combination thereof. For example, $NMe(C_{16}H_{33})_2$ is typically the major species in a commercial long chain amine composition which usually comprises a mixture of several amines. In one aspect, the Lewis base typically comprises NMe_2Ph , $NMe_2(CH_2Ph)$, NEt_2Ph , $NEt_2(CH_2Ph)$, or $NMe(C_{16}H_{33})_2$.

[0064] When a Lewis base is employed, it is expected that the base interacts with an active proton situated either on the support itself (pre-treatment) or on the $R^2_{3-n}Al(ER^3)_n$ -treated support (post-treatment), because the active proton is bonded to an oxygen atom. Any Lewis base such as an amine can be used that interacts with at least some of with an active proton, for example, by coordination, hydrogen-bonding, deprotonation, or the like. Thus, in this aspect, this invention encompasses an activator composition comprising the contact product of:

- a) a metal oxide support comprising surface hydrogen-bonded hydroxyl groups;
- b) an organoaluminum compound having at least one bulky functional ligand, which typically comprises an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate; and
- c) optionally, a Lewis base Q such as an amine;

wherein the metal oxide support, the organoaluminum compound, and the optional Lewis base are contacted in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion covalently bonded to the metal oxide support through two chelating oxygen atoms on the support and ionically bonded to a Brønsted acidic cation selected from H^+ and $[QH]^+$, where $[QH]^+$ is the ammonium ion corresponding to the protonated Lewis base Q. Optionally, an aluminate species comprising an aluminate anion bonded to the support through one oxygen atom can be present in the activator composition.

[0065] The use of the term ammonium ion or ammonium-type ion is not intended to limit the bonding or interaction to a particular type, as this terminology is used regardless of whether the amine coordinates, hydrogen-bonds to, deprotonates, deprotonates and ionically-bonds to, deprotonates and ion pairs with, ionically bonds to, or interacts in some other manner with the active proton of the support or the treated support. In one aspect, when an amine-treated support or activator is characterized as comprising the contact products of its precursors, these components are contacted in amounts sufficient and under conditions sufficient to form a composition wherein the active proton and Lewis base interact according to any of these interactions listed, which can be formally described as forming a composition comprising at least one aluminate anion and at least one Brønsted acidic cation of the formula $[QH]^+$. Similarly, describing the $[aluminate][QH]^+$ interaction as ionically-bonded, or according to any other of these possibilities, is also not intended to limit the interaction between the hydroxyaluminumoxane and amine to a particular type of interaction, but merely reflects a formal $[aluminate][QH]^+$ moiety that forms in this reaction. Similarly, terms such as bonding or interaction are also not intended as limited to a particular type of bonding or interaction.

[0066] In another aspect, the molar ratio of Lewis base Q to aluminum atoms in the activator composition, regardless of whether the base is added pre-treatment or post-treatment, can vary to a considerable extent. Typically, the Q:Al ratio employed is calculated on the basis of the moles of active OH present in the calcined support or the activator composition, such that an approximately equimolar base (Q):active OH (active proton) ratio is achieved. Thus, the molar ratio of Q:active OH can span a range from about 0 to about 1.5. The molar ratio of Q:active OH can also span a range from about 0 to about 1, from about 0.1 to about 1, or from about 0.5 to about 1.

Catalyst Precursors

[0067] Metallocene and non-metallocene single-site catalyst precursors, suitable for activation by activator compositions of this invention, can comprise one or more alkylated transition metal component having olefin polymerization potential. The alkyl ligand of the precursor functions as a leaving group upon reaction of the precursor with the proton of the Brønsted acid of the activator composition. For example, without limiting this invention, hydrocarbyl is a suitable alkylated

transition metal ligand. Provided that suitable alkylation agent is provided in situ, halogen, alkoxy, aryloxy, and amide transition metal components are all suitable.

[0068] Catalyst precursors can comprise catalyst precursor $ML_n X_{n-a}$.

[0069] M represents any transition metal catalyst compound in which the transition metal thereof is in Group 3 to 10, or in the lanthanide or actinide series, of the Periodic Table of Elements using the new IUPAC format, for example, the Periodic Table appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*. Suitable catalyst compounds can also be described as d- and f- block metal compounds. See, for example, the Periodic Table appearing on page 225 of Moeller, et al., *Chemistry*, Second Edition, Academic Press, copyright 1984. Metal constituent of M may comprise Fe, Co, Ni, and Pd, and may comprise metals of Groups 4-6 (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W).

[0070] Thus catalyst precursors used in this invention can be one or more of any Ziegler-Natta catalyst compound, any metallocene, any single-site non-metallocene, any compound of constrained geometry, any late transition metal complex, and any other transition metal compound or complex reported in the literature or otherwise generally known in the art to be an effective catalyst compound when suitably activated, including mixtures of at least two different types of such transition metal compounds or complexes, such as for example a mixture of a metallocene and a Ziegler-Natta olefin polymerization catalyst compound.

[0071] L represents group having ligand suitable for either Ziegler-Natta type catalyst precursor, or metallocene type catalyst precursor, or non-metallocene single-site catalyst precursor. At least one L may be group having cyclopentadienyl skeleton, or may be non-cyclopentadienyl; and a plurality of L may be the same or different and may be crosslinked to each other; X represents halogen, alkoxy, aryloxy, amide or hydrocarbyl group having 1 to about 20 carbon atoms; "a" represents a numeral satisfying the expression $0 < a \leq n$; and n represents valence of transition metal atom M.

[0072] In L in catalyst precursors, group having cyclopentadienyl skeleton can comprise, for example, cyclopentadienyl group, substituted cyclopentadienyl group or polycyclic group having cyclopentadienyl skeleton. Example substituted cyclopentadienyl groups include hydrocarbon group having 1 to about 20 carbon atoms, halogenated hydrocarbon group having 1 to about 20 carbon atoms, silyl group having 1 to about 20 carbon atoms and the like. Silyl group according to this invention can include $SiMe_3$ and the like. Examples of polycyclic group having cyclopentadienyl skeleton include indenyl group, fluorenyl group and the like. Examples of hetero atoms of the group having at least one hetero atom include nitrogen atom, oxygen atom, phosphorous atom, sulfur atom and the like.

[0073] Example non-metallocene d-block or f-block metal compounds that can be used in this invention include, but are not limited to, transition metal compounds suitable for olefin

polymerization such as Ziegler-Natta type catalysts. Typically, transition metal of Ziegler-Natta catalysts comprises at least two hydrocarbyl ligands. Examples of Ziegler-Natta catalyst systems are disclosed in U.S. Patent Application Number 2004/0102312, and are described herein as follows. Representative traditional Ziegler-Natta transition metal compounds include, but are not limited to, tetrabenzyl zirconium, tetrakis(trimethylsilylmethyl)zirconium, oxotris(trimethylsilylmethyl)vanadium, tetrabenzyl hafnium, tetrabenzyl titanium, bis(hexamethyl disilazido)dimethyl titanium, tris(trimethylsilylmethyl)niobium dichloride, tris(trimethylsilylmethyl)tantalum dichloride, and combinations thereof. Other Ziegler-Natta type systems that can be used in this invention include, but are not limited to, transition metal halides, oxyhalides or alkoxyhalides in the presence of an alkylating agent such as a dialkylaluminum alkoxide or trialkyl aluminum compound. Examples of this Ziegler-Natta type system include, but are not limited to, titanium and vanadium halides, oxyhalides or alkoxyhalides, such as titanium tetrachloride (TiCl₄), vanadium tetrachloride (VCl₄) and vanadium oxytrichloride (VOCl₃), and titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl group from 1 to 20 carbon atoms, or from 1 to 6 carbon atoms. Any chloride-containing catalyst precursor is suitable once alkylated, including via in-situ alkylation, by methods well-known to those skilled in the art.

[0074] In still another aspect, useful d-block or f-block metal compounds that can be used in this invention include, but are not limited to, the Group 15-containing compounds, such as those disclosed in U.S. Patent Application Number 2004/0102312, and defined above. Examples of Group 15-containing compounds include, but are not limited to, Group 4 imino-phenol complexes, Group 4 bis(amido) complexes, and Group 4 pyridyl-amide complexes that are active towards olefin polymerization to any extent. In one aspect, the Group 15-containing catalyst component can be described by the following formula:

$\beta_b(\alpha)_a\gamma_gMX_n$; wherein:

β and γ are groups that each comprise at least one Group 14 to Group 16 atom; and β (when present) and γ are groups bonded to M through from 1 to 4 Group 14 to Group 16 atoms, wherein at least two atoms are Group 15-containing atoms; more particularly: β and γ are groups selected from Group 14 and Group 15-containing (and their non-valent equivalents when not linked by a group α): alkyls, aryls, alkylaryls, and heterocyclic hydrocarbons, and chemically bonded combinations thereof in one aspect; and selected from Group 14 and Group 15-containing: C₁ to C₁₀ alkyls, C₆ to C₁₂ aryls, C₆ to C₁₈ alkylaryls, and C₄ to C₁₂ heterocyclic hydrocarbons, and chemically bonded combinations thereof in a further aspect; and selected from C₁ to C₁₀ alkylamines, C₁ to C₁₀ alkoxy, C₆ to C₂₀ alkylarylamines, C₆ to C₁₈ alkylaryloxys, and C₄ to C₁₂ nitrogen containing heterocyclic hydrocarbons,

and C₄ to C₁₂ alkyl substituted nitrogen containing heterocyclic hydrocarbons and chemically bonded combinations thereof in still another aspect; and selected from anilinylys, pyridyls, quinolylys, pyrrolyls, pyrimidylys, purinylys, imidazylys, indolylys, C₁ to C₆ alkyl substituted groups selected from anilinylys, pyridyls, quinolylys, pyrrolyls, pyrimidylys, purinylys, imidazylys, indolylys; C₁ to C₆ alkylamine substituted groups selected from anilinylys, pyridyls, quinolylys, pyrrolyls, pyrimidylys, purinylys, imidazylys, indolylys, amine substituted anilinylys, pyridyls, quinolylys, pyrrolyls, pyrimidylys, purinylys, imidazylys, and indolylys; hydroxy substituted groups selected from anilinylys, pyridyls, quinolylys, pyrrolyls, pyrimidylys, purinylys, imidazylys, and indolylys; methyl-substituted phenylamines, and chemically bonded combinations thereof in yet a further aspect: α can be a linking (or “bridging”) moiety that, when present, forms a chemical bond to each of β and γ , or to two γ moieties, thus forming a “ $\gamma\alpha\gamma$ ” or “ $\gamma\alpha\beta$ ” ligand bound to M; α can also include a Group 14 to Group 16 atom which can be bonded to M through the Group 14 to Group 16 atom in one aspect; and more particularly, α can be a divalent bridging group selected from alkylenes, arylenes, alkenylenes, heterocyclic arylenes, alkylarylenes, heteroatom containing alkylenes, heteroatom containing alkenylenes and heterocyclic hydrocarbonylenes in another aspect; and selected from C₁ to C₁₀ alkylenes, C₂ to C₁₀ alkenylenes, C₆ to C₁₂ arylenes, C₁ to C₁₀ divalent ethers, C₆ to C₁₂ O- or N-containing arylenes, C₂ to C₁₀ alkyleneamines, C₆ to C₁₂ aryleneamines, and substituted derivatives thereof in yet a further aspect;

a is typically 0 or 1;

b is typically an integer from 0 to 2;

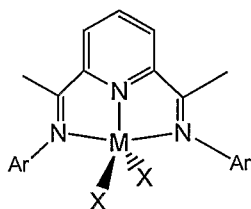
g is an integer from 1 to 2; wherein in one aspect, a is 1, b is 0, and g is 2;

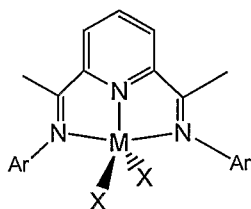
M is selected from Group 3 to Group 12 atoms in one aspect; and selected from Group 3 to Group 10 atoms in a further aspect; and selected from Group 3 to Group 6 atoms in yet another aspect; and selected from Ni, Cr, Ti, Zr and Hf in still a further aspect; and selected from Zr and Hf in yet one other aspect; each X represents halogen, alkoxy, aryloxy, amide or hydrocarbyl group having 1 to about 20 carbon atoms; and n is an integer from 0 to 4 in one aspect; and an integer from 1 to 3 in another aspect; and an integer from 2 to 3 in still another aspect.

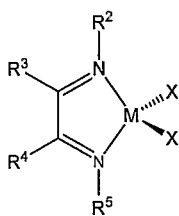
As used in this description, “chemically bonded combinations thereof” means that adjacent groups, (β and γ groups) can form a chemical bond between them; in one aspect, the β and γ groups are chemically bonded through one or more α groups therebetween.

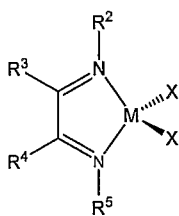
[0075] As used herein, the terms “alkyleneamines”, “aryleneamines”, describe alkylamines and arylamines (respectively) that are deficient by two hydrogens, thus capable of forming chemical bonds with two adjacent γ groups, or adjacent β and γ groups. Thus, examples of an alkyleneamine include, but are not limited to, $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2-$. Examples of a heterocyclic hydrocarbylene or aryleneamine include, but are not limited to, $-\text{C}_5\text{H}_3\text{N}-$ (divalent pyridine). An “alkylene-arylamine” includes a group such as, for example, $-\text{CH}_2\text{CH}_2(\text{C}_5\text{H}_3\text{N})\text{CH}_2\text{CH}_2-$.

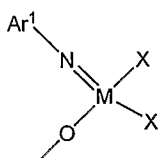
[0076] Examples of compounds having the general formula $\beta_b(\alpha)_a\gamma_b\text{MX}_n$ include, but are not limited to, the following compounds:

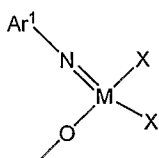


1. , including compounds such as those disclosed in WO 99/02472, wherein examples of Ar include 2-MeC₆H₄, 2,4,6-Me₃C₆H₂, 2-i-PrC₆H₄, and the like; and examples of M include Fe or Ni; and examples of X include Cl, Br, or a C₁ to C₁₂ hydrocarbyl;

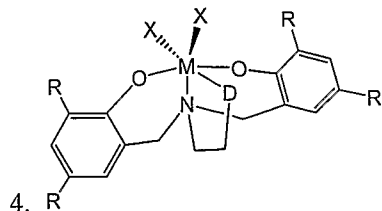


2.  including compounds such as those disclosed in U.S. Patent No. 5,880,241, wherein examples of R² and R⁵ include 2,6-i-Pr₂C₆H₃, 2,6-Me₂C₆H₃, and 2,4,6-Me₃C₆H₂; examples of R³ and R⁴ include methyl, ethyl, propyl, butyl, and benzyl; examples of M include Pd and Ni; and examples of X include Cl, Br, and a C₁ to C₁₂ hydrocarbyl such as Me;



3. , including compounds such as those disclosed in Nomura *et al.*, *Macromolecules*, 2005, in press (Abstract published by the American Chemical Society, *Macromolecules*, ASAP Article 10.1021/ma050629s; S0024-9297(05)00629-7; Web Release Date June 15, 2005), wherein examples of Ar¹ include 2,6-Me₂C₆H₃ and 2,6-i-Pr₂C₆H₃; examples of Ar² include 2,6-Me₂C₆H₃,

2,4,6-Me₃C₆H₂, 2,6-i-Pr₂C₆H₃, and 2,6-Ph₂C₆H₃; examples of M include V; and examples of X include Cl, Br, and a C₁ to C₁₂ hydrocarbyl;



4. , including compounds such as those disclosed in Waymouth *et al.*, *Macromolecules*, 2005, 38, 2552-2558, wherein examples of M include Zr or Hf; examples of X include a C₁ to C₁₂ hydrocarbyl such as CH₂C₆H₅; examples of R include Me, Ph, or t-Bu; and examples of D include NMe₂, OMe, and the like; and

5. any combination of the above compounds.

[0077] In each of these compounds, if X is a halide or alkoxide, these metal compounds typically are used in conjunction with an alkylating agent such as a trialkyl aluminum or alkoxyaluminum dialkyl reagent to convert these compounds to the corresponding dialkyl species.

[0078] Example substituted cyclopentadienyl groups include methylcyclopentadienyl group, ethylcyclopentadienyl group, n-propylcyclopentadienyl group, n-butylcyclopentadienyl group, isopropylcyclopentadienyl group, isobutylcyclopentadienyl group, sec-butylcyclopentadienyl group, tertbutylcyclopentadienyl group, 1,2-dimethylcyclopentadienyl group, 1,3-dimethylcyclopentadienyl group, 1,2,3-trimethylcyclopentadienyl group, 1,2,4-trimethylcyclopentadienyl group, tetramethylcyclopentadienyl group, pentamethylcyclopentadienyl group and the like.

[0079] Example polycyclic groups having cyclopentadienyl group include indenyl group, 4,5,6,7-tetrahydroindenyl group, fluorenyl group and the like.

[0080] Example groups having at least one hetero atom include methylamino group, tert-butylamino group, benzylamino group, methoxy group, tert-butoxy group, phenoxy group, pyrrolyl group, thiomethoxy group and the like.

[0081] One or more groups having cyclopentadienyl skeleton, or one or more group having cyclopentadienyl skeleton and one or more group having at least one hetero atom, may be crosslinked with (i) alkylene group such as ethylene, propylene and the like; (ii) substituted alkylene group such as isopropylidene, diphenylmethylene and the like; or (iii) silylene group or substituted silylene group such as dimethylsilylene group, diphenylsilylene group, methylsilylsilylene group and the like.

[0082] R in transition metal component comprises hydrogen or hydrocarbon group having 1 to about 20 carbon atoms. Examples of R include alkyl group having 1 to about 20 carbon atoms such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, benzyl group and the like.

[0083] Examples of transition metal component ML_nX_{n-a} , wherein M comprises zirconium, include bis(cyclopentadienyl)zirconiumdichloride, bis(methylcyclopentadienyl)zirconiumdichloride, bis(pentamethylcyclopentadienyl)zirconiumdichloride, bis(indenyl)zirconiumdichloride, bis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride, bis(fluorenyl)zirconiumdichloride, ethylenebis(indenyl)zirconiumdichloride, dimethylsilylene(cyclopentadienylfluorenyl)zirconiumdichloride, diphenylsilylenebis(indenyl)zirconiumdichloride, cyclopentadienyldimethylaminozirconiumdichloride, cyclopentadienylphenoxyzirconium dichloride, dimethyl(tert-butylamino)(tetramethylcyclopentadienyl) silanezirconiumdichloride, isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)zirconiumdichloride, dimethylsilylene(tetramethylcyclopentadienyl)(3-tertbutyl-5-methyl-2-phenoxy) zirconiumdichloride and the like.

[0084] Additional exemplary transition metal component ML_nX_{n-a} include components wherein zirconium is replaced with titanium or hafnium in the above zirconium components.

[0085] Alkylated catalyst precursors useful in this invention are: *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl; *rac*-dimethylsilylbis(2-methyl-1-indenyl) zirconium dimethyl; *rac*-dimethylsilylbis(2-methyl-4,5-benzoidenyl) zirconium dimethyl; ethylenebis-(tetrahydroindenyl)zirconium dimethyl, and ethylenebis(indenyl) zirconium dimethyl. Alkylated catalyst precursor can be generated *in-situ* through reaction of alkylation agent with the halogenated version of the catalyst precursor. For example, bis(cyclopentadienyl)zirconium dichloride can be treated with triisobutylaluminum (TIBA) and then combined with activator composition (A) of this invention.

[0086] Additional non-limiting and representative metallocene compounds that can be used in the present invention include mono-cyclopentadienyl compounds such as pentamethylcyclopentadienyl titanium trimethyl, pentamethylcyclopentadienyl titanium tribenzyl, dimethylsilyltetramethyl-cyclopentadienyl-tert-butylamido titanium dimethyl, dimethylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dimethyl, dimethylsilyltetramethylcyclopentadienyl-dodecylamido hafnium dihydride, dimethylsilyltetramethylcyclopentadienyl-dodecylamido hafnium dimethyl, unbridged biscyclopentadienyl compounds such as bis(1,3-butylmethylcyclopentadienyl) zirconium dimethyl, bis(1,3-butylmethylcyclopentadienyl)zirconium dibenzyl, pentamethylcyclopentadienyl-cyclopentadienyl zirconium dimethyl, (tetramethylcyclopentadienyl)(n-propylcyclopentadienyl)zirconium dimethyl; bridged bis-cyclopentadienyl compounds such as dimethylsilylbis(tetrahydroindenyl)zirconium dimethyl and silacyclobutyl(tetramethylcyclopentadienyl)(n-propyl-cyclopentadienyl) zirconium dimethyl; bridged bisindenyl compounds such as dimethylsilylbis(indenyl) zirconium dimethyl,

dimethylsilylbis(indenyl)zirconium dibenzyl, dimethylsilylbis(indenyl) hafnium dimethyl, dimethylsilylbis(2-methylbenzindenyl) zirconium dimethyl, dimethylsilylbis(2-methylbenzindenyl)zirconium dibenzyl; and fluorenyl ligand-containing compounds, for example, diphenylmethyl(fluorenyl)(cyclopentadienyl)zirconium dimethyl; and the additional mono- and bis-cyclopentadienyl compounds such as those listed and described in U.S. Patent Nos. 5,017,714 and 5,324,800, and in EP-A-0 591 756.

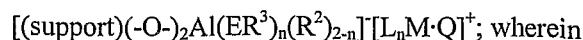
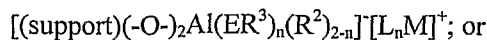
Catalyst Compositions

[0087] In one aspect, this invention provides a catalyst composition comprising a metal oxide support, an aluminate anion, a cationic d-block or f-block metal compound, and optionally a Lewis base, wherein:

- a) the aluminum atom of the aluminate anion is covalently bonded to the metal oxide support through two chelating oxygen atoms;
- b) the aluminum atom of the aluminate anion is covalently bonded to at least one bulky functional ligand, which is typically selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate;
- c) the aluminate anion is ionically bonded to the cationic d-block or f-block metal compound;
- d) the cationic d-block or f-block metal compound comprises at least one ligand capable of propagating olefin polymerization; and
- e) the Lewis base is optionally coordinated to the cationic d-block or f-block metal compound.

In this aspect, the cationic d-block or f-block metal compound has the formula $[L_nM]^+$ when not coordinated by the Lewis base and $[L_nM \cdot Q]^+$ when coordinated by the Lewis base, wherein: L_n comprises any set of ligands on M selected such that $[L_nM]^+$ is coordinatively unsaturated; and the at least one ligand of $[L_nM]^+$ capable of propagating olefin polymerization is hydrogen or a hydrocarbyl ligand having up to about 12 carbon atoms. Optionally, the aluminate species comprising an aluminate anion bonded to the support through one oxygen atom can be present in the activator composition.

[0088] Yet a further aspect of the present invention encompasses a catalyst composition comprising:



the support comprises silica;

n is 1 or 2;

R² is hydrogen or a hydrocarbyl ligand having up to about 20 carbon atoms;

R³ is a hydrocarbyl group or a silyl group, each said group having up to about 20 carbon atoms;

E is O, S, or NR⁴, wherein (i) R⁴ is (a) hydrogen or (b) a hydrocarbyl group or a silyl group, each said group having up to about 10 carbon atoms, or (ii) R³ and R⁴ together form a heterocyclic group having up to about 20 carbon atoms;

[L_nM]⁺ is a d-block or f-block metal compound cation capable of polymerizing olefins; and

Q is a Lewis base.

Such a catalyst composition can also comprise [(support)(-O-)Al(ER³)_n(R²)_{3-n}][L_nM]⁺ or [(support)(-O-)Al(ER³)_n(R²)_{3-n}][L_nM·Q]⁺. This aspect of the invention also encompasses a method for polymerizing olefins, comprising contacting at least one olefin monomer with the catalyst composition of this type.

[0089] In another aspect, this invention provides a catalyst composition comprising the contact product of:

- a) a metal oxide support comprising hydrogen bonded surface hydroxyl groups;
- b) at least one organoaluminum compound having at least one bulky functional ligand, which is typically selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate;
- c) optionally, a Lewis base Q; and
- d) at least one d-block or f-block metal compound comprising at least one ligand subject to protonolysis to form a catalytically-active cationic species;

wherein the metal oxide support, the organoaluminum compound, the optional Lewis base, and the d-block or f-block metal compound are contacted in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion covalently bonded to the metal oxide support through two chelating oxygen atoms and ionically bonded to the cationic transition metal compound. As used herein, any d-block or f-block metal compound comprising at least one ligand subject to protonolysis to form a catalytically-active cationic species can be termed a catalyst precursor. This disclosure also encompasses a method of preparing a catalyst composition comprising contacting the components recited above. This aspect further encompasses a method for polymerizing olefins, comprising contacting at least one olefin monomer with the catalyst composition of this type.

[0090] Accordingly, the present invention also encompasses a method of preparing a composition comprising a metallocene cation and a supported, Brønsted acidic, bulky aluminate activator comprising contacting the following constituents: a) at least one organoaluminum compound having the formula AlR^2_3 ; b) a compound of the formula HER^3 , c) optionally a Lewis base Q; and d) at least one metallocene comprising at least one leaving group; in amounts sufficient and under conditions sufficient to form a compound comprising an aluminate anion and a metallocene cation $[L_nM]^+$.

[0091] In one aspect, to produce the catalytically active catalyst compositions of this invention, the metallocene and the supported, Brønsted acidic, bulky aluminate activator were brought together in a slurry. In one aspect, the temperature of the reaction mixture is kept in the range of about -78°C to about 160°C , but typically can be in the range of about 20 - 90°C . Under typical conditions, the reaction is conducted under an inert atmosphere and in an inert environment such as in an anhydrous solvent slurry. Reaction times vary, but the protonation reactions are typically smooth and often proceed to completion within less than 24 hours. Various aspects of the metal oxide support were considered above.

[0092] In one aspect, contacting the catalyst precursor with the support can be carried in various ways to synthesize a supported catalyst of this invention. For example, the bulky aluminate activator, such as BAM-treated or DBAB-treated silica, can be pre-formed and isolated, then contacted with at least one metallocene to form a catalyst. Further, the bulky aluminate activator can be prepared in situ by contacting a suitable organoaluminum compound such as BAM or DBAB with the appropriate silica sample, the bulky aluminate activator then can be isolated and subsequently contacted with at least one catalyst precursor to form a catalyst. Alternatively, the bulky aluminate activator can be prepared in situ and not isolated, by contacting the organoaluminum compound with silica, and then at least one metallocene can be contacted with this mixture to form a catalyst.

Polymerization Processes

[0093] Additional aspects of the polymerization reaction conditions, aspects of the recovery of the active catalyst compositions, the finishing process that can be used in the preparation of the catalysts, the storage of recovered active catalyst compositions, polymerization processes using catalyst of this invention, suitable olefin monomers, extensive examples of useful metallocenes that can be employed in the practice of this invention, and the like, are all provided in detail in U.S. Patent No. 6,462,212.

[0094] As disclosed herein, the catalyst compositions of this invention can be used in solution or deposited on a solid support. When the catalyst compositions are used in solution polymerization reactions, where applicable, the solvent can simply constitute a large excess quantity of the liquid

olefinic monomer to be polymerized. Typically, however, an ancillary inert solvent, typically a hydrocarbon solvent, for example a liquid paraffinic or aromatic hydrocarbon solvent, can be used. Examples of the hydrocarbon solvents that can be employed in these polymerizations include, but are not limited to, heptane, isooctane, decane, toluene, xylene, ethylbenzene, mesitylene, mixtures of liquid paraffinic hydrocarbons, mixtures of liquid aromatic hydrocarbons, or any combination thereof. When the catalyst compositions of this invention are supported on a carrier, the solid support or carrier can be any suitable particulate solid, and typically comprises a porous support of some type. Examples include, but are not limited to, talc, zeolites, inorganic oxides, resinous support material such as polyolefins, or any combination thereof.

[0095] In one aspect of the present invention, the support material is typically an inorganic oxide in finely divided form. Suitable inorganic oxide support materials which can be employed in this invention include metal oxides. Examples of useful metal oxides include, but are not limited to, silica, alumina, silica-alumina, magnesia, titania, zirconia, and the like, and any combination thereof. Other suitable support materials include finely divided polyolefins such as finely divided polyethylene.

[0096] Polymers can be produced according to the present invention by homopolymerization of polymerizable olefins, typically 1-olefins (α -olefins) such as ethylene, propylene, 1-butene, styrene, and the like. Alternatively, polymers can be produced according to the present invention by co-polymerization of two or more co-polymerizable monomers, at least one of which is typically a 1-olefin. In the case of co-polymerization, in addition to a 1-olefin that is typically employed, the other monomer(s) used in forming such co-polymers can be one or more different 1-olefins, a diolefin, a polymerizable acetylenic monomer, and the like, including any combination thereof. The 1-olefins that can be polymerized in the presence of the catalysts of this invention typically include α -olefins having from 2 to about 20 carbon atoms, examples of which include, but are not limited to, ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The hydrocarbon co-monomers used, such as 1-olefins, diolefins, acetylene monomers, or any combination thereof, typically contain up to about 12 carbon atoms per molecule.

[0097] In another aspect, the 1-olefin monomers that are useful in the present invention include ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, and the like, including any combination thereof. In a further aspect, the supported or unsupported catalysts of this invention are useful in the polymerization of ethylene, propylene, or ethylene and at least one C_3 - C_8 1-olefin that is co-polymerizable with ethylene. Typical diolefin monomers that can be used to form terpolymers with ethylene and propylene include, but are not limited to, butadiene, hexadiene, norbornadiene, and similar co-polymerizable diene hydrocarbons. 1-Heptyne and 1-octyne are

illustrative of suitable co-polymerizable acetylenic monomers which can be used in the present invention.

[0098] Polymerization of ethylene or co-polymerization with ethylene and an α -olefin having from 3 to about 10 carbon atoms typically can be performed in either the gas or liquid phase, for example, in a solvent such as toluene or heptane. Such polymerizations can be conducted at conventional temperatures (for example from about 0°C to about 120°C) and at conventional pressures (for example, from about ambient pressure to about 50 kg/cm²) using conventional procedures as to molecular weight regulations and the like.

[0099] In yet another aspect of this invention, the heterogeneous catalysts of this invention can be used in polymerizations conducted as slurry processes, as gas phase processes, or by any other polymerization process that is known in the art. Typically, by "slurry" is meant that the particulate catalyst is used as a slurry or dispersion in a suitable liquid reaction medium which can comprise one or more ancillary solvents such as liquid aromatic hydrocarbons and the like, or an excess amount of liquid monomer to be polymerized in bulk. Generally, these polymerizations can be conducted at one or more temperatures in the range of about 0°C to about 160°C, and under atmospheric, sub-atmospheric, or super-atmospheric conditions. Conventional polymerization adjuvants, such as hydrogen, can be employed if desired. Typically, polymerizations conducted in a liquid reaction medium containing a slurry or dispersion of a catalyst of this invention can be conducted at temperatures in the range of about 40°C to about 110°C, and usual liquid diluents for such processes include, but are not limited to, hexane, toluene, and similar materials, although the compounds and compositions of this invention are applicable to any polymerization that is conducted outside these ranges and conditions. Typically, when conducting gas phase polymerizations, super-atmospheric pressures are often used and the reactions are often conducted at temperatures in the range of about 50°C to about 160°C. In one aspect, the gas phase polymerizations can be performed in a stirred or fluidized bed of catalyst in a pressure vessel adapted to permit the separation of product particles from unreacted gases. In addition to the typically thermostated ethylene and optional comonomer, hydrogen, an inert diluent gas such as nitrogen, or a combination thereof can be introduced or recirculated to maintain the particles at the desired polymerization reaction temperature. An optional aluminum alkyl such as triethylaluminum can be added as a scavenger of water, oxygen, and other impurities. Typically, the aluminum alkyl can be employed as a solution in a suitable dry liquid hydrocarbon solvent such as toluene or xylene. As an example, concentrations of such aluminum alkyl in hydrocarbon solutions in the range of about 5×10^{-5} molar are conveniently used, although solutions of greater or lesser concentrations are useful and can be employed if desired. The resulting polymer product can be withdrawn continuously or semi-continuously, typically at a rate that maintains a constant product inventory in the reactor.

[00100] The catalyst compositions of this invention can also be used along with small amounts of hydrocarbylborane compounds, examples of which include, but are not limited to, triethylborane, tripropylborane, tributylborane, trisecbutylborane, or any combination thereof. In this aspect, when hydrocarbylborane compounds are used, molar Al/B ratios in the range of about 1/1 to about 1/500 are typical, though higher and lower ratios are also useful.

[00101] Because of the high activity and productivity of the catalysts of this invention, the catalyst levels used in olefin polymerizations can be less than previously used in typical olefin polymerizations conducted on an equivalent scale using more traditional activator compositions. In general, the polymerizations and co-polymerizations conducted according to this invention are carried out using a catalytically-effective amount of the catalyst composition of this invention, which amount can be varied depending upon such factors as the type of polymerization being conducted, the monomers and co-monomers employed, the polymerization conditions being used, and the type of reaction equipment in which the polymerization is being conducted. In many cases, the amount of the catalyst of this invention used will be such as to provide in the range of from about 0.000001 to about 0.01 percent by weight of the d- or f-block metal, including metallocene, based on the weight of the monomer(s) being polymerized. However, the amount of the catalyst used in the practice of this invention can be more or less than the amounts encompassed by this range, again depending upon the type of polymerization and the conditions, the monomers and co-monomers employed, the type of reaction equipment employed, and the like, all of which will be readily understood by one of ordinary skill in the art.

[00102] After polymerization and deactivation of the catalyst in a conventional manner, the product polymer can be recovered from the polymerization reactor by any suitable means. When conducting the process with a slurry or dispersion of the catalyst in a liquid medium, the product typically is recovered by a physical separation technique such as by decantation or the like. The recovered polymer is usually washed with one or more suitably volatile solvents to remove residual polymerization solvent or other impurities, and then dried, typically under reduced pressure, optionally with the addition of heat. When conducting the process as a gas phase polymerization, the product after removal from the gas phase reactor is typically freed of residual monomer by means of a nitrogen purge, and often can be used without further catalyst deactivation or catalyst removal.

[00103] When preparing polymers according to this invention, conditions and catalysts can be employed for preparing unimodal or multimodal types of polymers. Thus, for example, mixtures of one or more catalysts of this invention, formed from two or more different metallocenes, two or more different activators, or any combination of different metallocenes and activators, can be employed in a single polymerization run. In this case, the different catalyst might be expected to exhibit different

propagation and termination rate constants for ethylene polymerizations and therefore can be used in preparing polymers having tailored molecular weight distributions of the multimodal type.

[00104] Further details on the polymerization chemistry and the method for polymerizing olefins is provided in many of the U.S. Patents that have been discussed herein, including, for example, U.S. Patent Nos. 6,562,991, 6,555,494, 6,492,292, 6,462,212, and 6,160,145.

Polymerization Tests Using DBAB-Treated and BAM-Treated Silica Activators and a Metallocene

[00105] The following experiments also provide data on which the reaction mechanisms or reaction schemes illustrated herein for both DBAB-treated and BAM-treated silica are established, and provide an experimental basis on which the appended claims are fully supported.

[00106] Example 10 and Table 6 summarize the propylene polymerization results obtained from using *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)-derived catalysts, in which either BAM-treated or DBAB-treated silica were used as activators. By examining Table 6 and comparing Entry 2 with Entry 3 and by comparing Entry 4 with Entry 5, the 600°C calcined silica provides higher activities for both the DBAB-derived and the BAM-derived catalyst systems. Regarding the types of silica OH moieties, comparing Entry 2 with Entry 3 clearly shows that active species derived from the H-bonded silica OH moieties, which richly populate the 600°C calcined silica, are more vigorous or potent than active species derived from the free OH moieties, which are the major OH species in the 800°C calcined silica. As noted, free OH can coordinate to a BAM molecule to form the active species N (Scheme 5). This species is dominant in the BAM treated, 800°C calcined silica based on the IR spectrum that shows no significant 3690cm⁻¹ peak (the chelated aluminate-proton ion-pair) but 3490cm⁻¹, a frequency related to BAM derived compounds (FIG. 4, spectrum 42). Since Entry 2 has the same Zr loading as Entry 3, we can conclude that the chelated, double siloxyl bonded aluminate-proton ion-pair (F, Scheme 3) is much more active than the single siloxyl bonded aluminate-proton ion-pair (N, Scheme 5). This notion can be confirmed by comparing Entry 4 with Entry 2, which reveals that the DBAB-derived catalyst from the 800°C calcined silica has insignificant activity. This observations likely results because DBAB cannot form an N type active species with free OH groups under ambient conditions due to the higher reactivity of secondary Al-R in DBAB, which causes an alkane elimination of the active proton with Al-R to form a neutral species (Scheme 1, E).

[00107] Table 6 also shows that a different support Silica II can also be used to make a highly active catalyst, although the calcination conditions can be different (Entry 1 vs. Entry 6). The data from Silica II in Table 6 also seem to indicate that if the hydrogen bonded OH content on Silica II is sufficient (for example, 0.80 mmol/g, Entry 1) and BAM, which is able to form a single siloxyl

bonded aluminate-proton ion-pair **N** with free OH, is used to construct the activator, even the resulting catalyst with a higher Zr loading (0.31%) does not provide a higher polymer productivity (12,300 g/g cat/hr). In comparison, upon allowing more hydrogen bonded OH content on Silica II (for example, 1.10 mmol/g) by shortening the calcination time, and using DBAB which only form chelated aluminate-proton ion-pair with two silica silyloxy groups to construct the active site, the productivity can be significantly increased even with significantly lower Zr loading (0.11 wt% Zr, 13,300 g/g cat/hr productivity). These data again are strong supporting evidence that the chelated aluminate-proton ion-pair is more active than the non-chelated one on silica.

[00108] Example 9 and Table 5 summarize the propylene polymerization results obtained from using four different metallocene-derived catalysts, in which BAM-treated silica was used as the activator. The catalyst analytical results and propylene polymerization results using these catalysts are provided in Table 5. Data were obtained for the following metallocenes that were used to prepare metallocene-based BAM-treated Silica I catalysts, according to the procedure detailed in the examples: *rac*-dimethylsilylbis(2-methyl-1-indenyl) zirconium dimethyl (**M2**); *rac*-dimethylsilylbis(2-methyl-4,5-benzindenyl) zirconium dimethyl (**M3**); and ethylenebis(tetrahydroindenyl)zirconium dimethyl (**M4**), along with *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**). The performance of both DBAB-derived and BAM-derived silica supported metallocene catalysts has been found to be sensitive to the metallocene structures, in that metallocene structures with less open ligand frameworks appear to perform better for propylene polymerization, consistent with the requirement of a bulky aluminate activator bearing a bulky functional group ER³ that influences the interaction of catalyst ion-pair [(support)(-O)₂Al(R)(ER³)]⁻[L_nM]⁺ to obtain a highly active catalytic system, although other deactivation factors such as the interaction of surface bridged oxygen atoms of silica with more open catalyst structures can also exist.

[00109] Polymerization tests were also conducted with *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)-based catalysts prepared from either BAM-treated or DBAB-treated silica, and both were observed to polymerize ethylene. Data for these tests are provided in Example 12.

Definitions and Abbreviations

[00110] In order to more clearly define the terms used herein, the following definitions are provided.

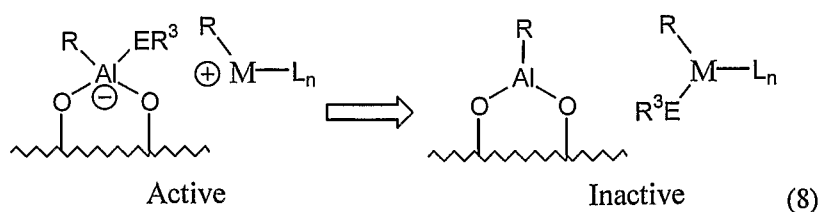
[00111] Unless specified otherwise, or unless the context requires otherwise, the term hydrocarbyl is used to specify a hydrocarbon radical group that includes, but is not limited to aryl, alkyl, cycloalkyl, alkenyl, cycloalkenyl, cycloalkadienyl, alkynyl, aralkyl, aralkenyl, aralkynyl, and


the like, and includes all substituted, unsubstituted, branched, linear, and heteroatom-substituted analogs thereof.

[00112] Unless specified otherwise, or unless the context requires otherwise, certain abbreviations that are used herein, include, but are not limited to the following: TIBA, triisobutyl aluminum; TEA, triethyl aluminum; TMA, trimethyl aluminum. Generally, ligand abbreviations are used herein to refer either to the parent neutral ligand or to the deprotonated anion, as the context requires. Thus, the abbreviation BHT refers either to the substituted phenol, butylated hydroxytoluene, HO-2,6-(*t*-Bu)₂-4-Me-C₆H₂, or to the deprotonated aryloxide anion, [(O-2,6-(*t*-Bu)₂-4-Me-C₆H₂)⁻], as the context requires.

[00113] The terms ammonium ion or ammonium-type ion are intended to encompass primary, secondary, and tertiary ammonium ions, as the context allows or requires.

[00114] The terms bulky functional group or bulky functional ligand, which are used to refer to ER³ or HER³, wherein E and R³ are as disclosed herein, can be defined as follows. A compound HER³ or a moiety ER³ is considered to be a "bulky" functional group or ligand when utilized with a particular d-block or f-block metal dialkyl compound if more than about 70% of the metal dialkyl compound has not reacted with HER³ after 3 hours in solution at room temperature. This criterion for the definition of "bulky" demonstrates that a particular ER³ functional ligand that is considered bulky when used with one d-block or f-block metal dialkyl compound, may not be considered bulky when used with another d-block or f-block metal dialkyl compound. As used herein, the bulky functional group or bulky functional ligand terminology is applicable because HER³ acts as a "functional" group to convert a primary aluminum alkyl AlR₂ to a secondary aluminum alkyl R₂Al(ER³) or even to a tertiary aluminum alkyl R²Al(ER³)₂, thereby lowering the reactivity of the organoaluminum compound such that an aluminate ion comprising a tertiary aluminum alkyl bonded to an active proton forms and is stable. This reaction, therefore, avoids an active proton in the presence of secondary aluminum alkyl groups in a species such as [support(-O)₂AlR₂]⁻[H]⁺, which would be expected to undergo alkane elimination to form [support(-O)₂AlR₂] and HR², and thereby deactivate. Also, the bulky functional group or bulky functional ligand terminology is applicable for ER³ and HER³ because the ER³ moiety acts to prevent the catalyst deactivation according to Reaction (8).



[00115] When included in structures shown in this application, the structural component "" denotes a catalyst support or carrier, as is further described herein. Thus, the steric bulk of the group R^3 is related to the catalyst structure and stability. Generally, a more open catalyst framework is easier to react with a given ER^3 to undergo catalyst deactivation as illustrated above. Therefore the reaction of the catalyst precursor L_nMR_2 with HER^3 , as disclosed above, can be used as a gauge to evaluate the R^3 bulkiness. Further to the protonolysis experiments described above, if HER^3 does not substantially react with L_nMR_2 but does react with AlR^2_3 under desired experimental conditions, then HER^3 is suitable for the construction of the aluminate-proton ion-pair on the support. Standard NMR spectroscopic methods can be used to monitor and quantify this reaction. Finally, the bulky functional ligand of this invention generally does not include the $-OB(C_6F_5)_2$ ligand, and the bulky functional ligand can be fluorinated, non-fluorinated, halogenated, or non-halogenated.

[00116] As used herein, any d-block or f-block metal compound comprising at least one ligand subject to protonolysis to form a catalytically-active cationic species can be termed a catalyst precursor.

[00117] When Applicants disclose or claim a range of any type, for example a range of temperatures, a range of numbers of atoms, a molar ratio, or the like, Applicants' intent is to disclose or claim individually each possible number that such a range could reasonably encompass. For example, when the Applicants disclose or claim a chemical moiety having a certain number of atoms, for example carbon atoms, Applicants' intent is to disclose or claim individually every possible number that such a range could encompass, consistent with the disclosure herein. Thus, by the disclosure that R^2 is selected independently from hydrogen or a hydrocarbyl group having up to about 20 carbon atoms, Applicants intent is to recite that R^2 can be selected independently from at least one of the following: hydrogen or a hydrocarbyl group having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, or about 20 carbon atoms. In another example, by the disclosure that the molar ratio of HER^3 to aluminum typically spans the range from about 0.5 to about 2.5, Applicants intend to recite that the molar ratio of HER^3 to aluminum can be at least one of the following, without limitation: about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1.0, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, or about 2.5. Further, Applicants reserve the right to proviso out or exclude any individual members of such a group, including any sub-ranges or combinations of sub-ranges within the group, that can be claimed according to a range or in any similar manner, if for any reason Applicants choose to claim less than the full measure of the disclosure, for example, to account for a reference that Applicants are unaware of at the time of the filing of the application.

[00118] Although methods, syntheses, and materials similar or equivalent to those described herein can be used in the practice or testing of this invention, typical methods, syntheses, and materials are described herein.

[00119] The references discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention.

[00120] For any particular compound disclosed herein, any general structure presented also encompasses all conformational isomers, regioisomers, and stereoisomers that can arise from a particular set of substituents. The general structure also encompasses all enantiomers, diastereomers, and other optical isomers whether in enantiomeric or racemic forms, as well as mixtures of stereoisomers, as the context requires. Applicants use standard abbreviations herein as are known to those skilled in the art, such as "Me" for "methyl", "Et" for "ethyl", "Bu" for "butyl", "Ph" for "phenyl", "i-Bu" for "isobutyl", and "t-Bu" for "tertiary butyl",

[00121] The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other aspects, embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to one of ordinary skill in the art without departing from the spirit of the present invention or the scope of the appended claims.

[00122] Unless specified otherwise, general procedures used in preparing, characterizing, and using the compounds and compositions of this invention are as follows. All preparations and analytical procedures related to the air-sensitive compounds and compositions, including air-sensitive silica compounds, were performed under a dry nitrogen (< 2ppm O₂) atmosphere, either in a nitrogen-filled drybox or using standard Schlenk line techniques. All aluminum alkyl compounds used, including trimethylaluminum (TMA) and triisobutylaluminum (TIBA), were commercial products of Albemarle Corporation and were used as received. Reagents such as benzylmagnesium chloride (PhCH₂MgCl) in THF, 4-fluorobenzylmagnesium chloride (FC₆H₄CH₂MgCl) in THF, MeLi with LiBr, BHT, carbazol, and the like, were purchased from Aldrich Chemical Company (Milwaukee, WI) and were used as received without further purification. Toluene, ethylene, propylene, and nitrogen used in the polymerization reactions were typically purified by passing through a series of three cylinders: molecular sieves, OXYCLEARoxygen absorbent, and alumina. Ethylene and propylene were polymer grade obtained from Matheson. Isohexane and toluene for activator and catalyst preparation and spectroscopy studies were Albemarle production anhydrous grade and were stored over sodium-potassium alloy. Hexane, C₆D₆, and similar hydrocarbon solvents were typically

Aldrich anhydrous grade and were dried with and stored over Na/K alloy. Unless otherwise indicated, the DBAB solutions used to treat silica were isohexane solutions.

[00123] The FT-infrared spectra were recorded on a NICOLET MAGNA-IR 560 spectrometer with a DRIFTS accessory under inert atmosphere, using a diffuse reflectance method. Samples were prepared by loading, in the drybox under an inert atmosphere, a dry, solid silica compound in an inert cell with KBr windows. NMR studies were undertaken on a BRUKERDPX 400 (400 MHz) instrument, where the NMR instrumental parameters were set up for both quantitative and qualitative measurements. Total Al content on silica was determined using standard Inductively Coupled Plasma (ICP) emission spectroscopy techniques.

[00124] The metallocenes used in the following Examples were prepared according to procedures given in the literature. The following treatises describe such methods: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. in *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic Press; New York, 1974.; Cardin, D. J.; Lappert, M. F.; and Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Halstead Press; New York, 1986; Cardin, D. J.; Lappert, M. F.; Raston, C. L.; and Riley, P. I. Cyclopentadienyl and other Anionic π -Ligand Complexes of Zirconium and Hafnium; in *Comprehensive Organometallic Chemistry: The Synthesis, Reactions, and Structures of Organometallic Compounds*; ed. Wilkinson, G.; Stone, F. G. A.; and Abel, E. W.; Pergamon Press; Oxford; 1982; Bottrill, M.; Gavens, P. D.; Kelland, J. W.; and McMeeking, J.; Anionic π -Bonded Derivatives of Titanium; in *Comprehensive Organometallic Chemistry: The Synthesis, Reactions, and Structures of Organometallic Compounds*; ed. Wilkinson, G.; Stone, F. G. A.; and Abel, E. W.; Pergamon Press; Oxford; 1982.

[00125] In one aspect, general properties of useful metal oxide supports in this invention are disclosed herein. Various silica samples were used in the following examples, and the following Table 1 provides some analytical data illustrating the range of properties for these silica samples that were used to develop the present invention. Silica I was a sample of silica sold under the trade name GRACE 952, and Silica II was a sample obtained from Ineos that is sold under the trade name ES70. Data for average particle sizes include an overall average particle size, and particles size for the weight percent fractions tabulated are provided. Further, any metal oxide or support as disclosed herein works well with this invention. Additional silicas that work well include, but are not limited to those sold under the trade names GRACE 948, ES70X, and ES70W, and similar silicas.

Table 1. Properties of Representative Silica Samples Used in Developing the Activators and Catalysts of this Invention.

Silica	Surface Area (m ² /g)	Pore Volume (cc/g)	Max or Ave. Pore Diameter (nm)	Average Particle Sizes (μm) (%)	Weight Loss (%) (Temp, °C)
Silica I	275	1.53	22.3	Overall Avg. 34.1; 14.8 (10), 30.9 (50), 57.3 (90)	4.00 (LOD), 6.57 (LOI) (raw) TGA: 3.56 (200°C), 5.69 (1000°C)
Silica II	12 (1-point)	1.58	23 (10-30)	Overall Avg. 38.6; 11.2 (10), 75.9 (90)	(500°C) (max 8)

EXAMPLE 1

Synthesis of (BHT)Al(i-Bu)₂ (DBAB) in Isohexane

[00126] Neat triisobutylaluminum (TIBA) 48.6 g (245 mmol) was charged in an 8 oz bottle with 46.6 g isohexane. To the TIBA solution was added dropwise a solution of 2,6-di-*t*-butyl-4-methylphenol (BHT) in isohexane, prepared from 54.0 g BHT (245 mmol) in 88.4 g isohexane, and this mixture was shaken vigorously. Gas evolution was observed upon the addition. When the addition was complete, an additional 22 g of isohexane was added to make a 36 wt% (1.0 mmol/g) solution of (BHT)Al(*i*-Bu)₂ (DBAB). The mixture was allowed to shake for another 30 minutes after the addition of BHT. ¹H NMR (400 MHz, 25°C, C₆D₆): δ 0.38 (4H, d, Al-CH₂CHMe₂); δ 0.5-1.8 (broad, m, isohexane C-H and ^tBu on BHT); δ 2.00 (2H, m, Al-CH₂CHMe₂); δ 2.25 (4H, s, CH₃-C₆H₂(^tBu)₂); δ 6.95 (2H, s, CH₃-C₆H₂(^tBu)₂).

EXAMPLE 2

Synthesis of DBAB-Treated Silica Samples with Different Al:OH Ratios and Determination of Their OH Content

[00127] The silica used in this example was the Silica I, calcined at 600°C which had an OH content of 0.78 mmol OH/g silica. Four (4) samples of DBAB-treated silica were prepared with Al:OH molar ratios of 0.36:0.78, 0.51:0.78, 0.73:0.78, and 0.85:0.78, as follows. In each of four, 20 mL vials were charged 1.0 g of the silica calcined as above (OH content 0.78 mmol/g) and 5.0 g of toluene. A 36 wt% DBAB solution (containing 1.0 mmol DBAB/g, from Example 1) was added to the four vials containing silica/toluene slurry in the amounts of 0.36 g, 0.51 g, 0.73 g, and 0.85 g, following by vigorously shaking each vial. These four samples were then transferred to a shaker to shake for a total of about 60 min. The mixture in each vial was filtered to isolate the treated silica, which was washed with 2×3 mL of toluene and 5 mL of isohexane, and then dried under vacuum for 16 hr.

[00128] The OH content of these four samples was determined by the Grignard titration method as provided herein, the results of which are summarized in Table 2. These titration results for OH contents on the silica, calcined at 600°C with various DBAB charges, clearly show that one DBAB consumes one OH on silica. Therefore, the OH content on the silica is observed to decrease in an amount corresponding to the amount of DBAB used to treat the silica.

Table 2. OH Contents on Silica Treated with Various DBAB Charges

Sample	DBAB (mmol/g SiO ₂)	OH (mmol/g SiO ₂)
1	0	0.78
2	0.36	0.42
3	0.51	0.30
4	0.73	0.04
5	0.85	Under detection limit

EXAMPLE 3

Synthesis of DBAB-Treated Silica Samples Calcined at Different Temperatures and Infrared Analysis of Each

[00129] Three raw silica samples of Silica I were calcined at 150°C, 600°C, and 800°C, respectively, for four hours. An OH content analysis of each silica sample was performed using the Grignard method, in which the silica was treated with an excess of benzyl magnesium chloride (PhCH₂MgCl) in THF, and the amount of toluene produced upon protonolysis of the benzyl Grignard was quantified using an internal standard of 1,2-diphenylethane after calibrating the amount of toluene originally present in the PhCH₂MgCl solution. This test provides the OH content for the silica samples calcined at various temperatures, which are provided in Table 3.

Table 3. OH Contents for Silica I Calcined at Various Temperatures

Entry	Calcination Temp (°C)	OH Content (mmol/g)
1	150	2.66
2	600	0.78
3	800	0.60

[00130] Each sample was also subjected to an infrared (IR) spectroscopic analysis. FIG. 1 illustrates the infrared (IR) spectra of the OH stretching region of Silica I after (a) calcining at 150°C (spectrum 10), (b) calcining at 600°C (spectrum 12), (c) calcining at 800°C (spectrum 14), and (d) calcining at 600°C followed by treatment of the silica with an excess of PhCH₂MgCl (spectrum 16), which is included for comparison. These data are used in comparisons with the OH stretching data

from this and other experiments. Each of these Silica I samples that were calcined at 150°C, 600°C, and 800°C, respectively, were then treated with varying amounts of a 36 wt% solution of (BHT)AlⁱBu₂ (DBAB), which were then dried and analyzed by IR spectroscopy, as follows.

[00131] A) 600°C Calcined Silica. As shown in Table 3, the OH content of this silica was measured at 0.78 mmol OH/g silica. Three separate treatments of this silica with 10, 50, and 95 mol% DBAB per mole of OH, based on the measured OH content, as follows. In three, 20 mL vials labeled as No. 1, 2, and 3 were charged 1.0 g, 2.0 g, and 2.0 g of silica, respectively, followed by 4.0 g, 8.0 g, and 8.0 g of toluene, respectively. To these mixtures was added 0.081 g (vial 1), 0.81 g (vial 2), and 1.53 g (vial 3) of 36% DBAB solution, following by vigorously shaking. The three samples were then placed on the shaker to shake for 16 hrs. The reaction mixture in No. 1 became light yellow over this time, while the other two developed an orange color. The treated silica from each of these reaction mixtures was filtered off, washed with 2×3mL of toluene and 5 mL of isohexane, and then dried under vacuum for 2 hrs. Each sample was subjected to an IR analysis. The IR spectra in the OH region of each sample is provided in FIG. 2, where IR results of silica from vial 1 (spectrum 22), vial 2 (spectrum 24), and vial 3 (spectrum 26) are shown along with the parent silica (spectrum 20) for comparison.

[00132] B) 150°C Calcined Silica. Another sample was prepared with a 95 mol% DBAB charge based on OH content on silica (OH = 2.66 mmol/g, from Table 3, Entry 1), using the 150°C calcined silica, as follows. A 20 mL vial was charged with 2.0 g silica (5.32 mmol OH total) and 8.0 g of toluene. To this mixture was added the 36 wt% DBAB solution 5.05 g (5.05 mmol) followed by vigorous shaking. The sample was then placed on the shaker to shake for 16 hrs. The treated silica was then filtered off, washed with 2×3 mL of toluene and 5 mL of isohexane, and dried under vacuum for 2 hrs. Although this sample was also subjected to an IR analysis, because the catalyst derived using this activator displayed relatively low activity (Table 4, Entry 1), this silica from 150°C calcination was not pursued further.

[00133] C) 800°C Calcined Silica. Another sample was prepared with a 95 mol% DBAB charge based on OH content on silica (OH = 0.60 mmol/g from Table 3, entry 3), using the 800°C calcined silica, as follows. A 20 mL vial was charged with 2.0 g silica (1.20 mmol OH total) and 8.0 g of toluene. To this mixture was added the 36 wt% DBAB solution 1.14 g (1.14 mmol) followed by vigorous shaking. The sample was then placed on the shaker to shake for 16 hrs. The treated silica was then filtered off, washed with 2×3 mL of toluene and 5 mL of isohexane, and dried under vacuum for 2 hrs. Although this sample was also subjected to an IR analysis, because the catalyst derived using this activator displayed relatively low activity (Table 4, Entry 3), this silica from 800°C calcination was not pursued further.

EXAMPLE 4

Supported Catalyst Preparation from DBAB-Treated Silica

[00134] A) DBAB-Treated Silica. A sample of silica (Silica I, 600°C calcined, 0.78 mmol OH/g), 5.0 g (3.9 mmol OH total), and 20 g of toluene were charged in a 4 oz. reaction bottle with a stirbar. This silica slurry was stirred slowly while 3.62 g of DBAB solution (3.7 mmol) was slowly added. Then the mixture was allowed to stir for another 2.3 hours, after which time the treated silica was filtered off through a coarse filter frit, washed with 2×10 mL of isohexane, and dried under vacuum until no liquid was observed to pass through the filter (about 30 seconds), which provided a somewhat wet DBAB-treated silica.

[00135] B) Catalyst Preparation. The wet DBAB-treated silica from above was added to a 4 oz. reaction bottle along with 26 g of toluene and a stirbar, stirring was commenced, and the slurry was mixed well. Then a mixture of 70 mg (0.12 mmol) of the metallocene *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**) (based on 0.19 wt% Zr) in 2 g of toluene was added at once to the slurry, and stirring was continued under ambient conditions for 1.5 hours. The deep red-brown material was then filtered through a coarse filter frit, washed with 3×10 mL of isohexane, and dried under vacuum for about 30 min. The yield of the resulting supported catalyst was 5.7g. Analytical data: Zr, 0.14 wt%; Al, 1.5 wt%. The propylene polymerization results using this catalyst are provided in Table 4, Entry 7a.

EXAMPLE 5

Determination of the Active Proton Content in DBAB- and BAM-Treated Silica Using ¹H NMR Spectroscopy

[00136] ¹H NMR Spectroscopy was used to determine the active proton content in the silica samples and the silica samples that had been treated with a BHT-modified aluminum alkyl compound, for example, DBAB-treated or BAM-treated Silica I. Treated silica samples that were free of toluene were first treated with excess benzyl magnesium chloride, and treated silica samples contained a toluene residue were first treated with 4-fluorobenzylmagnesium chloride. The analysis is based on the reaction of one active proton of the silica reacting with one benzylmagnesium chloride or one 4-fluorobenzylmagnesium chloride to produce one toluene, or one 4-fluorotoluene, respectively. From this reaction, the amounts of the produced toluene or 4-fluorotoluene were quantified by ¹H NMR spectroscopy with normalization to the THF peaks from the Grignard solvent, and the active proton contents was then derived. The NMR instrument employed in the analyses was a Bruker™ DPX 400 (400 MHz) instrument. The benzylmagnesium chloride (C₆H₅CH₂MgCl) and 4-fluorobenzylmagnesium chloride (4-FC₆H₄CH₂MgCl) Grignard solutions used were 2 M THF solutions, that were diluted to 0.1 M with THF that had been dried over Na/K alloy.

[00137] The following procedures were employed. A 0.200 g- to 0.400 g-sample of silica or treated silica was weighed into a 20 mL vial, to which was quickly added about 3.00 g of the 0.1 M Grignard stock solution, after which the vial was carefully sealed with a Teflon cap. The weights before and after silica sample and Grignard solution addition were recorded for accurate amounts of each component added. After the vial was charged and sealed, it was put on a shaker to shake for 30 minutes. The vial was then removed to allow the solids to settle. Because the Grignard reagents usually contain small amount of toluene (for $C_6H_5CH_2MgCl$) or 4-fluorotoluene (for $4-FC_6H_4CH_2MgCl$) arising from hydrolysis from adventitious water, these were taken into account in performing the calculations. Therefore, NMR samples of both the Grignard stock solution and a the supernatant of the Grignard-treated silica were prepared and their spectra compared. In both cases, a clean, dry 5 mm NMR tube was charged 0.5 mL of dry C_6D_6 . For the calibration sample, 0.3 mL of the Grignard stock solution (diluted to 0.1 M with THF) was quickly transferred into the NMR tube, and for the test sample, 0.3 mL of the supernatant from the Grignard-treated silica vial was used. These NMR tubes were quickly sealed with a cap. A solution height of about 1.4 to 1.8 inches in the NMR tube was desirable for good NMR spectrum resolution.

[00138] The 1H NMR spectra for the two samples were acquired using an identical set of instrumental parameters. A pulse delay of 90 seconds was used for good quantification. The peak separation between toluene and 4-fluorotoluene is small, therefore a good resolution of spectrum is required for accurate integration of peaks to quantify toluene or 4-fluorotoluene generated during the reaction of Grignard reagent with OH on silica compounds containing toluene residue. 1H NMR Peaks were identified and integrated as follows for the calibration sample: $C_6H_5CH_2MgCl$, multiplets at about 6.5 ppm (1 proton); $4-FC_6H_4CH_2MgCl$, multiplets at about 6.5 ppm (4 protons); THF, multiplets at about 3.6 ppm (4 protons); toluene, singlet at about 2.1 ppm (3 protons); 4-fluorotoluene, singlet at about 1.9 ppm (3 protons). 1H NMR Peaks were identified and integrated as follows for the supernatant sample: THF, multiplets at about 3.6 ppm (4 protons); toluene, singlet at about 2.1 ppm (3 protons); 4-fluorotoluene, singlet at about 1.9 ppm (3 protons). In each case, it was important to look for the resonances for excess Grignard reagent, to ensure that the protonolysis reaction had proceeded to completion for an accurate determination of the OH content. If no excess Grignard reagent was observed, the sample was discarded and more Grignard reagent was employed in the preparation of the subsequent sample.

[00139] Calculations of the OH content were performed as follows. First, the toluene and 4-fluorotoluene content in both the stock Grignard solution and in the supernatant of the Grignard-treated silica mixture were calculated. The difference in these contents is the amount of toluene or 4-fluorotoluene produced in the solution. Because one toluene or 4-fluorotoluene is produced from the reaction of one active proton with one $C_6H_5CH_2MgCl$ or $FC_6H_4CH_2MgCl$, the active proton content

on the silica compound can be calculated based on the amount of produced toluene or 4-fluorotoluene observed.

EXAMPLE 6

Propylene Polymerization Procedures

[00140] The general procedures for propylene polymerization were as follows. A 4-L autoclave reactor that had been dried under a nitrogen flow at a temperature of >100°C, was charged with 2 L of propylene and 25 mmol of hydrogen. The reactor temperature was raised to 70°C, while the sample was stirred at 700 rpm. A 2 mL-sample of a 10wt% TIBA solution in hexane (TEA was used in the comparative examples) was injected into the reactor followed by the injection of 40 mg of catalyst, using 300 mL as a flush. The reaction mixture was stirred at 70°C for one hour. At the end of the test, the polymerization was stopped by venting the reactor and opening it to the atmosphere, and the resulting polypropylene was collected.

EXAMPLE 7

Propylene Polymerization Results Using a Supported Catalyst Prepared from DBAB-Treated Silica and a Metallocene

[00141] Table 4 summarizes the propylene polymerization results obtained from using *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)-derived, DBAB-treated silica supported catalysts, comparing silica that was calcined at different temperatures, different DBAB charges, and different charges of metallocene **M1**. Any catalyst mentioned in an Entry in Table 4 for which the preparation has not been specifically described herein was prepared according to the procedure given in Example 4 (see entry 7a) and with the stoichiometry shown in Table 4 for that Entry.

Table 4. Polymerization Results for M1-Derived Silica Supported Catalysts¹

Entry	Silica	Calcnd Temp (°C)	SiO ₂ OH Residue (mmol/g)	DBAB Charge (mol% on OH)	OH on DBAB/SiO ₂ (mmol/g SiO ₂)	Zr charge/OH (mol:mol)	Zr Charge (wt%)	Zr Found (wt%)	Productivity (g/g cat/hr)
1	SiO ₂ I	150	2.66	95	0.13	1.10	0.77	-	3,000
2	SiO ₂ I	600	0.81	95	0.04	1.10	0.33	0.14	13,500
3	SiO ₂ I	800	0.60	95	0.03	1.10	0.27	-	300
4	SiO ₂ I	600	0.81	50	0.41	1.10	3.67	0.16	7,000
5	SiO ₂ I	600	0.78	60	0.31	0.13	0.22	0.19	9,300
6	SiO ₂ I	600	0.81	95	0.04	2.20	0.70	0.21	14,000
7a	SiO ₂ I	600	0.78	95	0.04	0.62	0.20	0.14	13,500
7b	SiO ₂ I	600	0.78	95	0.04	0.62	0.21	0.16	14,700
8	SiO ₂ I	600	0.78	128	<0.02	N/A	0.30	0.04	5,600
9	SiO ₂ II	600	0.80	66	0.27	0.8	0.26	0.24	7,400
10	SiO ₂ II	600 ²	1.10	82	0.20	0.17	0.24	0.13	14,000
11	SiO ₂ II	600 ²	1.10	95	0.06	0.45	0.18	0.11	13,300

¹ Conditions: 40-60 mg catalyst; 2 L propylene; 25 mmol H₂; 2 mL 10% TIBA in hexane; 70°C; 60 min; catalyst *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (M1).

² Calcined for a shorter period of time.

[00142] Entries 1-3 of Table 4 compare calcination temperatures for the treated silica, and show that the highest activity was obtained at a calcination temperature of about 600°C, when DBAB/OH and metallocene/OH ratios were identical across all three samples. The very low activity obtained from the catalyst derived from an 800°C calcined silica (Entry 3) indicates that hydrogen bonded OH groups are useful in formation of the highly active sites since IR spectrum of the 800°C calcined silica (FIG. 1, spectrum 14) revealed that free OH groups were dominant. Significantly lower activity that was obtained from the catalyst derived from the 150°C calcined silica also indicated that the presence of water was detrimental to the activity of the catalyst system, as the IR spectrum of the 150°C calcined silica (FIG. 1, spectrum 10) demonstrated the presence of a significant amount of water. Entry 2 and Entry 4 in Table 4, compare DBAB/OH ratios used to prepare the activator, and indicate higher activity was obtained at a DBAB/OH molar ratio of 95 mol% as compared to 50%. Reducing the DBAB charge to about 50-60 mol% of the OH concentration caused a significant drop in productivity, even the Zr loading is significantly higher (Entry 2 vs. Entry 4), apparently due to the deactivation of metallocene active species by excess active protons on the DBAB treated silica (Reaction (4)). An overcharge of DBAB causes low active proton contents and thus results in low Zr loading, although the Zr efficiency is very high (Entry 8), indicating that active protons are not only the activator to activate the catalyst precursor but also an anchor point to support the catalyst.

[00143] The polymerization results of Table 4 also indicated that not all active protons on DBAB-treated silica are equally active as indicated by the facts that the 62 and 110 mol% Zr charges based on the same residual OH content on DBAB treated silica show almost the same Zr loadings and the same productivities (Entry 2 vs. 7a), consistent with the IR observation as illustrated in FIG. 3. Finally, highly active catalysts can be prepared from different types of silica. For example, Silica II

derived from a similar preparation for the Silica I analog also resulted in active supported catalysts (Entry 9, 10, and 11), although the treatment of silica could be slightly different.

EXAMPLE 8

Supported Catalyst Preparation from BAM-Treated Silica Calcined at 600 °C

[00144] The following catalysts comprising a metallocene **M1**-derived catalyst supported on a BAM-treated Silica I or Silica II are compared to the same catalyst supported on DBAB-treated Silica I at Table 4, Entry 7a and Silica II at Table 4, Entry 11.

[00145] A) Metallocene **M1** BAM-Treated Silica II Catalyst. The preformed supported activator, BAM treated silica (Silica II, 600°C calcined, 0.80 mmol OH/g, treated with 1.0 mmol/g BAM), 2.0 g, was suspended in 20 g of toluene. This suspension was stirred while a slurry of metallocene *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**) 82mg (0.14 mmol) in 2 mL of toluene was slowly added. The resulting mixture turned dark and was stirred at RT for 12 hours, over which time the mixture turned even darker. The resulting catalyst of **M1** supported on BAM-treated Silica II was isolated by decantation or filtration through a coarse filter frit, rinsed with toluene and then cyclohexane, and dried under vacuum for about 6 hours. The resulting supported catalyst was characterized by the following analytical data: Al, 1.40%; Zr, 0.31 wt%. The propylene polymerization productivity of this catalyst was observed to be 12,000 g/g cat/hr. Data from this sample are provided in Table 6, Entry 1.

[00146] B) Metallocene **M1** BAM-Treated Silica I Catalyst. A 2.0-g sample of silica (Silica I, calcined at 600°C, 0.78 mmol OH/g) was placed in a 2 oz bottle and slurried in 12 g of toluene. To this slurry was added 1.0 g of BAM (2.08 mmol), which caused the slurry to change from colorless to orange in color. The resulting mixture was shaken on a mechanical shaker for 1 hour. The metallocene *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**), 0.080 g (0.14 mmol), was then added to the slurry, which was shaken for an additional 1 hour, over the course of which the slurry changed color from yellow to orange to brown. The resulting solid was then isolated by filtration, washed with isohexane and dried under vacuum at room temperature for 1 hour. The resulting supported catalyst was characterized by the following analytical data: Al, 1.07%; Zr, 0.18 wt%. The propylene polymerization productivity of this catalyst was observed to be 13,500 g/g cat/hr. Data from this sample are provided in Table 6, Entry 2.

EXAMPLE 9

Synthesis of Additional Metallocene BAM-Treated Silica Catalysts and Their Propylene Polymerization Activity

[00147] The following metallocenes were used to prepare corresponding metallocene-based BAM-treated Silica I catalysts, according to the procedure used in Example 8B: *rac*-dimethylsilylbis(2-methyl-1-indenyl) zirconium dimethyl (**M2**); *rac*-dimethylsilylbis(2-methyl-4,5-benzoindenyl) zirconium dimethyl (**M3**); and ethylenebis(tetrahydroindenyl)zirconium dimethyl (**M4**), along with *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**).

[00148] The analytical and propylene polymerization results of these catalysts are provided in Table 5.

Table 5. Polymerization Results Using Various Metallocene-Derived Silica Supported Catalysts¹

Entry	Metallocene	BAM (mmol/g)	Zr (wt%)	Productivity (g/g cat/hr)
1	M1	1.00	0.18	13,500
2	M2	1.00	0.19	6,000
3	M3	1.00	0.22	600
4	M4	1.00	0.25	Low

¹ Conditions: 40-60 mg catalyst; 2 L propylene; 25 mmol H₂; 2 mL 10% TIBA in hexane; 70°C; 60 min; support Silica I, 600°C calcined.

Other metallocenes that could be used in this aspect of the invention include the listing of additional metallocene compounds provided in the disclosure.

EXAMPLE 10

Propylene Polymerization Results Using a Supported Catalyst Prepared from BAM- and DBAB-Treated Silica and a Metallocene

[00149] Table 6 summarizes the propylene polymerization results obtained from using *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (**M1**)-derived, BAM- or DBAB-treated silica supported catalysts.

Table 6. Polymerization Results for M1-Derived Silica Supported Catalysts¹

Entry	Silica	Calcnd Temp (°C)	OH on Silica (mmol/g)	BAM Charge (mmol/g SiO ₂)	OH Residue (mmol/g)	Zr (wt%)	Productivity (g/g cat/hr)
1	Silica II	600	0.80	1.00	0.32	0.31	12,000
2	Silica I	600	0.78	1.00	0.15	0.18	13,500
3	Silica I	800	0.60	1.00	-	0.18	4,000
				DBAB (mmol/g)			
4	Silica I	600	0.78	0.74	0.04	0.11	13,500
5	Silica I	800	0.60	0.57	0.03 ²	-	300
6	Silica II	600 ³	1.10	1.04	0.06 ²	0.11	13,300

¹ Conditions: 40-60 mg catalyst; 2 L propylene; 25 mmol H₂; 2 mL 10% TIBA in hexane; 70°C; 60 min; catalyst *rac*-dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dimethyl (M1).

² Estimated based on the stoichiometric reaction of DBAB with OH (see Table 6).

³ Calcined for a shorter period of time.

[00150] As seen from Table 6, the 600°C calcined silica provides higher activities for both the DBAB-derived and the BAM-derived catalyst systems (Entry 2 versus Entry 3 and Entry 4 versus Entry 5). Regarding the types of silica OH moieties, comparing Entry 2 with Entry 3 clearly shows that active species derived from the H-bonded silica OH moieties, which richly populate the 600°C calcined silica, are more vigorous or potent than active species derived from the free OH moieties, which are the major OH species in the 800°C calcined silica. As disclosed herein, free OH can coordinate to a BAM molecule to form the active species N (Scheme 5). This species is dominant in the BAM treated, 800°C calcined silica based on the IR spectrum that shows no significant 3690cm⁻¹ peak (the chelated aluminate-proton ion-pair) but rather a 3490cm⁻¹, a frequency related to BAM derived compounds (FIG. 4, spectrum 42). Since Entry 2 has the same Zr loading as Entry 3, these data show that the chelated double siloxyl bonded aluminate-proton ion-pair (F, Scheme 3) is much more active than the single siloxyl bonded aluminate-proton ion-pair (N, Scheme 5). This notion can be confirmed by Entry 5, which reveals that the DBAB-derived catalyst from the 800°C calcined silica has insignificant activity. This observations reflects DBAB which does not form an N type active species with free OH groups under ambient conditions, due to the higher reactivity of secondary Al-R in DBAB that results in alkane elimination of the active proton with Al-R to form a neutral species (Scheme 1, E).

EXAMPLE 11

Synthesis of DBAB-Treated Silica Samples with Different Al:OH Ratios and Determination of Their Reaction By-Products

[00151] The reaction by-products resulting from the treatment of 600°C calcined Silica I with DBAB were examined for different DBAB amounts and different reaction times, to determine stoichiometries of the by-products, and examine kinetic versus thermodynamic products produced from this reaction. Silica I, which was calcined at 600°C, had an OH content of 0.78 mmol OH/g silica, and was used for the experiments reported in Table 7. Given sufficient reaction time, one mole of DBAB reacted with one mole of OH to release one mole of isobutane (abbreviated iC_4). With shorter reaction times, where a mixture of kinetic and thermodynamic products are present, both isobutane iC_4 and free BHT phenol were observed. Thus, BHT is produced relatively quickly in these reactions, but itself reacts to form iC_4 in an equimolar amount. As Table 7 indicates, NMR studies showed that the sum of the moles of iC_4 and moles of free BHT equals to the same number of moles of DBAB used in the reaction.

Table 7. Quantification of Byproducts from Reactions of DBAB with Silica

Entry	DBAB Charge (mmol/g SiO ₂)	Rxn Time (hr)	iC_4 (Isobutane) (mmol/g SiO ₂)	Free BHT (mmol/g SiO ₂)	(BHT+ iC_4)/DBAB (mol/mol)
1	0.42	0.5	0.36	0.08	1.05
2		1	0.43	0	1.02
3	0.78	0.5	0.41	0.32	0.99
4		1	0.49	0.24	0.99
5		19	0.74	0.02	1.03

[00152] The data in Table 7 support the mechanisms shown in Schemes 1 and 2, that is, at 0.5 hr, both **E** and **D** in Scheme 1 and **E'** and **D'** in Scheme 2 are present. After 1 hr for a low DBAB charge (0.42 mmol/g silica) or after 19 hrs for a high DBAB charge (0.78 mmol/g silica), only **E** and **E'** are present.

EXAMPLE 12

Application of BAM-Treated and DBAB-Treated Metallocene Catalysts to Ethylene Polymerization

[00153] Polymerization tests were conducted with *rac*-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dimethyl (**M1**)-based catalysts prepared from either BAM-treated or DBAB-treated silica, and both were observed to polymerize ethylene, although with significantly lower activities than ethylene polymerization using the more open metallocene ethylenebis(tetrahydroindenyl)zirconium dimethyl (**M4**) activated with MAO. Thus, a supported **M1**

catalyst prepared using DBAB-treated silica was run under the following polymerization conditions: 40 mg catalyst; 2 mL of 10% TIBA; 40 mL of hexene; 80°C; 320 psi ethylene pressure; in a 4 L autoclave reactor. The activity of this catalyst was observed to be 1,700 g/g cat/hr productivity, whereas the productivity of this same catalyst in the polypropylene polymerization test was observed to be 9,500 g/g cat/hr.

EXAMPLE 13

Comparative Polymerization Example 1

[00154] Silica (5 g, Silica I, dried at 600°C) was placed in a 2 oz bottle and slurried in 28 g of toluene. To this slurry was added N,N-diethylaniline (0.34 g, 2.3 mmol) and $B(C_6F_5)_3$ (1.09 g, 2.1 mmol). After shaking this mixture for 10 min, 0.37 g of metallocene **M1** was added and the slurry was shaken for an additional 2 hr. The resulting deep red slurry was filtered, the isolated product was washed twice with isohexane, and dried under vacuum. This sample was characterized by the following analytical and propylene polymerization data. Analysis: 0.74 wt% Zr. Polymerization Productivity, 9000 g/g cat/hr.

EXAMPLE 14

Comparative Polymerization Example 2

[00155] Silica (2 g, Silica I, dried at 600°C) was placed in a 2 oz bottle and slurried in 13 g of toluene. To this slurry was added $B(C_6F_5)_3$ (0.50 g, 0.98 mmol), but in contrast to the previous example, no N,N-diethylaniline was added. After shaking this mixture for 1 hr, 0.103 g of metallocene **M1** was added and the slurry was shaken for an additional 1 hr. The resulting orange slurry was filtered, the isolated product was washed with toluene and isohexane, and dried under vacuum. This sample was characterized by the following analytical and propylene polymerization data. Analysis: 0.77 wt% Zr. Polymerization Productivity, 0 g/g cat/hr.

EXAMPLE 15

Post-Amination of a Supported DBAB-Treated Aluminate Activator and Catalysts Prepared Therefrom

[00156] A 2-g sample of Silica I (600°C) was suspended in toluene (20 g) and treated with DBAB (1.48 mmol), while being stirred at room temperature for about 1 hr. After this time, the resulting slurry was treated with benzyldimethylamine (1.5 mmol) and stirred at room temperature for an additional 2 hr. The supernatant from this reaction was decanted from the reaction mixture, fresh toluene (20 g) was added, and the resulting slurry was treated with metallocene **M1** (0.051 mmol).

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This slurry was stirred at room temperature for another 1 hr, the solid was isolated by filtration, and washed with toluene and then cyclohexane. Analysis: 1.47 wt% Al; 0.15 wt% Zr. Polymerization productivity: 11,500g/g cat/hr.

CLAIMS

1. An activator composition derived from at least:
 - a) metal oxide support having at least one surface hydrogen-bonded hydroxyl group;
and
 - b) organoaluminum compound having at least one bulky functional ligand comprising an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate;
wherein the metal oxide support and the organoaluminum compound are combined in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion that is covalently bonded to the metal oxide support through two chelating oxygen atoms and ionically bonded to a H^+ .
2. The activator composition of Claim 1, wherein the metal oxide support comprises silica, alumina, or silica-alumina.
3. The activator composition of Claim 1, wherein the organoaluminum compound is $R^2_{3-n}Al(ER^3)_n$, wherein R^2 is hydrogen or a hydrocarbyl group having up to about 20 carbon atoms; R^3 is a hydrocarbyl group or a silyl group, each said group having up to 20 carbon atoms; and E is O, S, or NR^4 , wherein (i) R^4 is (a) hydrogen or (b) a hydrocarbyl group or a silyl group, each said group having up to about 10 carbon atoms, or (ii) R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms; and n is 1 or 2.
4. The activator composition of Claim 3, wherein R^2 comprises methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, n-hexyl, n-heptyl, or n-octyl.
5. The activator composition of Claim 1, wherein the at least one bulky functional ligand has the formula (ER^3) , wherein: i) R^3 is a hydrocarbyl group having up to 20 carbon atoms; and ii) E is O, S, or NR^4 , wherein R^4 is hydrogen or a hydrocarbyl group having up to 10 carbon atoms; or R^3 and R^4 together form a heterocyclic group having up to 20 carbon atoms.
6. A composition derived from at least:
 - a) the activator composition of Claim 1; and
 - b) a d-block or f-block metal compound comprising at least one ligand subject to protonolysis to form a cationic d-block or f-block metal compound.

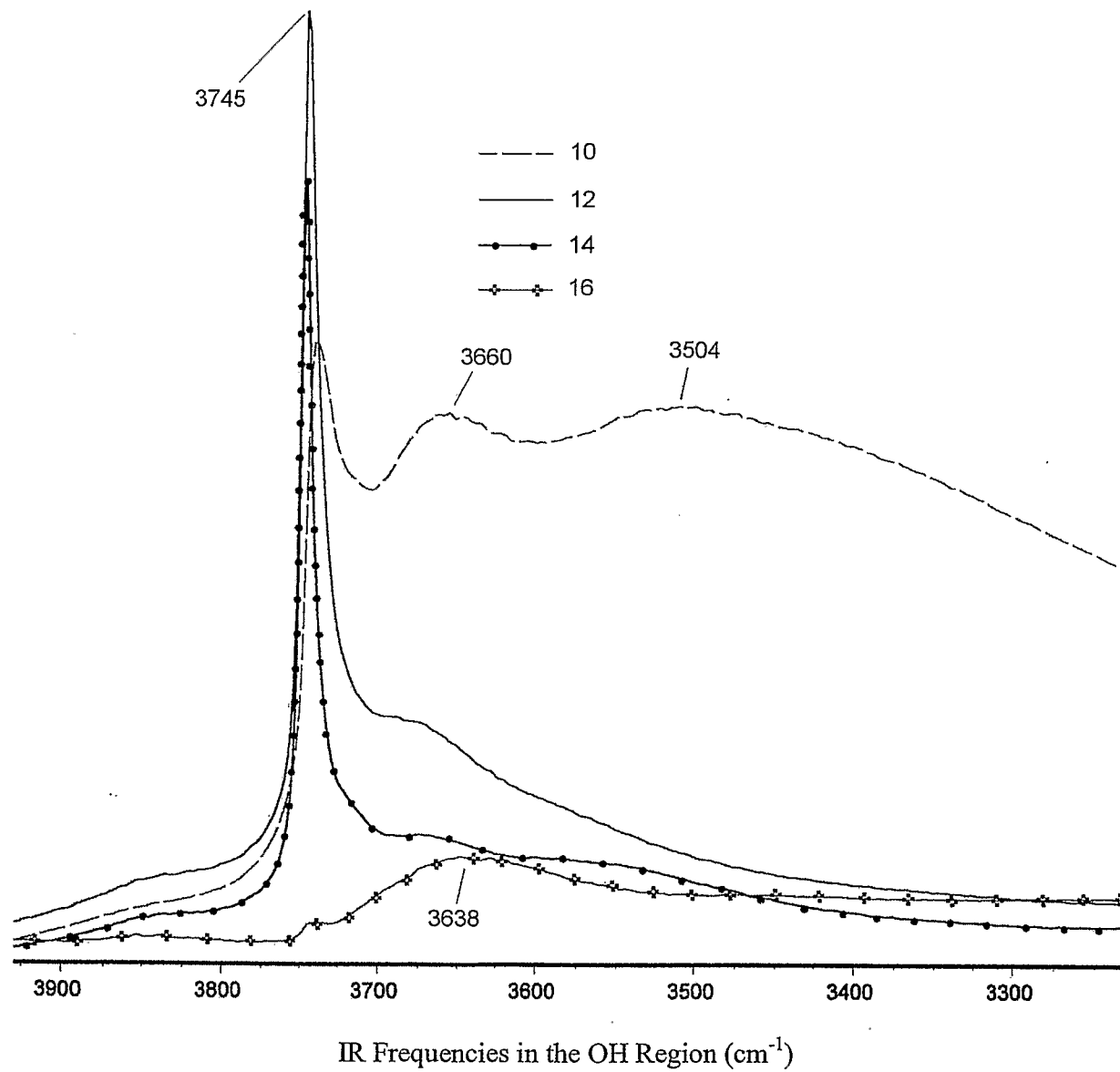
7. An activator composition derived from at least:
- metal oxide support having at least one surface hydrogen-bonded hydroxyl group;
 - organoaluminum compound having at least one bulky functional ligand comprising an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate; and
 - Lewis base
- wherein the metal oxide support, the organoaluminum compound, and the Lewis base are combined in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion that is covalently bonded to the metal oxide support through two chelating oxygen atoms and ionically bonded to a H^+ .
8. The activator composition of Claim 7, wherein the Lewis base is NR^1_3 , and R^1 in each occurrence is independently a hydrocarbyl group having up to 20 carbon atoms, or hydrogen.
9. The activator composition of Claim 7 wherein the Lewis base comprises NMe_2Ph , $NMe_2(CH_2Ph)$, NEt_2Ph , $NEt_2(CH_2Ph)$, $NMe(C_nH_{2n+1})(C_mH_{2m+1})$, $NMe_2(C_nH_{2n+1})$, $NEt(C_nH_{2n+1})(C_mH_{2m+1})$, or $NEt_2(C_nH_{2n+1})$, wherein n and m are selected independently from an integer from 3 to 20.
10. A composition derived from at least:
- the activator composition of Claim 7; and
 - a d-block or f-block metal compound comprising at least one ligand subject to protonolysis to form a cationic d-block or f-block metal compound.
11. An activator composition comprising a metal oxide support, an aluminate anion, and a Brønsted acidic cation, wherein:
- the aluminum atom of the aluminate anion is covalently bonded to the metal oxide support through two chelating oxygen atoms on the support;
 - the aluminum atom of the aluminate anion is covalently bonded to at least one bulky functional ligand;
 - the aluminate anion is ionically bonded to the Brønsted acidic cation; and
 - the Brønsted acidic cation is selected from H^+ or $[QH]^+$, wherein Q is a Lewis base.

12. The activator composition of Claim 11, wherein the at least one bulky functional ligand comprises an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate.
13. The activator composition of Claim 11, wherein the metal oxide support comprises hydrogen-bonded hydroxyl groups.
14. The activator composition of Claim 11, wherein the metal oxide support comprises silica, alumina, or silica-alumina.
15. The activator composition of Claim 11, wherein the Brønsted acidic cation comprises H^+ or $[HNR^1_3]^+$, and R^1 in each occurrence is independently a hydrocarbyl group having up to 20 carbon atoms, or hydrogen.
16. The activator composition of Claim 11, wherein the bulky functional ligand is (ER^3) , wherein: I) R^3 is a hydrocarbyl group or a silyl group, each said group having up to about 20 carbon atoms; and II) E is O, S, or NR^4 , wherein (i) R^4 is (a) hydrogen or (b) a hydrocarbyl group or a silyl group, each said group having up to about 10 carbon atoms; or (ii) R^3 and R^4 together form a heterocyclic group having up to 20 carbon atoms.
17. A method of preparing an activator composition comprising combining at least:
- a metal oxide support comprising at least one surface hydrogen-bonded hydroxyl group; and
 - an organoaluminum compound having at least one bulky functional ligand selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate;
- wherein the metal oxide support and the organoaluminum compound are contacted in amounts sufficient and under contact conditions sufficient to form at least one aluminate anion covalently bonded to the metal oxide support through two chelating oxygen atoms on the support and ionically bonded to a H^+ .
18. A catalyst composition comprising a metal oxide support, an aluminate anion, a cationic d-block or f-block metal compound, wherein:
- the aluminum atom of the aluminate anion is covalently bonded to the metal oxide support through two chelating oxygen atoms on the support;

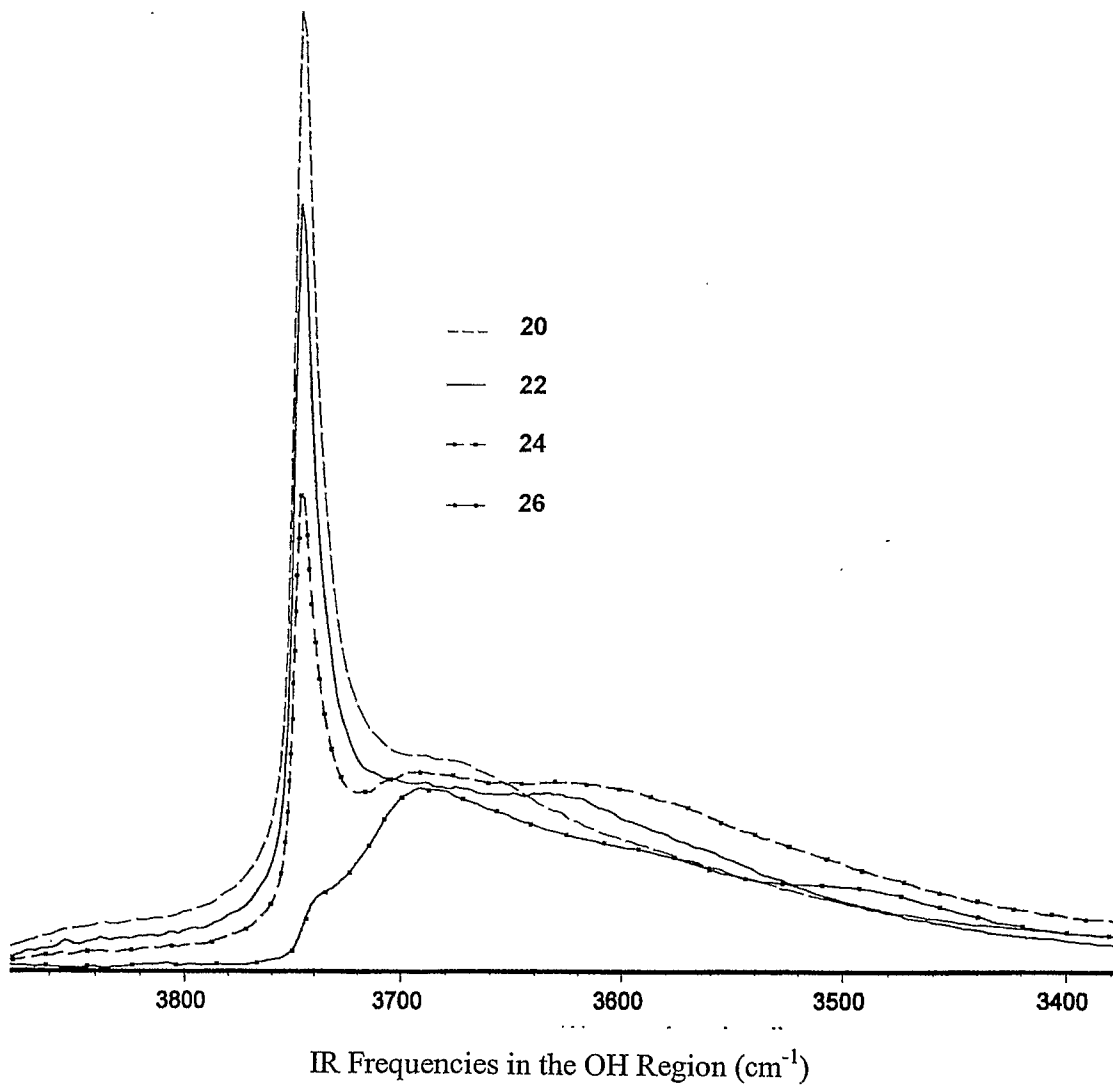
- b) the aluminum atom of the aluminate anion is covalently bonded to at least one bulky functional ligand selected from an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, and an aryl thiolate;
 - c) the aluminate anion is ionically bonded to the cationic d-block or f-block metal compound; and
 - d) the cationic d-block or f-block metal compound comprises at least one ligand capable of propagating olefin polymerization.
19. The catalyst composition of Claim 18, wherein the metal oxide support comprises silica, alumina, or silica-alumina.
20. The catalyst composition of Claim 18, wherein the bulky functional ligand is (ER^3) , wherein:
i) R^3 is a hydrocarbyl group or silyl group, each said group having up to about 20 carbon atoms; and
ii) E is O, S, or NR^4 , wherein (i) R^4 is (a) hydrogen or (b) a hydrocarbyl group or silyl group, each said group having up to about 10 carbon atoms; or (ii) R^3 and R^4 together form a heterocyclic group having up to about 20 carbon atoms.
21. A method for polymerizing olefins, comprising contacting at least one olefin monomer with the catalyst composition of Claim 18.
22. A catalyst composition comprising a metal oxide support, an aluminate anion, a cationic d-block or f-block metal compound, and a Lewis base wherein:
a) the aluminum atom of the aluminate anion is covalently bonded to the metal oxide support through two chelating oxygen atoms on the support;
b) the aluminum atom of the aluminate anion is covalently bonded to a bulky functional ligand comprising an alkoxide, an aryloxy, an alkyl amide, an aryl amide, an alkyl aryl amide, a dialkyl amide, a diaryl amide, an alkyl thiolate, or an aryl thiolate;
c) the aluminate anion is ionically bonded to the cationic d-block or f-block metal compound;
d) the cationic d-block or f-block metal compound comprises at least one ligand capable of propagating olefin polymerization; and
e) the Lewis base is coordinated to the cationic d-block or f-block metal compound.
23. The catalyst composition of Claim 22, wherein the Lewis base is NR^1_3 , and R^1 in each occurrence is independently a hydrocarbyl group having up to about 20 carbon atoms, or hydrogen.

24. The catalyst composition of Claim 22, wherein the Lewis base comprises NMe_2Ph , $\text{NMe}_2(\text{CH}_2\text{Ph})$, NEt_2Ph , $\text{NEt}_2(\text{CH}_2\text{Ph})$, $\text{NMe}(\text{C}_n\text{H}_{2n+1})(\text{C}_m\text{H}_{2m+1})$, $\text{NMe}_2(\text{C}_n\text{H}_{2n+1})$, $\text{NEt}(\text{C}_n\text{H}_{2n+1})(\text{C}_m\text{H}_{2m+1})$, or $\text{NEt}_2(\text{C}_n\text{H}_{2n+1})$, and n and m are independently an integer from 3 to 20.

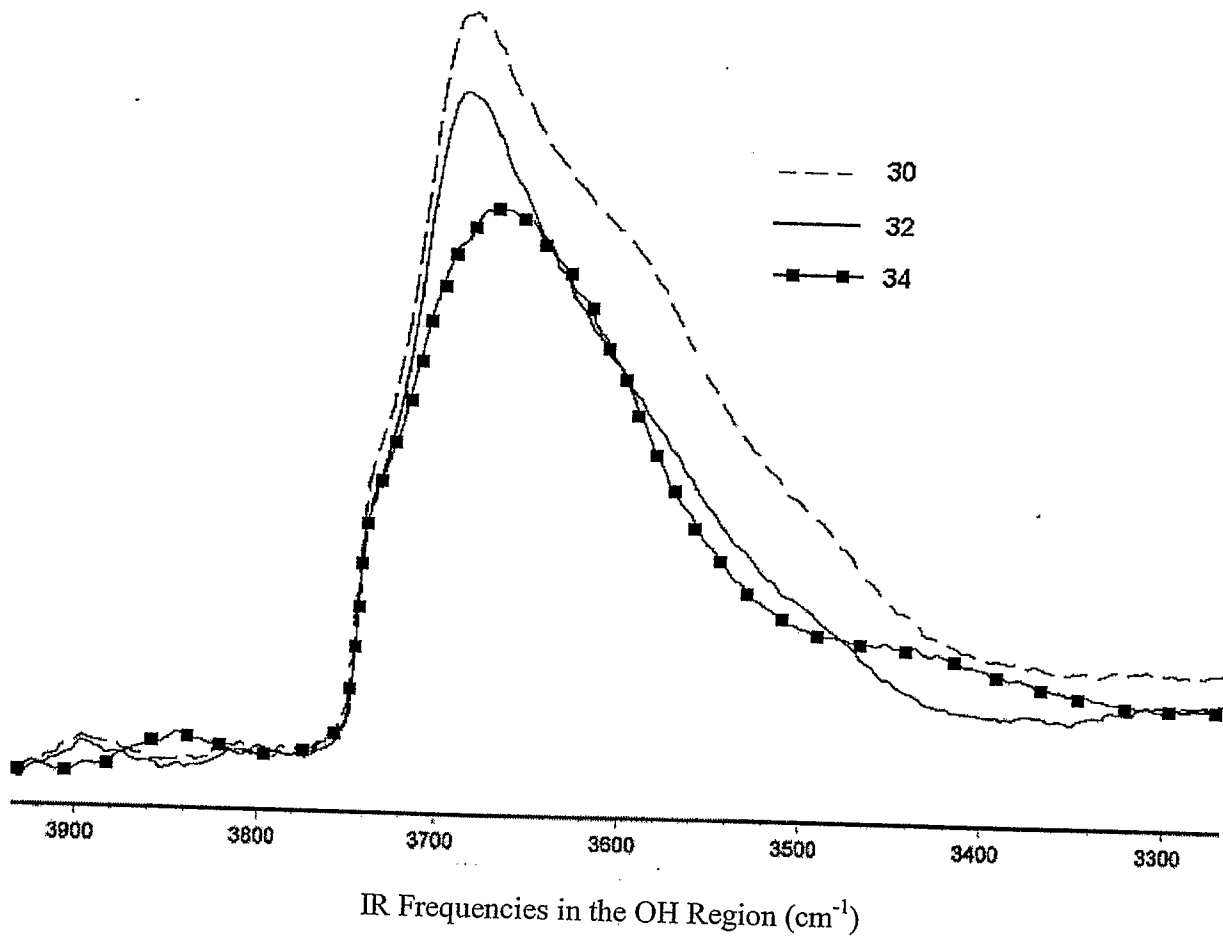
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