Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2497676 A1 2004/03/18

(21) 2 497 676

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2003/08/12
(87) Date publication PCT/PCT Publication Date: 2004/03/18
(85) Entrée phase nationale/National Entry: 2005/03/03
(86) N° demande PCT/PCT Application No.: US 2003/025281
(87) N° publication PCT/PCT Publication No.: 2004/022607
(30) Priorités/Priorities: 2002/09/04 (60/408,430) US;
2003/02/18 (10/368,818) US

(51) Cl.Int.^{7}/Int.Cl.^{7} C08F 4/02, C08F 4/642, C08F 4/60, C08F 110/02, C08F 4/44, C08F 210/02

(71) Demandeur/Applicant:
UNIVATION TECHNOLOGIES, LLC, US

(72) Inventeurs/Inventors:
KUO, CHI-I, US;
MCCULLOUGH, LAUGHLIN G., US;
SHIRODKAR, PRADEEP P., US;
EHRMAN, FRED D., US;
SHANNON, PORTER C., US;
SANTANA, ROBERT L., US;
...

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PROCEDE DE PRODUCTION DE POLYOLEFINES BIMODALES ET FILMS ASSOCIES
(54) Title: BIMODAL POLYOLEFIN PRODUCTION PROCESS AND FILMS THEREFROM

(57) Abrégé/Abstract:
A process of producing a bimodal polyolefm composition is described, which includes in one embodiment contacting monomers with a supported bimetallic catalyst composition for a time sufficient to form a bimodal polyolefm composition that includes a high molecular weight polyolefin component and a low molecular weight polyolefin component; wherein the supported bimetallic catalyst includes a first catalyst component that is preferably nonmetallocene, and a second catalyst component that includes a metallocene catalyst compound having at least one fluoride or fluorine containing leaving group, wherein the bimetallic catalyst is supported by an enhanced silica, dehydrated at a temperature of 800 °C or more in one embodiment.

CA 2497676 A1 2004/03/18

(21) 2 497 676

(13) A1

(72) **Inventeurs(suite)/Inventors(continued)**: ACKERMAN, STEVEN K., US; O'NEIL, DANIEL G., US

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number
WO 2004/022607 A1

(51) International Patent Classification[7]: C08F 4/02, 4/44, 4/60, 4/642, 110/02, 210/02

(21) International Application Number:
PCT/US2003/025281

(22) International Filing Date: 12 August 2003 (12.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/408,430	4 September 2002 (04.09.2002)	US
10/368,818	18 February 2003 (18.02.2003)	US

(71) Applicant: UNIVATION TECHNOLOGIES, LLC [US/US]; 5555 San Felipe, Suite 1950, Houston, TX 77056 (US).

(72) Inventors: KUO, Chi-I; 19410 Cluster Oaks Drive, Humble, TX 77346 (US). MCCULLOUGH, Laughlin, G.; 114 Crystal Reef Drive, League City, TX 77573 (US). SHIRODKAR, Pradeep, P.; 3118 Willow Wood Trail, Kingwood, TX 77345 (US). EHRMAN, Fred, D.; 14226 Ridgewood Lake Court, Houston, TX 77062 (US). SHANNON, Porter, C.; 1129 Carriage Court, Seabrook, TX 77586 (US). SANTANA, Robert, L.; 6126 Cajun Way, Baytown, TX 77520 (US). ACKERMAN, Steven, K.; 117 wEST aRCHER rOAD, Baytown, TX 77521 (US). ONEIL, Daniel, G.; 209 Rose Street, Metuchen, NJ 08840 (US).

(74) Agents: FAULKNER, Kevin, M. et al.; 5555 San Felipe, Suite 1950, Houston, TX 77056 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BIMODAL POLYOLEFIN PRODUCTION PROCESS AND FILMS THEREFROM

(57) Abstract: A process of producing a bimodal polyolefm composition is described, which includes in one embodiment contacting monomers with a supported bimetallic catalyst composition for a time sufficient to form a bimodal polyolefm composition that includes a high molecular weight polyolefin component and a low molecular weight polyolefin component; wherein the supported bimetallic catalyst includes a first catalyst component that is preferably nonmetallocene, and a second catalyst component that includes a metallocene catalyst compound having at least one fluoride or fluorine containing leaving group, wherein the bimetallic catalyst is supported by an enhanced silica, dehydrated at a temperature of 800 °C or more in one embodiment.

WO 2004/022607 A1

BIMODAL POLYOLEFIN PRODUCTION PROCESS AND FILMS THEREFROM

FIELD OF INVENTION

[0001] The present invention relates to bimodal polyolefin production, and more particularly, to bimodal polyolefins in producing films, wherein the bimodal polyolefin is produced in a single reactor using a bimetallic catalyst in a desirable embodiment.

BACKGROUND

[0002] Bimodal polymers produced using two or more different catalyst types—bimetallic catalysts—are of increasing interest, especially in producing polyethylene and other polyolefins. See, for example, US 5,525,678. However, problems exist in using these bimetallic catalysts, especially in the gas phase. One problem is catalyst activity, which should be as high as possible in order to economize the process, as catalysts costs are significant.

[0003] One method of improving catalyst efficiency in gas phase processes is to improve upon the catalyst used in the process. A promising class of single-site catalysts for commercial use includes those wherein the metal center has at least one extractable fluorine (or fluorine "leaving group"). Disclosures of such catalysts include US 20020032287; WO 97/07141; DE 43 32 009 A1; EP-A2 0 200 351; EP-A1 0 705 849; E.F. Murphy, et al., *Synthesis and spectroscopic characterization of a series of substituted cyclopentadienyl Group 4 fluorides; crystal structure of the acetylacetonato complex* $[(acac)_2(\eta^5\text{-}C_5Me_5)Zr(\mu\text{-}F)SnMe_3Cl]$, DALTON, 1983 (1996); A. Herzog, et al., *Reactions of* $(\eta^5\text{-}C_5Me_5)ZrF_3$, $(\eta^5\text{-}C_5Me_4Et)ZrF_3$, $(\eta^5\text{-}C_5M4_5)_2ZrF_2$, $(\eta^5\text{-}C_5Me_5)HfF_3$, *and* $(\eta^5\text{-}C_5Me_5)TaF_4$ *with* $AlMe_3$, *Structure of the First Hafnium-Aluminum-Carbon Cluster*, 15 ORGANOMETALLICS 909-917 (1996); F. Garbassi, et al., JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL 101 199-209 (1995); and W. Kaminsky, et al., *Fluorinated Half-Sandwich Complexes as Catalysts in Syndiospecific Styrene Polymerization*, 30(25) MACROMOLECULES 7647-7650 (1997). Use of such single site catalyst components in a olefin polymerization system is desirable, especially in gas-phase polyethylene polymerization. It would be desirable to further improve upon this system, especially for bimodal gas phase polymerization processes. The present invention is directed towards solving this and other problems.

SUMMARY

[0004] The present invention provides a method for bimodal polyolefin production, preferably using bimetallic catalysts, and polyolefins films made from bimodal polyolefin compositions. At least one embodiment of the invention is directed to a process of producing a bimodal polyolefin composition that includes contacting monomers with a supported bimetallic catalyst composition for a time sufficient to form a bimodal polyolefin composition; wherein the supported bimetallic catalyst includes a first catalyst component and a second catalyst component that includes a metallocene catalyst compound having at least one fluoride or fluorine containing leaving group.

[0005] Another specific embodiment of the invention is directed to a process of producing a bimodal polyolefin composition comprising contacting monomers with a supported bimetallic catalyst composition for a time sufficient to form the bimodal polyolefin composition that includes a high molecular weight polyolefin component and a low molecular weight polyolefin component; wherein the supported bimetallic catalyst includes a first catalyst component that includes a fluorinated metallocene represented by the formula Cp_2MF_2 wherein Cp is a substituted or unsubstituted cyclopentadienyl ring or derivative thereof, M is a Group 4, 5, or 6 transition metal and a support material comprising silica dehydrated at a temperature of 800 °C or more.

[0006] Yet another specific embodiment of the invention is directed to a process of producing a bimodal polyolefin composition, including providing a particulate support material comprising silica; heating the particulate support material to a temperature of 800 °C or more for a time sufficient to form a dehydrated support material including dehydrated silica; combining the dehydrated support material with a non-polar hydrocarbon to provide a support slurry; providing a first catalyst component that is a non-metallocene catalyst; providing a second catalyst component that includes a metallocene catalyst compound having at least one fluoride or fluorine containing leaving group; combining the support slurry with the first and second catalyst components to form a supported bimetallic catalyst composition; and contacting monomers with the bimetallic catalyst composition for a time sufficient to form a bimodal polyolefin composition having a density of from 0.86 g/cm^3 to 0.97 g/ cm^3, a

molecular weight distribution of from 5 to 80, a I_2 of from 0.01 dg/min to 50 dg/min, and a melt index ratio of from 40 to 500.

[0007] In certain aspects, a film made from one or more of the bimodal polyolefin compositions disclosed herein has a Dart Drop Impact F50 Value of at least 100 [g] on 25.4 micron film and 75 [g] on 12.5 micron film.

[0008] In certain aspects, a film made from one or more of the bimodal polyolefin compositions disclosed herein has an MD Tear value of at least 0.4 g/micron on 25.4 micron film and at least 0.2 g/micron on 12.5 micron film.

[0009] In certain aspects, a film made from one or more of the bimodal polyolefin compositions disclosed herein has a TD Tear value of at least 1.5 g/micron on 24.5 micron film and 1.0 g/micron on 12.5 micron film.

[0010] In particular embodiments, the support material useful in the process of the invention has been enhanced, in that it includes silica dehydrated at a temperature of 800°C or more. In a more particular embodiment, the support material includes silica dehydrated at a temperature of 830 °C or more. In yet a more particular embodiment, the support material includes silica dehydrated at a temperature of 875 °C or more.

DETAILED DESCRIPTION

General Definitions

[0011] As used herein, in reference to Periodic Table "Groups" of Elements, the "new" numbering scheme for the Periodic Table Groups are used as in the CRC HANDBOOK OF CHEMISTRY AND PHYSICS (David R. Lide ed., CRC Press 81st ed. 2000).

[0012] As used herein, the phrase "catalyst system" includes at least one "catalyst component" and at least one "activator", both of which are described further herein. The catalyst system may also include other components, such as supports, etc., and is not limited to the catalyst component and/or activator alone or in combination. The catalyst system may

include any number of catalyst components in any combination as described herein, as well as any activator in any combination as described herein.

[0013] As used herein, the phrase "catalyst compound" includes any compound that, once appropriately activated, is capable of catalyzing the polymerization or oligomerization of olefins, the catalyst compound comprising at least one Group 3 to Group 12 atom, and optionally at least one leaving group bound thereto.

[0014] As used herein, the phrase "leaving group" refers to one or more chemical moieties bound to the metal center of the catalyst component that can be abstracted from the catalyst component by an activator, thus producing the species active towards olefin polymerization or oligomerization. The activator is described further below.

[0015] As used herein, the term "fluorinated catalyst component" or "fluorided catalyst component" means a catalyst compound having at least one fluoride or fluorine containing leaving group, preferably a metallocene or metallocene-type catalyst compound having at least one fluoride or fluorine containing leaving group.

[0016] As used herein, a "hydrocarbyl" includes aliphatic, cyclic, olefinic, acetylenic and aromatic radicals (*i.e.*, hydrocarbon radicals) comprising hydrogen and carbon that are deficient by one hydrogen. A "hydrocarbylene" is deficient by two hydrogens.

[0017] As used herein, an "alkyl" includes linear, branched and cyclic paraffin radicals that are deficient by one hydrogen. Thus, for example, a $-CH_3$ group ("methyl") and a CH_3CH_2- group ("ethyl") are examples of alkyls.

[0018] As used herein, an "alkenyl" includes linear, branched and cyclic olefin radicals that are deficient by one hydrogen; alkynyl radicals include linear, branched and cyclic acetylene radicals deficient by one hydrogen radical.

[0019] As used herein, "aryl" groups includes phenyl, naphthyl, pyridyl and other radicals whose molecules have the ring structure characteristic of benzene, naphthylene,

phenanthrene, anthracene, etc. For example, a $C_6H_5^-$ aromatic structure is an "phenyl", a $C_6H_4^{2-}$ aromatic structure is an "phenylene". An "arylalkyl" group is an alkyl group having an aryl group pendant therefrom; an "alkylaryl" is an aryl group having one or more alkyl groups pendant therefrom.

[0020] As used herein, an "alkylene" includes linear, branched and cyclic hydrocarbon radicals deficient by two hydrogens. Thus, $-CH_2-$ ("methylene") and $-CH_2CH_2-$ ("ethylene") are examples of alkylene groups. Other groups deficient by two hydrogen radicals include "arylene" and "alkenylene".

[0021] As used herein, the phrase "heteroatom" includes any atom other than carbon and hydrogen that can be bound to carbon, and in one embodiment is selected from the group consisting of B, Al, Si, Ge, N, P, O, and S. A "heteroatom-containing group" is a hydrocarbon radical that contains a heteroatom and may contain one or more of the same or different heteroatoms, and from 1 to 3 heteroatoms in a particular embodiment. Non-limiting examples of heteroatom-containing groups include radicals of imines, amines, oxides, phosphines, ethers, ketones, oxoazolines heterocyclics, oxazolines, thioethers, and the like.

[0022] As used herein, an "alkylcarboxylate", "arylcarboxylate", and "alkylarylcarboxylate" is an alkyl, aryl, and alkylaryl, respectively, that possesses a carboxyl group in any position. Examples include $C_6H_5CH_2C(O)O^-$, $CH_3C(O)O^-$, etc.

[0023] As used herein, the term "substituted" means that the group following that term possesses at least one moiety in place of one or more hydrogens in any position, the moieties selected from such groups as halogen radicals (*esp.*, Cl, F, Br), hydroxyl groups, carbonyl groups, carboxyl groups, amine groups, phosphine groups, alkoxy groups, phenyl groups, naphthyl groups, C_1 to C_{10} alkyl groups, C_2 to C_{10} alkenyl groups, and combinations thereof. Examples of substituted alkyls and aryls includes, but are not limited to, acyl radicals, alkylamino radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- and dialkyl-carbamoyl radicals, acyloxy radicals, acylamino radicals, arylamino radicals, and combinations thereof.

[0024] As used herein, structural formulas are employed as is commonly understood in the chemical arts; lines ("——") used to represent associations between a metal atom ("M", Group 3 to Group 12 atoms) and a ligand or ligand atom (*e.g.*, cyclopentadienyl, nitrogen, oxygen, halogen ions, alkyl, etc.), as well as the phrases "associated with", "bonded to" and "bonding", are not limited to representing a certain type of chemical bond, as these lines and phrases are meant to represent a "chemical bond"; a "chemical bond" defined as an attractive force between atoms that is strong enough to permit the combined aggregate to function as a unit, or "compound".

[0025] A certain stereochemistry for a given structure or part of a structure should not be implied unless so stated for a given structure or apparent by use of commonly used bonding symbols such as by dashed lines and/or heavy lines.

[0026] Unless stated otherwise, no embodiment of the present invention is herein limited to the oxidation state of the metal atom "M" as defined below in the individual descriptions and examples that follow. The ligation of the metal atom "M" is such that the compounds described herein are neutral, unless otherwise indicated.

[0027] As used herein, the term "bimodal," when used to describe a polymer or polymer composition (*e.g.*, polyolefins such as polypropylene or polyethylene, or other homopolymers, copolymers or terpolymers) means "bimodal molecular weight distribution," which is understood as having the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents. For example, a single composition that includes polyolefins with at least one identifiable high molecular weight distribution and polyolefins with at least one identifiable low molecular weight distribution is considered to be a "bimodal" polyolefin, as that term is used herein. In a particular embodiment, other than having different molecular weights, the high molecular weight polyolefin and the low molecular weight polyolefin are essentially the same type of polymer, for example, polypropylene or polyethylene.

[0028] As used herein, the term "productivity" means the weight of polymer produced per weight of the catalyst used in the polymerization process (*e.g.*, grams polymer/gram catalyst).

[0029] As used herein, the term "dehydrated" is understood as having the broadest definition persons in the pertinent art have given that term in describing catalyst support materials, for example, silica, as reflected in printed publications and issued patents, and includes any material, for example, a support particle, from which a majority of the contained/adsorbed water has been removed.

Gas-phase polymerization using bimetallic catalysts comprising a fluorided metallocene catalyst component

[0030] The present invention provides a process for producing a bimodal polyolefin composition comprising: contacting olefin monomers with a bimetallic catalyst composition to form a bimodal polyolefin composition; wherein the bimetallic catalyst composition comprises: a first catalyst component; and metallocene catalyst compound having at least one fluoride or fluorine containing leaving group. In a particular embodiment, the bimetallic catalyst is supported. The bimetallic catalyst, each of its components, and the method of polymerization are set out in greater detail below.

[0031] In one aspect of the invention, the method of making bimodal polymers is characterized in that the monomers are contacted with the bimetallic catalyst in a single reactor vessel and form the bimodal polyolefin composition in the same reactor vessel.

[0032] The present invention also provides a bimodal film composition comprising a polyolefin having a density of from 0.86 g/cm^3 to 0.97 g/cm^3, a molecular weight distribution of from 5 to 80, a melt index of from 0.01 dg/min to 50 dg/min, and a melt index ratio of from 40 to 500. The film composition, or film, is formed from the bimetallic catalyst of the invention, and has certain desirable features as set out further below.

Bimetallic Catalyst

[0033] As used herein, the term "bimetallic catalyst" or "bimetallic catalyst system" refers to two or more catalyst components used in combination with at least one activator, and optionally a support material, that is useful in polymerizing olefins. The "supported bimetallic catalyst" or "supported bimetallic catalyst composition" refers the bimetallic catalyst system as used in combination with a support material, wherein one or more of the components that make up the bimetallic catalyst system may be bound to the support. In a particular embodiment, the bimetallic catalyst of the invention includes two catalyst components. In a more particular embodiment, the bimetallic catalyst component includes a "first catalyst component" and a "second catalyst component".

[0034] As used herein, the term "first catalyst component" refers to any catalyst component other than the second catalyst component. Preferably, the first catalyst component is a non-metallocene catalyst component, examples of which include titanium or vanadium based Ziegler-Natta catalysts compounds as described further herein.

[0035] As used herein, the term "non-metallocene compound" refers any catalyst that is neither a metallocene nor one of the metallocene-type catalyst compounds identified below.

[0036] As used herein, the term "second catalyst component" refers to any catalyst that is different from a first catalyst component, a metallocene catalyst component in a particular embodiment. In a particular embodiment, the second catalyst component includes a fluorided metallocene component which comprises at least one fluoride ion leaving group or fluorine containing group.

[0037] Certain embodiments of the present invention involve contacting monomers with the bimetallic catalyst component. In a particular embodiment, each different catalyst compound that comprises the bimetallic catalyst resides, or is supported on a single type of support such that, on average, each particle of support material includes both the first and second catalyst components. In another embodiment, the first catalyst component is supported separately from the second catalyst component such that on average any given particle of support material comprises only the first or the second catalyst component. In this later

embodiment, each supported catalyst may be introduced into the polymerization reactor sequentially in any order, alternately in parts, or simultaneously.

[0038] In a particular embodiment, the first catalyst component includes a titanium non-metallocene catalyst component, from which a higher molecular weight resin (*e.g.*, > ca 100,000 amu) can be produced. In a particular embodiment, the second catalyst component includes a metallocene component, from which a lower molecular weight resin (*e.g.*, < ca 100,000 amu) can be produced. Accordingly, polymerization in the presence of the first and second catalyst components provides a bimodal polyolefin composition that includes a low molecular weight component and a high molecular weight component. The two catalyst components reside on a single support particle in a particular embodiment, and they can be affixed to the support in a variety of ways.

[0039] In one embodiment, an "enhanced silica" is prepared as described herein and constitutes the support; the first catalyst component is a non-metallocene compound that is first combined with the enhanced silica, to provide a supported non-metallocene composition; the supported non-metallocene composition is combined with the second catalyst component, for example, a fluorided metallocene (a metallocene having at least one fluorine ion leaving group), resulting in a fluorinated bimetallic catalyst composition having enhanced productivity when used in production of a bimodal polyolefin composition.

[0040] Various methods of affixing two different catalyst components (albeit a different combination of catalysts) to a support can be used. In general, one procedure for preparing a supported bimetallic catalyst can include providing a supported first catalyst component, contacting a slurry that includes the first catalyst component in a non-polar hydrocarbon with a solution that includes the second catalyst component, which may also include an activator, and drying the resulting product that includes the first and second catalyst components and recovering a bimetallic catalyst composition.

First Catalyst Component

[0041] As noted above, the bimetallic catalyst composition includes a first catalyst component, which is (or includes) a non-metallocene compound. However, it is contemplated

that for certain applications the first catalyst component may alternatively be a metallocene compound, or even one of the metallocene-type catalyst compounds identified below that is different in structure from the second catalyst component as described herein. In a particular embodiment, the first catalyst component is a Ziegler-Natta catalyst compound. Ziegler-Natta catalyst components are well known in the art and described by, for example, in ZIEGLER CATALYSTS 363-386 (G. Fink, R. Mulhaupt and H.H. Brintzinger, eds., Springer-Verlag 1995). Examples of such catalysts include those comprising $TiCl_4$ and other such transition metal oxides and chlorides.

[0042] The first catalyst component is combined with a support material in one embodiment, either with or without the second catalyst component. The first catalyst component can be combined with, placed on or otherwise affixed to a support in a variety of ways. In one of those ways, a slurry of the support in a suitable non-polar hydrocarbon diluent is contacted with an organomagnesium compound, which then dissolves in the non-polar hydrocarbon diluent of the slurry to form a solution from which the organomagnesium compound is then deposited onto the carrier. The organomagnesium compound can be represented by the formula RMgR', where R' and R are the same or different C_2-C_{12} alkyl groups, or C_4-C_{10} alkyl groups, or C_4-C_8 alkyl groups. In at least one specific embodiment, the organomagnesium compound is dibutyl magnesium. In one embodiment, the amount of organomagnesium compound included in the silica slurry is only that which will be deposited, physically or chemically, onto the support, for example, being bound to the hydoxyl groups on the support, and no more than that amount, since any excess organomagnesium compound may cause undesirable side reactions. Routine experimentation can be used to determine the optimum amount of organomagnesium compound. For example, the organomagnesium compound can be added to the slurry while stirring the slurry, until the organomagnesium compound is detected in the support solvent. Alternatively, the organomagnesium compound can be added in excess of the amount that is deposited onto the support, in which case any undeposited excess amount can be removed by filtration and washing. The amount of organomagnesium compound (moles) based on the amount of dehydrated silica (grams) generally range from 0.2 mmol/g to 2 mmol/g in one embodiment.

[0043] Optionally, the organomagnesium compound-treated slurry is contacted with an electron donor, such as tetraethylorthosiloxane (TEOS) or an organic alcohol R"OH, where R" is a C_1-C_{12} alkyl group, or a C_1 to C_8 alkyl group, or a C_2 to C_4 alkyl group. In a particular embodiment, R"OH is n-butanol. The amount of alcohol used in an amount effective to provide an R"OH:Mg mol/mol ratio of from 0.2 to 1.5, or from 0.4 to 1.2, or from 0.6 to 1.1, or from 0.9 to 1.0.

[0044] The organomagnesium and alcohol-treated slurry is contacted with a non-metallocene transition metal compound. Suitable non-metallocene transition metal compounds are compounds of Group 4 and 5 metals that are soluble in the non-polar hydrocarbon used to form the silica slurry. Suitable non-metallocene transition metal compounds include, for example, titanium and vanadium halides, oxyhalides or alkoxyhalides, such as titanium tetrachloride ($TiCl_4$), vanadium tetrachloride (VCl_4) and vanadium oxytrichloride ($VOCl_3$), and titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl group of 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms. Mixtures of such transition metal compounds may also be used. The amount of non-metallocene transition metal compound used is sufficient to give a transition metal to magnesium mol/mol ratio of from 0.3 to 1.5, or from 0.5 to 0.8. The diluent can then be removed in a conventional manner, such as by evaporation or filtering, to obtain the dry, supported first catalyst component.

[0045] The first and second catalyst components may be contacted with the support in any order. In a particular embodiment of the invention, the first catalyst component is reacted first with the support as described above, followed by contacting this supported first catalyst component with a second catalyst component.

Process for Making a Fluorinated Catalyst Compound

[0046] Embodiments of the invention include a process of producing a fluorinated catalyst compound, and in particular, a fluorided metallocene catalyst component. The fluorided metallocene itself is described in more detail below. The fluorided metallocene catalyst component can be (or include) any fluorided metallocene catalyst component, but is preferably a fluorided metallocene catalyst component. The fluorided metallocene catalyst component can be, for example, any one of the catalysts described in greater detail below, or

the "second catalyst component" of the bimodal catalyst. The fluorided catalyst compound is preferably a metallocene type compound having the general formula $(Cp(R)_p)_mMX_nF_r$ (which can include, for example, a partially fluorinated metallocene), wherein Cp is a cyclopentadienyl ligand or ligand isolobal to cyclopentadienyl (as described further below) that can be substituted in any position by a group R as set out below, M is a Group 4, 5, or 6 transition metal in a particular embodiment, X is an anionic ligand such as a halogen, carboxylate, acetylacetonate, alkoxide, hydroxide, or oxide; p is an integer from 0 to 10, m is an integer from 1 to 3, n is an integer from 0 to 3, and r is an integer from 1 to 3.

[0047] The process includes contacting a metallocene catalyst compound with a fluoriding agent, and more particularly, a fluorinated inorganic salt, for a time sufficient to form the fluorided metallocene catalyst compound. The metallocene catalyst compound preferably has the same general formula as the desired fluorinated metallocene compound, with the exception that the one or more leaving groups X are an anionic ligand (*e.g.*, chlorine or bromine) rather than fluorine. The metallocene compound that is contacted with the fluoriding agent may be commercially available, or may be prepared by methods known to one skilled in the art.

[0048] The metallocene compound may include a cyclopentadienyl ligand or ligand isolobal to Cp, either substituted or unsubstituted. The amount of substitution on Cp may affect the yield of the fluorinated metallocene compound. Therefore, at least one Cp of the metallocene is substituted in one embodiment, and two Cps are substituted in another embodiment, wherein the metallocene is a sandwich metallocene as set out below. In a particular embodiment, the substituent group (R) is not an aryl group such as phenyl, indenyl or fluorenyl. In at least certain embodiments, it has been discovered that benzene substituent groups correspond to reduced product yields. For example, when R is indenyl, the product yield may be as low as zero. Preferably, the substituent groups include hydrocarbyl groups. In a preferred embodiment, alkyl substitution results in surprisingly high yields, for example, 95% or more.

[0049] In one embodiment, the fluoriding agent is a fluorinated inorganic salt or combination of salts described by the general formula (a):

$$[\alpha]_a[\beta]_b, \qquad (a)$$

wherein α is a cationic species selected from the group consisting of Group 1 and 2 cations; anilinium and substituted versions thereof; and NH_4^+, NH_3R, NH_2R_2, and NHR_3^+ wherein R is selected from the group consisting of hydride, chloride, C_1 to C_{10} alkyl and C_6 to C_{12} aryls;

β is an anionic species selected from the group consisting of fluorine ions and compounds comprising fluorine and one or more elements selected from the group consisting of hydrogen, silicon, carbon, phosphorous, oxygen, aluminum and boron; and

a and b are integers from 1 to 10.

[0050] In a particular embodiment, the fluorinated inorganic salt is a compound characterized in that it is capable of generating fluoride ions when contacted with water or other protic diluent. Non-limiting examples of the fluorinated inorganic salt include $(NH_4)_3AlF_6$, NH_4HF_2, NaF, KF, NH_4F, $(NH_4)_2\ SiF_6$ and combinations thereof.

[0051] The fluorinated inorganic salt compound may include a fluorinated inorganic salt mixture. The fluorinated inorganic salt compound is preferably soluble or partially soluble in a diluent. Therefore, the mixture may include the fluorinated inorganic salt and a diluent, that is, the fluorinated inorganic salt may be dissolved in a diluent prior to contacting the metallocene catalyst compound. The diluent may include an organic diluent. In a particular embodiment, the diluent is water or water in combination with some other polar diluent that is miscible with water (*e.g.*, ethers, ketones, aldehydes, etc). In another embodiment, the diluent is any desirable protic medium. In a particular embodiment, the fluorinated inorganic salt is combined with a diluent that is at least 50 wt% water, and at least 60 wt% water in another embodiment, and at least 70 wt% water in yet another embodiment, and at least 80 wt% water in yet another embodiment, and at least 90 wt% in a particular embodiment, and at least 99 wt% water in a more particular embodiment.

[0052] The metallocene compound that is contacted with the fluoriding agent may be initially charged in an inert or non-protic diluent. The inert diluent may include one of, or a mixture of, aliphatic and aromatic hydrocarbons or a halogenated solvent. Suitable hydrocarbons include substituted and unsubstituted aliphatic hydrocarbons and substituted and unsubstituted aromatic hydrocarbons. In a particular embodiment, the inert diluent is selected from the group consisting of C_3 to C_{30} hydrocarbons and C_1 to C_{10} halogenated hydrocarbons and mixtures thereof in a particular embodiment. Non-limiting examples of suitable inert diluents include hexane, heptane, octane, decane, toluene, xylene, dichloromethane, dichloroethane, chloroform and 1-chlorobutane.

[0053] In a particular embodiment of the method of fluoriding metallocenes described herein, the fluorinated inorganic salt combined with a protic diluent is reacted with the metallocene combined with an inert diluent. In a more particular embodiment, the fluorinated inorganic salt in at least 50% water is combined with the metallocene to be fluorided dissolved/suspended in a hydrocarbon or halogenated hydrocarbon diluent. The combined reactants may form two or more phases in contact with one another. The fluoriding reaction then takes place under desirable mixing and temperature conditions.

[0054] In embodiments of the fluoriding step wherein the fluoriding agent is immiscible or only partially miscible with the diluent, it is within the scope of the invention to use a reagent that will assist the transport of the fluoriding agent to the alkylated catalyst component or the diluent phase in which the alkylated catalyst component exists, or assist in the reaction between the fluoriding agent and alkylated catalyst component. Such reagents—phase-transfer catalysts—are known in the art and are used in reactions wherein, for example, an aqueous or polar diluent phase is in contact with a non-polar or hydrocarbon diluent phase, and the reactants are separated as such. Non-limiting examples of such phase-transfer catalysts include quaternary ammonium salts (*e.g.*, quaternary ammonium bisulfate), crown ethers, and others common in the art.

[0055] Depending on the desired degree of substitution, the ratio of fluorine (of the fluoriding agent) to metallocene combined to react is from 1 equivalent to 20 equivalents in one embodiment, and from 2 to 10 equivalents in another embodiment, and from 2 to 8

equivalents in yet another embodiment, and from 2 to 5 equivalents in yet another embodiment, wherein a desirable range comprises any combination of any upper limit with any lower limit. While excess fluorinated inorganic salt may not be detrimental, the molar ratio of the reactants is preferably determined by the number of anionic ligands to be substituted in the metallocene compound, that is, the number of anionic ligands to be replace by fluorine or fluoride atoms. In a particular embodiment, the number of anionic ligands to be substituted is 2.

[0056] Stated another way, the desired amount of fluoriding agent, based on the equivalents of fluorine in the fluoriding agent, that is combined with the metallocene catalyst compound ranges from 1, or 2, or 3, or 4, or 5 to 6, or 7, or 8, or 10, or 12, or 14 or 15 or 18 or 20, wherein a desirable range comprises any combination of any upper limit with any lower limit described herein. In another embodiment, the desired amount of fluoriding agent, based on the equivalents of fluoriding agent as a whole, ranges from 1, or 2, or 3, or 4 to 5 or 6, or 7, or 8, or 9, or 10, wherein a desirable range comprises any combination of any upper limit with any lower limit described herein.

[0057] The fluorinated inorganic salt may be reacted with the metallocene compound by vigorously stirring the compounds. The reaction may occur at any temperature that affords the desired mono-, di- or trifluorided metallocene, including temperatures of from –80 °C to 120 °C in one embodiment, and from 0 to 100 °C in a more particular embodiment, and from 10 to 60°C in yet a more particular embodiment, and from 15 to 40°C in yet a more particular embodiment. At those temperatures, reaction times of 0.05 hour to 8 hours are sufficient to form a fluorinated metallocene compound, but routine experimentation may be desirable to arrive at an optimum temperature. Generally, the reaction time is dependent upon the amount of reactants reacted. In one embodiment, the reaction time is from 0.1 hour to 3 hours.

[0058] The diluent, along with reaction by-products, can be removed from the mixture in a conventional manner, such as by evaporation or filtering, to obtain the dry, fluorinated metallocene compound. For example, the fluorided metallocene may be dried in the presence of magnesium sulfate. The filtrate, which contains the fluorinated metallocene compound in high purity and yield, can without further processing be directly used in the polymerization of olefins if the solvent is a hydrocarbon.

[0059] Contacting the metallocene compound with the fluorinated inorganic salt, an aqueous fluorinated inorganic salt, results in a product yield of 50% or more in a particular embodiment. The product yield is 80% or more in yet a more particular embodiment. The product yield is 90% or more in yet a more particular embodiment. Unexpectedly, contacting the metallocene compound with the aqueous solution of fluorinated inorganic salt results in a fluorided metallocene compound having high productivities.

Fluorided Metallocene Catalyst Component

[0060] The bimetallic catalyst system useful in the present invention includes a second catalyst component that comprises at least one fluorided metallocene catalyst component as described herein. Metallocene catalyst compounds are generally described throughout in, for example, 1 & 2 METALLOCENE-BASED POLYOLEFINS (John Scheirs & W. Kaminsky eds., John Wiley & Sons, Ltd. 2000); G.G. Hlatky in 181 COORDINATION CHEM. REV. 243-296 (1999) and in particular, for use in the synthesis of polyethylene in 1 METALLOCENE-BASED POLYOLEFINS 261-377 (2000). The metallocene catalyst compounds as described herein include "half sandwich" and "full sandwich" compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl) bound to at least one Group 3 to Group 12 metal atom, and one or more leaving group(s) bound to the at least one metal atom. Hereinafter, these compounds will be referred to as "metallocenes" or "metallocene catalyst components". The fluorided metallocene components are those wherein at least one leaving group bound to M is a fluoride ion or a fluorine-containing group. The metallocene catalyst component is supported on a support material in a particular embodiment as described further below, and may be supported with or without the first catalyst component, with the first catalyst component in a particular embodiment.

[0061] The Cp ligands are typically π-bonded and/or fused ring(s) or ring systems. The ring(s) or ring system(s) typically comprise atoms selected from the group consisting of Groups 13 to 16 atoms, and more particularly, the atoms that make up the Cp ligands are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum and combinations thereof, wherein carbon makes up at least 50% of the ring members. Even more particularly, the Cp ligand(s) are selected from the group consisting

of substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentaphenanthreneyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (*e.g.*, 4,5,6,7-tetrahydroindenyl, or "H_4Ind"), substituted versions thereof, and heterocyclic versions thereof. In a particular embodiment, the metallocenes useful in the present invention are selected from those including one or two, two in a more particular embodiment, of the same or different Cp rings selected from the group consisting of cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, and substituted versions thereof.

[0062] The metal atom "M" of the metallocene catalyst compound, as described throughout the specification and claims, may be selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms in one embodiment; and selected from the group consisting of Groups 3 through 10 atoms in a more particular embodiment, and selected from the group consisting of Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni in yet a more particular embodiment; and selected from the group consisting of Groups 4, 5 and 6 atoms in yet a more particular embodiment, and a Ti, Zr, Hf atoms in yet a more particular embodiment, and Zr in yet a more particular embodiment. The oxidation state of the metal atom "M" may range from 0 to +7 in one embodiment; and in a more particular embodiment, is +1, +2, +3, +4 or +5; and in yet a more particular embodiment is +2, +3 or +4. The groups bound the metal atom "M" are such that the compounds described below in the formulas and structures are electrically neutral, unless otherwise indicated. The Cp ligand(s) form at least one chemical bond with the metal atom M to form the "metallocene catalyst compound". The Cp ligands are distinct from the leaving groups bound to the catalyst compound in that they are not highly susceptible to substitution/abstraction reactions.

[0063] In one aspect of the invention, the one or more metallocene catalyst components of the invention are represented by the formula (I):

$$Cp^ACp^BMX_n \qquad (I)$$

wherein M is as described above; each X is chemically bonded to M; each Cp group is chemically bonded to M; and n is an integer from 0 to 4, and either 1 or 2 in a particular embodiment.

[0064] The ligands represented by Cp^A and Cp^B in formula (I) may be the same or different cyclopentadienyl ligands or ligands isolobal to cyclopentadienyl, either or both of which may contain heteroatoms and either or both of which may be substituted by a group R. In one embodiment, Cp^A and Cp^B are independently selected from the group consisting of the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, and substituted derivatives of each.

[0065] Independently, each Cp^A and Cp^B of formula (I) may be unsubstituted or substituted with any one or combination of substituent groups R. Non-limiting examples of substituent groups R as used in structure (I) as well as ring substituents in structures (Va-d) include groups selected from the group consisting of hydrogen radicals, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, and combinations thereof.

[0066] More particular non-limiting examples of alkyl substituents R associated with formula (I) through (V) include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl, phenyl, methylphenyl, and tert-butylphenyl groups and the like, including all their isomers, for example tertiary-butyl, isopropyl, and the like. Other possible radicals include substituted alkyls and aryls such as, for example, fluoromethyl, fluroethyl, difluroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted Group 15 radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, Group 16 radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide.

Other substituents R include olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example 3-butenyl, 2-propenyl, 5-hexenyl and the like. In one embodiment, at least two R groups, two adjacent R groups in one embodiment, are joined to form a ring structure having from 3 to 30 atoms selected from the group consisting of carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron and combinations thereof. Also, a substituent group R group such as 1-butanyl may form a bonding association to the element M.

[0067] At least one X in the formula (I) above and for the formulas/structures (II) through (V) below is independently selected from the group consisting of fluoride ions, fluorinated C_6 to C_{24} aryls, C_7 to C_{25} alkylaryls and fluorinated C_1 to C_{12} alkyls, wherein "fluorinated" means at least one, and up to 100% of the hydrogen atoms of the group are replaced by fluorine atoms, and from 50 to 100% of the hydrogen atoms in a particular embodiment; selected independently from fluoride ions, methyl, ethyl, propyl, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls) in yet a more particular embodiment; and are fluoride ions in yet a more particular embodiment. In a particular embodiment, all X groups on the metallocene are fluorine or fluorine containing groups as described, and in yet a more particular embodiment, all of the X groups on the metallocene useful in the invention are fluorine ions.

[0068] Non-limiting examples of other X groups include alkyls, amines, phosphines, ethers, carboxylates, dienes, hydrocarbon radicals having from 1 to 20 carbon atoms; fluorinated hydrocarbon radicals (*e.g.*, $-C_6F_5$ (pentafluorophenyl)), fluorinated alkylcarboxylates (*e.g.*, $CF_3C(O)O^-$), hydrides and halogen ions and combinations thereof. Other examples of X ligands include alkyl groups such as cyclobutyl, cyclohexyl, methyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylidene, methyoxy, ethyoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like. In one embodiment, two or more X's form a part of a fused ring or ring system.

[0069] In another aspect of the invention, the metallocene catalyst component includes those of formula (I) where Cp^A and Cp^B are bridged to each other by at least one bridging group, (A), such that the structure is represented by formula (II):

$$Cp^A(A)Cp^BMX_n \qquad (II)$$

[0070] These bridged compounds represented by formula (II) are known as "bridged metallocenes". Cp^A, Cp^B, M, X and n in structure (II) are as defined above for formula (I); and wherein each Cp ligand is chemically bonded to M, and (A) is chemically bonded to each Cp. Non-limiting examples of bridging group (A) include divalent hydrocarbon groups containing at least one Group 13 to 16 atom, such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom and combinations thereof; wherein the heteroatom may also be C_1 to C_{12} alkyl or aryl substituted to satisfy neutral valency. The bridging group (A) may also contain substituent groups R as defined above (for formula (I)) including halogen radicals and iron. More particular non-limiting examples of bridging group (A) are represented by C_1 to C_6 alkylenes, substituted C_1 to C_6 alkylenes, oxygen, sulfur, $R'_2C=$, $R'_2Si=$, $-Si(R')_2Si(R'_2)-$, $R'_2Ge=$, $R'P=$ (wherein "=" represents two chemical bonds), where R' is independently selected from the group consisting of hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 atoms, substituted Group 16 atoms, and halogen radical; and wherein two or more R' may be joined to form a ring or ring system. In one embodiment, the bridged metallocene catalyst component of formula (II) has two or more bridging groups (A).

[0071] Other non-limiting examples of bridging group (A) include methylene, ethylene, ethylidene, propylidene, isopropylidene, diphenylmethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylsilyl, diethylsilyl, methyl-ethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di(n-butyl)silyl, di(n-propyl)silyl, di(i-propyl)silyl, di(n-hexyl)silyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di(t-butylphenyl)silyl, di(p-tolyl)silyl and the corresponding moieties wherein the Si atom is replaced by a Ge or a C atom; dimethylsilyl, diethylsilyl, dimethylgermyl and diethylgermyl.

[0072] In another embodiment, bridging group (A) may also be cyclic, comprising, for example 4 to 10, 5 to 7 ring members in a more particular embodiment. The ring members may be selected from the elements mentioned above, from one or more of B, C, Si, Ge, N and O in a particular embodiment. Non-limiting examples of ring structures which may be present as or part of the bridging moiety are cyclobutylidene, cyclopentylidene, cyclohexylidene, cycloheptylidene, cyclooctylidene and the corresponding rings where one or two carbon atoms are replaced by at least one of Si, Ge, N and O, in particular, Si and Ge. The bonding arrangement between the ring and the Cp groups may be either cis-, trans-, or a combination.

[0073] The cyclic bridging groups (A) may be saturated or unsaturated and/or carry one or more substituents and/or be fused to one or more other ring structures. If present, the one or more substituents are selected from the group consisting of hydrocarbyl (*e.g.*, alkyl such as methyl) and halogen (*e.g.*, F, Cl) in one embodiment. The one or more Cp groups which the above cyclic bridging moieties may optionally be fused to may be saturated or unsaturated and are selected from the group consisting of those having 4 to 10, more particularly 5, 6 or 7 ring members (selected from the group consisting of C, N, O and S in a particular embodiment) such as, for example, cyclopentyl, cyclohexyl and phenyl. Moreover, these ring structures may themselves be fused such as, for example, in the case of a naphthyl group. Moreover, these (optionally fused) ring structures may carry one or more substituents. Illustrative, non-limiting examples of these substituents are hydrocarbyl (particularly alkyl) groups and halogen atoms.

[0074] The ligands Cp^A and Cp^B of formulae (I) and (II) are different from each other in one embodiment, and the same in another embodiment.

[0075] In yet another aspect of the invention, the metallocene catalyst components include bridged mono-ligand metallocene compounds (*e.g.*, mono cyclopentadienyl catalyst components). In this embodiment, the at least one metallocene catalyst component is a bridged "half-sandwich" metallocene represented by the formula (III):

$$Cp^A(A)QMX_n \qquad (III)$$

wherein Cp^A is defined above and is bound to M; (A) is a bridging group bonded to Q and Cp^A; and wherein an atom from the Q group is bonded to M; and n is an integer 0, 1 or 2. In formula (III) above, Cp^A, (A) and Q may form a fused ring system. The X groups and n of formula (III) are as defined above in formula (I) and (II). In one embodiment, Cp^A is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted versions thereof, and combinations thereof.

[0076] In formula (III), Q is a heteroatom-containing ligand in which the bonding atom (the atom that is bonded with the metal M) is selected from the group consisting of Group 15 atoms and Group 16 atoms in one embodiment, and selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur atom in a more particular embodiment, and nitrogen and oxygen in yet a more particular embodiment. Non-limiting examples of Q groups include alkylamines, arylamines, mercapto compounds, ethoxy compounds, carboxylates (*e.g.*, pivalate), carbamates, azenyl, azulene, pentalene, phosphoyl, phosphinimine, pyrrolyl, pyrozolyl, carbazolyl, borabenzene other compounds comprising Group 15 and Group 16 atoms capable of bonding with M.

[0077] In yet another aspect of the invention, the at least one metallocene catalyst component is an unbridged "half sandwich" metallocene represented by the formula (IVa):

$$Cp^AMQ_qX_n \qquad \text{(IVa)}$$

wherein Cp^A is defined as for the Cp groups in (I) and is a ligand that is bonded to M; each Q is independently bonded to M; X is a leaving group as described above in (I); n ranges from 0 to 3, and is 0 or 3 in one embodiment; q ranges from 0 to 3, and is 0 or 3 in one embodiment. In one embodiment, Cp^A is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted version thereof, and combinations thereof.

[0078] In formula (IVa), Q is selected from the group consisting of ROO^-, RO–, R(O)–, –NR–, $-CR_2-$, –S–, $-NR_2$, $-CR_3$, –SR, $-SiR_3$, $-PR_2$, –H, and substituted and unsubstituted aryl groups, wherein R is selected from the group consisting of C_1 to C_6 alkyls, C_6 to C_{12} aryls, C_1 to C_6 alkylamines, C_6 to C_{12} alkylarylamines, C_1 to C_6 alkoxys, C_6 to C_{12} aryloxys, and the

like. Non-limiting examples of Q include C_1 to C_{12} carbamates, C_1 to C_{12} carboxylates (*e.g.*, pivalate), C_2 to C_{20} allyls, and C_2 to C_{20} heteroallyl moieties.

[0079] Described another way, the "half sandwich" metallocenes above can be described as in formula (IVb), such as described in, for example, US 6,069,213:

$$Cp^AM(Q_2GZ)X_n \quad \text{or} \quad T(Cp^AM(Q_2GZ)X_n)_m \qquad \text{(IVb)}$$

wherein M, Cp^A, X and n are as defined above;

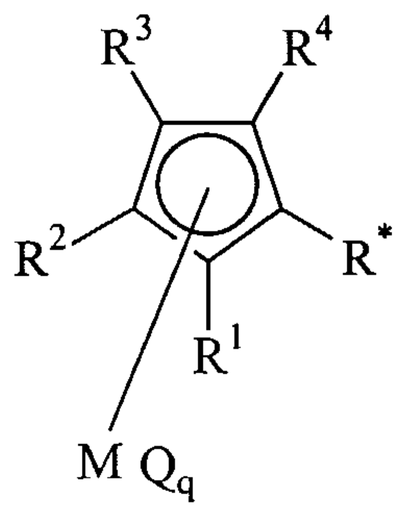
Q_2GZ forms a polydentate ligand unit (*e.g.*, pivalate), wherein at least one of the Q groups form a bond with M, and is defined such that each Q is independently selected from the group consisting of –O–, –NR–, $–CR_2—$ and –S–; G is either carbon or silicon; and Z is selected from the group consisting of R, –OR, $–NR_2$, $–CR_3$, –SR, $–SiR_3$, $–PR_2$, and hydride, providing that when Q is –NR–, then Z is selected from the group consisting of –OR, $–NR_2$, –SR, $–SiR_3$, $–PR_2$; and provided that neutral valency for Q is satisfied by Z; and wherein each R is independently selected from the group consisting of C_1 to C_{10} heteroatom containing groups, C_1 to C_{10} alkyls, C_6 to C_{12} aryls, C_6 to C_{12} alkylaryls, C_1 to C_{10} alkoxys, and C_6 to C_{12} aryloxys;

n is 1 or 2 in a particular embodiment; and

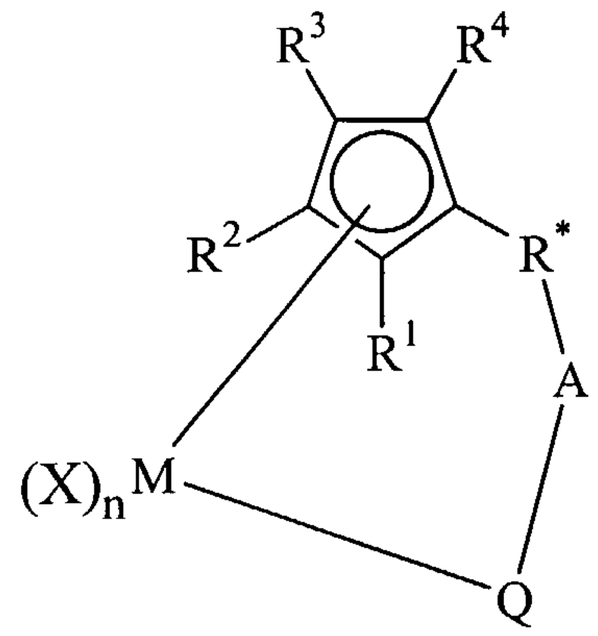
T is a bridging group selected from the group consisting of C_1 to C_{10} alkylenes, C_6 to C_{12} arylenes and C_1 to C_{10} heteroatom containing groups, and C_6 to C_{12} heterocyclic groups; wherein each T group bridges adjacent "$Cp^AM(Q_2GZ)X_n$" groups, and is chemically bonded to the Cp^A groups.

m is an integer from 1 to 7; m is an integer from 2 to 6 in a more particular embodiment.

[0080] In another aspect of the invention, the at least one fluorided metallocene catalyst component can be described more particularly in structures (Va), (Vb), (Vc) and (Vd):

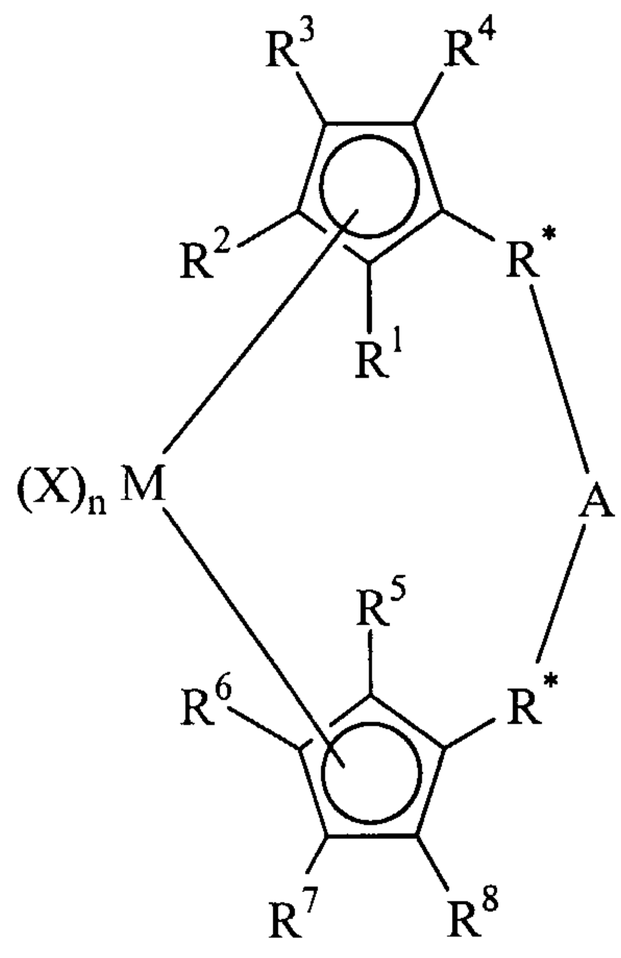


(Va-i)

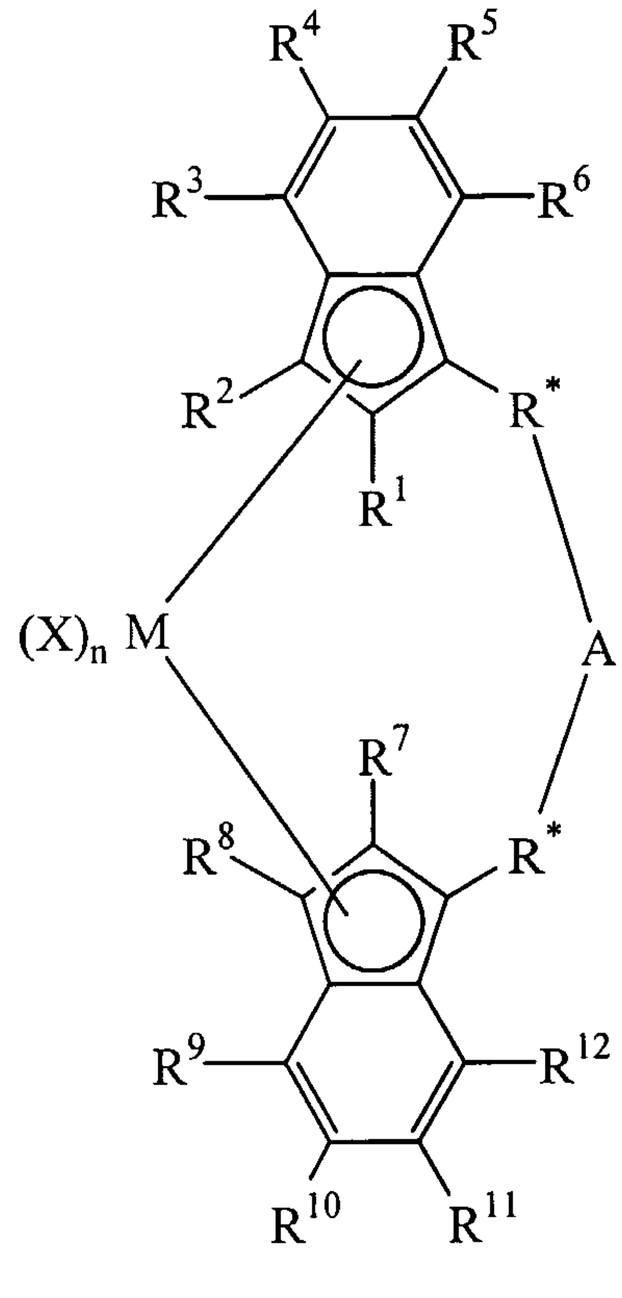


(Va-ii)

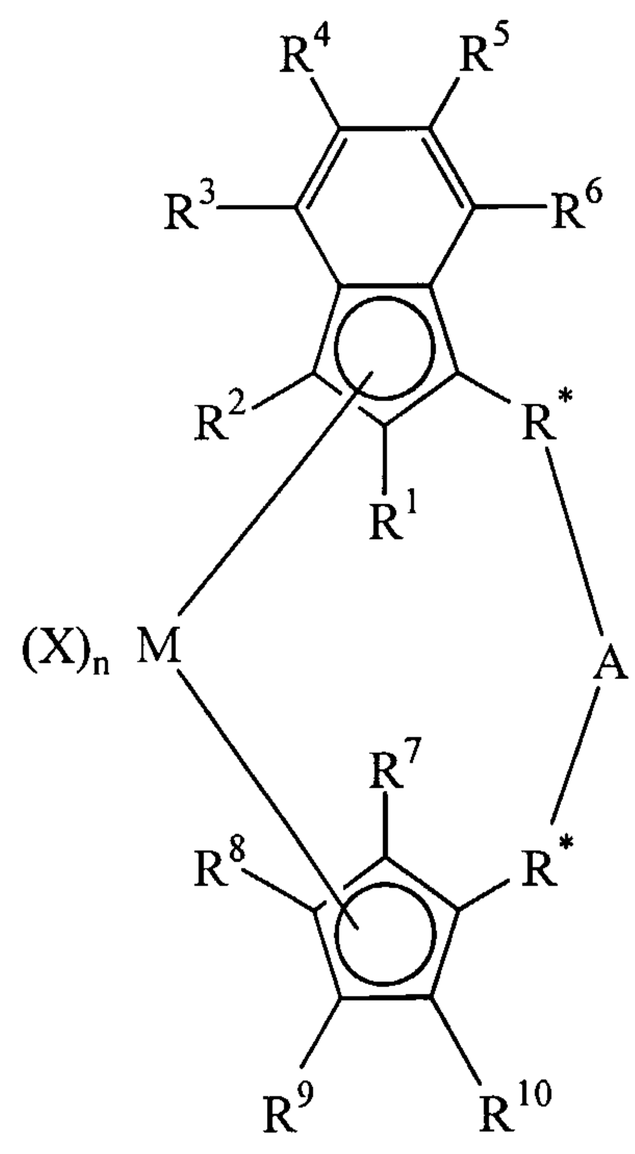
5



(Vb)



(Vc)



(Vd)

wherein in structures (Va) to (Vd) M is selected from the group consisting of Group 3 to Group 12 atoms, and selected from the group consisting of Group 3 to Group 10 atoms in a more particular embodiment, and selected from the group consisting of Group 3 to

Group 6 atoms in yet a more particular embodiment, and selected from the group consisting of Group 4 atoms in yet a more particular embodiment, and selected from the group consisting of Zr and Hf in yet a more particular embodiment; and is Zr in yet a more particular embodiment;

wherein Q in (Va-i) and (Va-ii) is selected from the group consisting of halogen ions, alkyls, alkylenes, aryls, arylenes, alkoxys, aryloxys, amines, alkylamines, phosphines, alkylphosphines, substituted alkyls, substituted aryls, substituted alkoxys, substituted aryloxys, substituted amines, substituted alkylamines, substituted phosphines, substituted alkylphosphines, carbamates, heteroallyls, carboxylates (non-limiting examples of suitable carbamates and carboxylates include trimethylacetate, trimethylacetate, methylacetate, p-toluate, benzoate, diethylcarbamate, and dimethylcarbamate), fluorinated alkyls, fluorinated aryls, and fluorinated alkylcarboxylates;

q is an integer ranging from 1 to 3;

wherein each R^* is independently: selected from the group consisting of hydrocarbyls and heteroatom-containing hydrocarbyls in one embodiment; and selected from the group consisting of alkylenes, substituted alkylenes and heteroatom-containing hydrocarbyls in another embodiment; and selected from the group consisting of C_1 to C_{12} alkylenes, C_1 to C_{12} substituted alkylenes, and C_1 to C_{12} heteroatom-containing hydrocarbons in a more particular embodiment; and selected from the group consisting of C_1 to C_4 alkylenes in yet a more particular embodiment; and wherein both R* groups are identical in another embodiment in structures (Vb-d);

A is as described above for (A) in structure (II), and more particularly, selected from the group consisting of –O–, –S–, $–SO_2–$, –NR–, $=SiR_2$, $=GeR_2$, $=SnR_2$, $—R_2SiSiR_2—$, RP=, C_1 to C_{12} alkylenes, substituted C_1 to C_{12} alkylenes, divalent C_4 to C_{12} cyclic hydrocarbons and substituted and unsubstituted aryl groups in one embodiment; and selected from the group consisting of C_5 to C_8 cyclic hydrocarbons, $–CH_2CH_2–$, $=CR_2$ and $=SiR_2$ in a more particular embodiment; wherein and R is selected from the group consisting of

alkyls, cycloalkyls, aryls, alkoxys, fluoroalkyls and heteroatom-containing hydrocarbons in one embodiment; and R is selected from the group consisting of C_1 to C_6 alkyls, substituted phenyls, phenyl, and C_1 to C_6 alkoxys in a more particular embodiment; and R is selected from the group consisting of methoxy, methyl, phenoxy, and phenyl in yet a more particular embodiment;

wherein *A* may be absent in yet another embodiment, in which case each R* is defined as for R^1-R^{12};

each X is as described above in (I);

n is an integer from 0 to 4, and from 1 to 3 in another embodiment, and 1 or 2 in yet another embodiment; and

R^1 through R^{12} are independently: selected from the group consisting of hydrogen radical, halogen radicals, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, and C_1 to C_{12} heteroatom-containing hydrocarbons and substituted derivatives thereof in one embodiment; selected from the group consisting of hydrogen radical, fluorine radical, chlorine radical, bromine radical, C_1 to C_6 alkyls, C_2 to C_6 alkenyls, C_7 to C_{18} alkylaryls, C_1 to C_6 fluoroalkyls, C_2 to C_6 fluoroalkenyls, C_7 to C_{18} fluoroalkylaryls in a more particular embodiment; and hydrogen radical, fluorine radical, chlorine radical, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, hexyl, phenyl, 2,6-di-methylpheyl, and 4-tertiarybutylpheyl groups in yet a more particular embodiment; wherein adjacent R groups may form a ring, either saturated, partially saturated, or completely saturated.

[0081] The structure of the metallocene catalyst component represented by (Va) may take on many forms such as disclosed in, for example, US 5,026,798, US 5,703,187, and US 5,747,406, including a dimer or oligomeric structure, such as disclosed in, for example, US 5,026,798 and US 6,069,213.

[0082] In a particular embodiment of the metallocene represented in (Vd), R^1 and R^2 form a conjugated 6-membered carbon ring system that may or may not be substituted.

[0083] Non-limiting examples of metallocene catalyst components consistent with the description herein include:

cyclopentadienylzirconium X_n,
indenylzirconium X_n,
(1-methylindenyl)zirconium X_n,
(2-methylindenyl)zirconium X_n,
(1-propylindenyl)zirconium X_n,
(2-propylindenyl)zirconium X_n,
(1-butylindenyl)zirconium X_n,
(2-butylindenyl)zirconium X_n,
(methylcyclopentadienyl)zirconium X_n,
tetrahydroindenylzirconium X_n,
(pentamethylcyclopentadienyl)zirconium X_n,
cyclopentadienylzirconium X_n,
pentamethylcyclopentadienyltitanium X_n,
tetramethylcyclopentyltitanium X_n,
1,2,4-trimethylcyclopentadienylzirconium X_n,
dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium X_n,
dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2,3-trimethyl-cyclopentadienyl)zirconium X_n,
dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2-dimethyl-cyclopentadienyl)zirconium X_n,
dimethylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(2-methylcyclopentadienyl)zirconium X_n,
dimethylsilyl(cyclopentadienyl)(indenyl)zirconium X_n,
dimethylsilyl(2-methylindenyl)(fluorenyl)zirconium X_n,
diphenylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(3-propylcyclopentadienyl)zirconium X_n,
dimethylsilyl (1,2,3,4-tetramethylcyclopentadienyl) (3-t-butylcyclopentadienyl)zirconium X_n,
dimethylgermyl(1,2-dimethylcyclopentadienyl)(3-isopropylcyclopentadienyl)zirconium X_n,
dimethylsilyl(1,2,3,4-tetramethyl-cyclopentadienyl)(3-methylcyclopentadienyl) zirconium X_n,
diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium X_n,
diphenylmethylidene(cyclopentadienyl)(indenyl)zirconium X_n,
iso-propylidenebis(cyclopentadienyl)zirconium X_n,
iso-propylidene(cyclopentadienyl)(9-fluorenyl)zirconium X_n,
iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium X_n,
ethylenebis(9-fluorenyl)zirconium X_n,
meso-ethylenebis(1-indenyl)zirconium X_n,
ethylenebis(1-indenyl)zirconium X_n,
ethylenebis(2-methyl-1-indenyl)zirconium X_n,
ethylenebis(2-methyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
ethylenebis(2-propyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
ethylenebis(2-isopropyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,

ethylenebis(2-butyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
ethylenebis(2-isobutyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
dimethylsilyl(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
diphenyl(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n,
dimethylsilylbis(cyclopentadienyl)zirconium X_n,
dimethylsilylbis(9-fluorenyl)zirconium X_n,
dimethylsilylbis(1-indenyl)zirconium X_n,
dimethylsilylbis(2-methylindenyl)zirconium X_n,
dimethylsilylbis(2-propylindenyl)zirconium X_n,
dimethylsilylbis(2-butylindenyl)zirconium X_n,
diphenylsilylbis(2-methylindenyl)zirconium X_n,
diphenylsilylbis(2-propylindenyl)zirconium X_n,
diphenylsilylbis(2-butylindenyl)zirconium X_n,
dimethylgermylbis(2-methylindenyl)zirconium X_n
dimethylsilylbis(tetrahydroindenyl)zirconium X_n,
dimethylsilylbis(tetramethylcyclopentadienyl)zirconium X_n,
dimethylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium X_n,
diphenylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium X_n,
diphenylsilylbis(indenyl)zirconium X_n,
cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium X_n,
cyclotetramethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl) zirconium X_n,
cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(2-methylindenyl)zirconium X_n,
cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(3-methylcyclopentadienyl)zirconium X_n,
cyclotrimethylenesilylbis(2-methylindenyl)zirconium X_n,
cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(2,3,5-
trimethylcyclopentadienyl)zirconium X_n,
cyclotrimethylenesilylbis(tetramethylcyclopentadienyl)zirconium X_n,
dimethylsilyl(tetramethylcyclopentadieneyl)(N-tert-butylamido)titanium X_n,
bis(cyclopentadienyl)chromium X_n,
bis(cyclopentadienyl)zirconium X_n,
bis(n-butylcyclopentadienyl)zirconium X_n,
bis(n-dodecyclcyclopentadienyl)zirconium X_n,
bis(ethylcyclopentadienyl)zirconium X_n,
bis(iso-butylcyclopentadienyl)zirconium X_n,
bis(iso-propylcyclopentadienyl)zirconium X_n,
bis(methylcyclopentadienyl)zirconium X_n,
bis(n-oxtylcyclopentadienyl)zirconium X_n,
bis(n-pentylcyclopentadienyl)zirconium X_n,
bis(n-propylcyclopentadienyl)zirconium X_n,
bis(trimethylsilylcyclopentadienyl)zirconium X_n,
bis(1,3-bis(trimethylsilyl)cyclopentadienyl)zirconium X_n,
bis(1-ethyl-2-methylcyclopentadienyl)zirconium X_n,
bis(1-ethyl-3-methylcyclopentadienyl)zirconium X_n,
bis(pentamethylcyclopentadienyl)zirconium X_n,
bis(pentamethylcyclopentadienyl)zirconium X_n,
bis(1-propyl-3-methylcyclopentadienyl)zirconium X_n,
bis(1-n-butyl-3-methylcyclopentadienyl)zirconium X_n,

bis(1-isobutyl-3-methylcyclopentadienyl)zirconium X_n,
bis(1-propyl-3-butylcyclopentadienyl)zirconium X_n,
bis(1,3-n-butylcyclopentadienyl)zirconium X_n,
bis(4,7-dimethylindenyl)zirconium X_n,
bis(indenyl)zirconium X_n,
bis(2-methylindenyl)zirconium X_n,
cyclopentadienylindenylzirconium X_n,
bis(n-propylcyclopentadienyl)hafnium X_n,
bis(n-butylcyclopentadienyl)hafnium X_n,
bis(n-pentylcyclopentadienyl)hafnium X_n,
(n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl)hafnium X_n,
bis[(2-trimethylsilylethyl)cyclopentadienyl]hafnium X_n,
bis(trimethylsilyl cyclopentadienyl)hafnium X_n,
bis(2-n-propylindenyl)hafnium X_n,
bis(2-n-butylindenyl)hafnium X_n,
dimethylsilylbis(n-propylcyclopentadienyl)hafnium X_n,
dimethylsilylbis(n-butylcyclopentadienyl)hafnium X_n,
bis(9-n-propylfluorenyl)hafnium X_n,
bis(9-n-butylfluorenyl)hafnium X_n,
(9-n-propylfluorenyl)(2-n-propylindenyl)hafnium X_n,
bis(1-n-propyl-2-methylcyclopentadienyl)hafnium X_n,
(n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)hafnium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n,
dimethylsilyl(tetramethyleyclopentadienyl)(cyclobutylamido)titanium X_n,
dimethylsilyl(tetramethyleyclopentadienyl)(cyclopentylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium X_n,
dimethylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium, X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium X_n,

methylphenylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium X_n,
methylphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n,
diphenylsilyl(tetramethyleyclopentadienyl)(n-octylamido)titanium X_n,
diphenylsilyl(tetramethyleyclopentadienyl)(n-decylamido)titanium X_n,
diphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n, and derivatives thereof.

[0084] Wherein the value of n is 1, 2 or 3, and at least one X is a fluoride ion. By "derivatives thereof", it is meant any substitution or ring formation as described above for structures (Va-d) in one embodiment; and in particular, replacement of the metal "M" (Cr, Zr, Ti or Hf) with an atom selected from the group consisting of Cr, Zr, Hf and Ti; and replacement of the "X" group with any of C_1 to C_5 alkyls, C_6 aryls, C_6 to C_{10} alkylaryls, fluorine, chlorine, or bromine. In a particular embodiment, each of the above metallocenes is a fluorided metallocene wherein one or more of the X groups is a fluoride; and all X groups are fluorides in yet a more particular embodiment.

[0085] More particularly, non-limiting examples of the fluorided catalyst components useful in the method of the invention are as follows:

Bis(methylcyclopentadienyl)zirconium difluoride,
Bis(ethylcyclopentadienyl)zirconium difluoride,
Bis(propylcyclopentadienyl)zirconium difluoride,
Bis(isopropylcyclopentadienyl)zirconium difluoride,
Bis(butylcyclopentadienyl)zirconium difluoride,
Bis(isobutylcyclopentadienyl)zirconium difluoride,
Bis(neopentylcyclopentadienyl)zirconium difluoride,
Bis(cyclopentylcyclopentadienyl)zirconium difluoride,
Bis(cyclohexylmethylcyclopentadienyl)zirconium difluoride,
Bis(allylcyclopentadienyl)zirconium difluoride,
Bis((3-butenyl)cyclopentadienyl)zirconium difluoride,
Bis(trimethylsilylcyclopentadienyl)zirconium difluoride,

Bis(trimethylgermylcyclopentadienyl)zirconium difluoride,
Bis(trimethylsilylmethylcyclopentadienyl)zirconium difluoride,
Bis(1,2-dimethylcyclopentadienyl)zirconium difluoride,
Bis(1,3-dimethylcyclopentadienyl)zirconium difluoride,
Bis(1,2,3-trimethylcyclopentadienyl)zirconium difluoride,
Bis(1,2,4-trimethylcyclopentadienyl)zirconium difluoride,
Bis(tetramethylcyclopentadienyl)zirconium difluoride,
Bis(1,3-methylethylcyclopentadienyl)zirconium difluoride,
Bis(1,3-methylpropylcyclopentadienyl)zirconium difluoride,
Bis(1,3-methylbutylcyclopentadienyl)zirconium difluoride,
Bis(phenylcyclopentadienyl)zirconium difluoride,
Bis(1,3-methylphenylcyclopentadienyl)zirconium difluoride,
Bis(benzylcyclopentadienyl)zirconium difluoride,
Bis(1,3-methylbenzylcyclopentadienyl)zirconium difluoride,
Bis(phenethylcyclopentadienyl)zirconium difluoride,
Bis((3-phenylpropyl)cyclopentadienyl)zirconium difluoride,
(Tetramethylcylopentadienyl)(propylcyclopentadienyl)zirconium difluoride,
(Pentamethylcylopentadienyl)(propylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(propylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(butylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(cyclopentylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl (tetrahydroindenyl)zirconium difluoride,
Cyclopentadienyl(1,3-methylbutylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(tetramethylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(propyltetramethylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(butyltetramethylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(cyclopentyltetramethylcyclopentadienyl)zirconium difluoride,
Cyclopentadienyl(indenyl)zirconium difluoride,
Cyclopentadienyl(1-methylindenyl)zirconium difluoride,
Cyclopentadienyl(fluorenyl)zirconium difluoride,
Cyclopentadienyl(tetrahydrofluorenyl)zirconium difluoride,
Cyclopentadienyl(octahydrofluorenyl)zirconium difluoride,
Bis(tetrahydroindenyl)zirconium difluoride,
Bis(trihydropentalenyl)zirconium difluoride,
Bis(pentahydroazulenyl)zirconium difluoride,
Dimethylsilylbis(tetrahydroindenyl)zirconium difluoride,
Ethylenebis(tetrahydroindenyl)zirconium difluoride,
Bis(indenyl)zirconium difluoride,
Bis(1-methylindenyl)zirconium difluoride,
Bis(2-methylindenyl)zirconium difluoride,
Bis(4,7-dimethylindenyl)zirconium difluoride,
Bis(5,6-dimethylindenyl)zirconium difluoride,
Bis(1-phenylindenyl)zirconium difluoride,
Bis(2-phenylindenyl)zirconium difluoride,
Bis(fluorenyl)zirconium difluoride,
Bis(1-methylfluorenyl)zirconium difluoride,
Bis(2,7-di-t-butylfluorenyl)zirconium difluoride,
Dimethylsilylbis(3-methylcyclopentadienyl)zirconium difluoride,

Dimethylsilylbis(3-propylcyclopentadienyl)zirconium difluoride,
Dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconium difluoride,
Dimethylsilylbis(2,3,5-trimethylcyclopentadienyl)zirconium difluoride,
Dimethylsilylbis(tetramethylcyclopentadienyl)zirconium difluoride,
Dimethylsilylbis(indenyl)zirconium difluoride,
Dimethylsilylbis(2-methylindenyl)zirconium difluoride,
Dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium difluoride,
Dimethylsilylbis(2-methyl-4-(3,5-di-t-butyl)phenylindenyl)zirconium difluoride,
Dimethylsilylbis(2-methyl-4-naphthylindenyl)zirconium difluoride,
Dimethylsilyl(cyclopentadienyl)(indenyl)zirconium difluoride,
Dimethylsilyl(tetramethylcyclopentadienyl)(indenyl)zirconium difluoride,
Silacyclobutyl(tetramethylcyclopentadienyl)(indenyl)zirconium difluoride,
Silacyclopentyl(tetramethylcyclopentadienyl)(indenyl)zirconium difluoride,
Ethylenebis(indenyl)zirconium difluoride,
Ethylenebis(2-methylindenyl)zirconium difluoride,
Isopropylidene(cyclopentadienyl)(fluorenyl)zirconium difluoride,
Diphenylmethylidene(cyclopentadienyl)(fluorenyl)zirconium difluoride,
Dimethylsilyl(cyclopentadienyl)(fluorenyl)zirconium difluoride,
Diphenylsilyl(cyclopentadienyl)(fluorenyl)zirconium difluoride,
Dimethylsilylbis(fluorenyl)zirconium difluoride,
Ethylenebis(fluorenyl)zirconium difluoride,
Bis(methylcyclopentadienyl)hafnium difluoride,
Bis(ethylcyclopentadienyl)hafnium difluoride,
Bis(propylcyclopentadienyl)hafnium difluoride,
Bis(butylcyclopentadienyl)hafnium difluoride,
Bis(isobutylcyclopentadienyl)hafnium difluoride,
Bis(neopentylcyclopentadienyl)hafnium difluoride,
Bis(cyclopentylcyclopentadienyl)hafnium difluoride,
Bis(allylcyclopentadienyl)hafnium difluoride,
Bis((3-butenyl)cyclopentadienyl)hafnium difluoride,
Bis(cyclohexylmethylcyclopentadienyl)hafnium difluoride,
Bis(trimethylsilylmethylcyclopentadienyl)hafnium difluoride,
Bis((3-phenylpropyl)cyclopentadienyl)hafnium difluoride,
Bis(1,3-methylbutylcyclopentadienyl)hafnium difluoride,
Bis(1,3-methylpropylcyclopentadienyl)hafnium difluoride,
Ethylenebis(indenyl)hafnium difluoride,
Dimethylsilylbis(3-propylcyclopentadienyl)hafnium difluoride,
Dimethylsilylbis(2,4-methylpropylcyclopentadienyl)hafnium difluoride,
Dimethylsilylbis(tetramethylcyclopentadienyl)hafnium difluoride,
Dimethylsilylbis(indenyl)hafnium difluoride,
Diphenylsilylbis(indenyl)hafnium difluoride,
Bis(cyclopentadienyl)titanium difluoride,
Bis(methylcyclopentadienyl)titanium difluoride,
Bis(ethylcyclopentadienyl)titanium difluoride,
Bis(propylcyclopentadienyl)titanium difluoride,
Bis(butylcyclopentadienyl)titanium difluoride,
Bis(isobutylcyclopentadienyl)titanium difluoride,
Bis(neopentylcyclopentadienyl)titanium difluoride,

Bis(cyclopentylcyclopentadienyl)titanium difluoride,
Ethylenebis(indenyl)titanium difluoride,
Dimethylsilylbis(indenyl)titanium difluoride,
Diphenylsilyl(cyclopentadienyl)(fluorenyl)titanium difluoride, (cyclopentadienyl)zirconium trifluoride,
(indenyl)zirconium trifluoride,
(1-methylindenyl)zirconium trifluoride,
(2-methylindenyl)zirconium trifluoride,
(1-propylindenyl)zirconium trifluoride,
(2-propylindenyl)zirconium trifluoride,
(1-butylindenyl)zirconium trifluoride,
(2-butylindenyl)zirconium trifluoride,
(methylcyclopentadienyl)zirconium trifluoride,
(tetrahydroindenyl)zirconium trifluoride,
(pentamethylcyclopentadienyl)zirconium trifluoride,
(cyclopentadienyl)zirconium trifluoride,
pentamethylcyclopentadienyltitanium trifluoride,
tetramethylcyclopentyldienyltitanium trifluoride,
1,2,4-trimethylcyclopentadienylzirconium trifluoride, and mixtures thereof.

[0086] It is contemplated that the metallocene catalysts components described above include their structural or optical or enantiomeric isomers (racemic mixture), and may be a pure enantiomer in one embodiment.

[0087] As used herein, a single, bridged, asymmetrically substituted metallocene catalyst component having a racemic and/or meso isomer does not, itself, constitute at least two different bridged, metallocene catalyst components.

[0088] The "metallocene catalyst component" useful in the present invention may comprise any combination of any "embodiment" described herein.

[0089] When combined to form the bimetallic catalyst component, the molar ratio of metal from the first catalyst component to the second catalyst component (*e.g.*, molar ratio of Ti:Zr) is a value of from 0.1 to 20 in one embodiment; and from 1 to 18 in another embodiment, and from 2 to 15 in yet another embodiment, and from 3 to 12 in yet another embodiment; and from 4 to 10 in yet another embodiment, and from 4 to 8 in yet another embodiment; wherein a desirable molar ratio of first catalyst component metal:second catalyst component metal is any combination of any upper limit with any lower limit described herein.

Activator

[0090] As used herein, the term "activator" is defined to be any compound or combination of compounds, supported or unsupported, which can activate a catalyst compound (*e.g.*, Ziegler-Natta, metallocenes, Group 15-containing catalysts, etc.), such as by creating a cationic species from the catalyst component. Typically, this involves the abstraction of at least one leaving group (X group in the formulas/structures above) from the metal center of the catalyst component. The catalyst components of the present invention are thus activated towards olefin polymerization using such activators. Embodiments of such activators include Lewis acids such as cyclic or oligomeric poly(hydrocarbylaluminum oxides), alkylaluminum compounds and so called non-coordinating ionic activators ("NCA") (alternately, "ionizing activators" or "stoichiometric activators"), or any other compound that can convert a neutral metallocene catalyst component to a metallocene cation that is active with respect to olefin polymerization.

[0091] More particularly, it is within the scope of this invention to use Lewis acids such as alumoxane (*e.g.*, "MAO"), modified alumoxane (*e.g.*, "TIBAO"), and alkylaluminum compounds as activators, and/or ionizing activators (neutral or ionic) such as tri (n-butyl)ammonium tetrakis(pentafluorophenyl)boron and/or a trisperfluorophenyl boron metalloid precursors to activate desirable metallocenes described herein. MAO and other aluminum-based activators are well known in the art. Ionizing activators are well known in the art and are described by, for example, Eugene You-Xian Chen & Tobin J. Marks, *Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure-Activity Relationships* 100(4) CHEMICAL REVIEWS 1391-1434 (2000). The activators may be associated with or bound to a support, either in association with the catalyst component (*e.g.*, metallocene) or separate from the catalyst component, such as described by Gregory G. Hlatky, *Heterogeneous Single-Site Catalysts for Olefin Polymerization* 100(4) CHEMICAL REVIEWS 1347-1374 (2000).

[0092] Non-limiting examples of aluminum alkyl compounds which may be utilized as activators for the catalyst precursor compounds for use in the methods of the present invention

include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

[0093] Examples of neutral ionizing activators include Group 13 tri-substituted compounds, in particular, tri-substituted boron, tellurium, aluminum, gallium and indium compounds, and mixtures thereof. The three substituent groups are each independently selected from the group consisting of alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. In one embodiment, the three groups are independently selected from the group consisting of halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof. In another embodiment, the three groups are selected from the group consisting of alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls), and combinations thereof. In yet another embodiment, the three groups are selected from the group consisting of alkyls having 1 to 4 carbon groups, phenyl, naphthyl and mixtures thereof. In yet another embodiment, the three groups are selected from the group consisting of highly halogenated alkyls having 1 to 4 carbon groups, highly halogenated phenyls, and highly halogenated naphthyls and mixtures thereof By "highly halogenated", it is meant that at least 50% of the hydrogens are replaced by a halogen group selected from the group consisting of fluorine, chlorine and bromine. In yet another embodiment, the neutral stoichiometric activator is a tri-substituted Group 13 compound comprising highly fluorided aryl groups, the groups being highly fluorided phenyl and highly fluorided naphthyl groups.

[0094] In another embodiment, the neutral tri-substituted Group 13 compounds are boron compounds such as a trisperfluorophenyl boron, trisperfluoronaphthyl boron, tris(3,5-di(trifluoromethyl)phenyl)boron, tris(di-t-butylmethylsilyl)perfluorophenylboron, and other highly fluorinated trisarylboron compounds and combinations thereof, and their aluminum equivalents. Other suitable neutral ionizing activators are described in US 6,399,532 B1, US 6,268,445 B1, and in 19 ORGANOMETALLICS 3332-3337 (2000), and in 17 ORGANOMETALLICS 3996-4003 (1998).

[0095] Illustrative, not limiting examples of ionic ionizing activators include trialkyl-substituted ammonium salts such as triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-trifluoromethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like; dialkyl ammonium salts such as di-(isopropyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron and the like; and triaryl phosphonium salts such as triphenylphosphonium tetra(phenyl)boron, tri(methylphenyl)phosphonium tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like, and their aluminum equivalents.

[0096] In yet another embodiment of the activator of the invention, an alkylaluminum can be used in conjunction with a heterocyclic compound. The ring of the heterocyclic compound may includes at least one nitrogen, oxygen, and/or sulfur atom, and includes at least one nitrogen atom in one embodiment. The heterocyclic compound includes 4 or more ring members in one embodiment, and 5 or more ring members in another embodiment.

[0097] The heterocyclic compound for use as an activator with an alkylaluminum may be unsubstituted or substituted with one or a combination of substituent groups. Examples of suitable substituents include halogen, alkyl, alkenyl or alkynyl radicals, cycloalkyl radicals, aryl radicals, aryl substituted alkyl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or any combination thereof. The substituents groups may also be substituted with halogens, particularly fluorine or bromine, or heteroatoms or the like.

[0098] Non-limiting examples of hydrocarbon substituents include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other examples of substituents include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl or chlorobenzyl.

[0100] In one embodiment, the heterocyclic compound is unsubstituted. In another embodiment one or more positions on the heterocyclic compound are substituted with a halogen atom or a halogen atom containing group, for example a halogenated aryl group. In one embodiment the halogen is selected from the group consisting of chlorine, bromine and fluorine, and selected from the group consisting of fluorine and bromine in another embodiment, and the halogen is fluorine in yet another embodiment.

[0101] Non-limiting examples of heterocyclic compounds utilized in the activator of the invention include substituted and unsubstituted pyrroles, imidazoles, pyrazoles, pyrrolines, pyrrolidines, purines, carbazoles, and indoles, phenyl indoles, 2,5,-dimethylpyrroles, 3-pentafluorophenylpyrrole, 4,5,6,7-tetrafluoroindole or 3,4-difluoropyrroles.

[0102] In one embodiment, the heterocyclic compound described above is combined with an alkyl aluminum or an alumoxane to yield an activator compound which, upon reaction with a catalyst component, for example a metallocene, produces an active polymerization catalyst. Non-limiting examples of alkylaluminums include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-iso-octylaluminum, triphenylaluminum, and combinations thereof.

[0103] Other activators include those described in WO 98/07515 such as tris (2, 2', 2"-nonafluorobiphenyl) fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations. Other activators include aluminum/boron complexes, perchlorates, periodates and iodates including their hydrates; lithium (2,2'-bisphenyl-ditrimethylsilicate)·4THF; silylium salts in combination with a non-coordinating compatible anion. Also, methods of activation such as using radiation, electro-chemical oxidation, and the like are also contemplated as activating methods for the

purposes of rendering the neutral metallocene-type catalyst compound or precursor to a metallocene-type cation capable of polymerizing olefins. Other activators or methods for activating a metallocene-type catalyst compound are described in for example, US 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775.

[0104] In general, the activator and catalyst component(s) are combined in mole ratios of activator to catalyst component from 1000:1 to 0.1:1 in one embodiment, and from 300:1 to 1:1 in a more particular embodiment, and from 150:1 to 1:1 in yet a more particular embodiment, and from 50:1 to 1:1 in yet a more particular embodiment, and from 10:1 to 0.5:1 in yet a more particular embodiment, and from 3:1 to 0.3:1 in yet a more particular embodiment, wherein a desirable range may include any combination of any upper mole ratio limit with any lower mole ratio limit described herein. When the activator is a cyclic or oligomeric poly(hydrocarbylaluminum oxide) (*e.g.*, "MAO"), the mole ratio of activator to catalyst component ranges from 2:1 to 100,000:1 in one embodiment, and from 10:1 to 10,000:1 in another embodiment, and from 50:1 to 2,000:1 in a more particular embodiment. When the activator is a neutral or ionic ionizing activator such as a boron alkyl and the ionic salt of a boron alkyl, the mole ratio of activator to catalyst component ranges from 0.5:1 to 10:1 in one embodiment, and from 1:1 to 5:1 in yet a more particular embodiment.

[0105] More particularly, the molar ratio of Al/metallocene-metal (Al from MAO) ranges from 40 to 500 in one embodiment; and ranges from 50 to 400 in another embodiment; and ranges from 60 to 300 in yet another embodiment, and ranges from 70 to 200 in yet another embodiment; and ranges from 80 to 175 in yet another embodiment; and ranges from 90 to 125 in yet another embodiment, wherein a desirable molar ratio of Al(MAO) to metallocene-metal "M" can be any combination of any upper limit with any lower limit described herein.

Supports

[0106] A support may also be present as part of the bimetallic catalyst system of the invention. Supports, methods of supporting, modifying, and activating supports for single-site catalyst such as metallocenes is discussed in, for example, 1 METALLOCENE-BASED POLYOLEFINS 173-218 (J. Scheirs & W. Kaminsky eds., John Wiley & Sons, Ltd. 2000). The terms "support" or "carrier", as used herein, are used interchangeably and refer to any support

material, a porous support material in one embodiment, including inorganic or organic support materials. Non-limiting examples of support materials include inorganic oxides and inorganic chlorides, and in particular such materials as talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide, thoria, aluminum phosphate gel, glass beads, and polymers such as polyvinylchloride and substituted polystyrene, functionalized or crosslinked organic supports such as polystyrene divinyl benzene polyolefins or polymeric compounds, and mixtures thereof, and graphite, in any of its various forms.

[0107] The support may be contacted with the other components of the catalyst system in any number of ways. In one embodiment, the support is contacted with the activator to form an association between the activator and support, or a "bound activator". In another embodiment, the catalyst component may be contacted with the support to form a "bound catalyst component". In yet another embodiment, the support may be contacted with the activator and catalyst component together, or with each partially in any order. The components may be contacted by any suitable means as in a solution, slurry, or solid form, or some combination thereof, and may be heated to any desirable temperature to effectuate a desirable chemical/physical transformation.

[0108] Desirable carriers are inorganic oxides that include Group 2, 3, 4, 5, 13 and 14 oxides and chlorides in one embodiment, and more particularly, inorganic oxides and chlorides of Group 13 and 14 atoms. Yet more particularly, support materials include silica, alumina, silica-alumina, magnesium chloride, graphite, and mixtures thereof. Other useful supports include magnesia, titania, zirconia, montmorillonite (EP 0 511 665 B1), phyllosilicate, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. Additional support materials may include those porous acrylic polymers described in EP 0 767 184 B1.

[0109] In one aspect of the support useful in the invention, the support possess a surface area in the range of from 10 to 700 m^2/g, pore volume in the range of from 0.1 to 4.0 cm^3/g and average particle size in the range of from 5 to 500 μm. In another embodiment, the surface area of the carrier is in the range of from 50 to 500 m^2/g, pore volume of from 0.5 to 3.5 cm^3/g and average particle size of from 10 to 200 μm. In yet another embodiment, the

surface area of the carrier is in the range is from 100 to 400 m^2/g, pore volume from 0.8 to 3.0 cm^3/g and average particle size is from 5 to 100 μm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000Å, from 50 to 500Å in another embodiment, and from 75 to 350Å in yet another embodiment.

[0110] In one embodiment of the support, graphite is used as the support. The graphite is a powder in one embodiment. In another embodiment, the graphite is flake graphite. In another embodiment, the graphite and has a particle size of from 1 to 500 microns, from 1 to 400 microns in another embodiment, and from 1 to 200 in yet another embodiment, and from 1 to 100 microns in yet another embodiment.

[0111] Dehydration or calcining of the support may or may also be carried out. In one embodiment, the support is calcined prior to reaction with the fluorine or other support-modifying compound. In another embodiment, the support is calcined and used without further modification, or calcined, followed by contacting with one or more activators and/or catalyst components. Suitable calcining temperatures range from 100°C to 1500°C in one embodiment, and from 200°C to 1200°C in another embodiment, and from 300°C to 1000°C in another embodiment, and from 350°C to 900°C in yet another embodiment, and from 400°C to 850°C in yet a more particular embodiment, and from 800°C to 900°C in yet a more particular embodiment, and from 810°C to 890°C in yet a more particular embodiment, wherein a desirable range comprises any combination of any upper temperature limit with any lower temperature limit. Calcining may take place in the absence of oxygen and moisture by using, for example, an atmosphere of dry nitrogen.

[0112] The support, especially an inorganic support or graphite support, may be pretreated such as by a halogenation process or other suitable process that, for example, associates a chemical species with the support either through chemical bonding, ionic interactions, or other physical or chemical interaction. In one embodiment, the support is fluorided. The fluorine compounds suitable for providing fluorine for the support are desirably inorganic fluorine containing compounds. Such inorganic fluorine containing compounds may be any compound containing a fluorine atom as long as it does not contain a carbon atom. Particularly desirable are inorganic fluorine containing compounds selected from the group

consisting of NH_4BF_4, $(NH_4)_2SiF_6$, NH_4PF_6, NH_4F, $(NH_4)_2TaF_7$, NH_4NbF_4, $(NH_4)_2GeF_6$, $(NH_4)_2SmF_6$, $(NH_4)_2TiF_6$, $(NH_4)_2ZrF_6$, MoF_6, ReF_6, GaF_3, SO_2ClF, F_2, SiF_4, SF_6, ClF_3, ClF_5, BrF_5, IF_7, NF_3, HF, BF_3, NHF_2 and NH_4HF_2.

[0113] A desirable method of treating the support with the fluorine compound is to dry mix the two components by blending at a concentration of from 0.01 to 10.0 millimole F/g of support in one embodiment, and in the range of from 0.05 to 6.0 millimole F/g of support in another embodiment, and in the range of from 0.1 to 3.0 millimole F/g of support in yet another embodiment. The fluorine compound can be dry mixed with the support either before or after charging to the vessel for dehydration or calcining the support. Accordingly, the fluorine concentration present on the support is in the range of from 0.2 to 5 wt% in one embodiment, and from 0.6 to 3.5 wt% of support in another embodiment.

[0114] Another method of treating the support with the fluorine compound is to dissolve the fluorine in a solvent, such as water, and then contact the support with the fluorine containing solution. When water is used and silica is the support, it is desirable to use a quantity of water that is less than the total pore volume of the support. Desirably, the support and, for example, fluorine compounds are contacted by any suitable means such as by dry mixing or slurry mixing at a temperature of from 100°C to 1000°C in one embodiment, and from 200°C to 800°C in another embodiment, and from 300°C to 600°C in yet another embodiment, the contacting in any case taking place for between two to eight hours.

[0115] It is within the scope of the present invention to co-contact (or "co-immobilize") more than one catalyst component with a support. Non-limiting examples of co-immobilization of catalyst components include two or more of the same or different metallocene catalyst components, one or more metallocene with a Ziegler-Natta type catalyst, one or more metallocene with a chromium or "Phillips" type catalyst, one or more metallocenes with a Group 15 containing catalyst, and any of these combinations with one or more activators. More particularly, co-supported combinations include metallocene A/metallocene A; metallocene A/metallocene B; metallocene/Ziegler Natta; metallocene/Group 15 containing catalyst; metallocene/chromium catalyst; metallocene/Ziegler Natta/Group 15-

containing catalyst; metallocene/chromium catalyst/Group 15 containing catalyst, any of the these with an activator, and combinations thereof.

[0116] Further, the catalyst system of the present invention can include any combination of activators and catalyst components, either supported or not supported, in any number of ways. For example, the catalyst component may include any one or both of metallocenes and/or Group 15-containing catalysts components (*e.g.*, US 6,265,505; US 5,707,913; EP 0 893 454; and WO 99/01460), and may include any combination of activators, any of which may be supported by any number of supports as described herein. Non-limiting examples of catalyst system combinations useful in the present invention include MN + NCA; MN:S + NCA; NCA:S + MN; MN:NCA:S; MN + AlA; MN:S + AlA; AlA:S + MN; MN:AlA:S; AlA:S + NCA + MN; NCA:S + MN + AlA; G15 + NCA; G15:S + NCA; NCA:S + G15; G15:NCA:S; G15 + AlA; G15:S + AlA; AlA:S + G15; G15:AlA:S; AlA:S + NCA + G15; NCA:S + G15 + AlA; MN + NCA + G15; MN:S + NCA + G15; NCA:S + MN + G15; MN:NCA:S + G15; MN + G15 + AlA; MN:S + AlA + G15; AlA:S + MN + G15; MN:AlA:S + G15; AlA:S + NCA + MN + G15; NCA:S + MN + AlA + G15; MN + NCA; G15:MN:S + NCA; G15:NCA:S + MN; G15:MN:NCA:S; G15:MN:S + AlA; G15:AlA:S + MN; G15:MN:AlA:S; G15:AlA:S + NCA + MN; G15:NCA:S + MN + AlA; MN + ZN + NCA; MN:S + ZN + NCA; NCA:S + ZN + MN; ZN:MN:NCA:S; MN + ZN + AlA; MN:ZN:S + AlA; AlA:S + ZN + MN; MN:AlA:ZN:S; AlA:ZN:S + NCA + MN; MN:AlA:S + ZN; wherein "MN" is metallocene component, "ZN" is a Ziegler-Natta catalyst component, such as described above for the first catalyst component, "NCA" is a non-coordinating activator including ionic and neutral boron and aluminum based compounds as described above, "AlA" is an aluminum alkyl and/or alumoxane based activator, "G15" is a Group 15-containing catalyst component as described above, and "S" is a support; and wherein the use of ":" with "S" means that that those groups next to the colon are associated with ("supported by") the support as by pretreatment and other techniques known in the art, and the "+" sign means that the additional component is not directly bound to the support but present with the support and species bound to the support, such as present in a slurry, solution, gas phase, or another way, but is not meant to be limited to species that have no physico-chemical interaction with the support and/or supported species. Thus, for example, the embodiment "MN:NCA:S + G15"

means that a metallocene and NCA activator are bound to a support, and present in, for example, a gas phase polymerization with a Group 15 containing catalyst component.

[0117] In a particular embodiment, the catalyst system is selected from the group consisting of MN:ZN:NCA:S; MN:ZN:AlA:S; MN:AlA:S + ZN; ZN:AlA:S + MN; MN:NCA:S + ZN; and ZN:MN:AlA:NCA:S. The components may be combined in any order desirable to achieve the highest polymerization activity. In one embodiment, the ZN catalyst is immobilized prior to immobilizing the metallocene; in another embodiment, the metallocene is first immobilized, and in yet another embodiment, an activator is first immobilized, followed by either the metallocene and/or the ZN catalyst. In yet another embodiment, both the MN and ZN catalyst components are immobilized simultaneously on the support, the support being pretreated with activator in one embodiment, and treated after catalyst component treatment in yet another embodiment.

[0118] One embodiment of the support useful in the present invention is a so called "enhanced support", prepared by heating support particles at a dehydration temperature of at least 800°C or more, and between 800°C and 1000°C in another embodiment, resulting in an enhanced support having a modified chemical structure. In a particular embodiment, the heating of the support takes place in an inert (*e.g.*, N_2 or Ar) atmosphere, and in the absence of water. In preferred embodiments, increased productivity is achieved when the enhanced support is combined with the other parts of the bimetallic catalyst discussed herein, to form a supported bimetallic catalyst, which is then contacted with monomers during polymerization to produce a bimodal polyolefin compositions.

[0119] In one or more specific embodiments, an enhanced support is first prepared, preferably in the manner described below; then that enhanced support is treated (*e.g.*, combined with ingredients that form the first catalyst) to provide a supported catalyst that includes the first catalyst component. In specific embodiments, that supported first catalyst is then treated in the presence of the second catalyst component to provide a supported bimetallic catalyst.

[0120] The enhanced support is prepared by any suitable means, and more particularly, by any means wherein water is removed from the support, such as by heating, exposure to low

pressure, chemical treatment, or combinations thereof. Heating the support at a dehydration temperature of at least 800°C, and between 800°C and 1000°C in a particular embodiment, provides an enhanced support, for example, enhanced silica, which provides surprisingly improved results over support that is dehydrated at lower temperatures, that is, below 800°C, even slightly lower temperatures, for example, 760°C. While not immediately apparent from the enhancement procedure itself, it is contemplated that the heat treatment results in an actual chemical and/or physical change in the support structure itself, which only reveals its beneficial structure when combined with a first and second catalyst components described herein, and placed in the context of an actual polymerization. For example, when the enhanced silica is combined with both the first catalyst component and the second catalyst component to form a supported bimetallic catalyst composition, that supported bimetallic catalyst composition, including the enhanced silica, has been discovered as having desirably high productivity when used in a polymerization process for making bimodal polyolefin in a single reactor. For example, a productivity of at least 3000 grams polymer/gram catalyst can be achieved. More preferably, the bimetallic catalyst that includes the enhanced support has a productivity of at least 3500 grams polymer/gram catalyst. Even more preferably yet, a bimetallic catalyst having the enhanced support has a productivity of at least 4000 grams polymer/gram catalyst. Other specific embodiments of the invention include bimetallic catalysts with productivities of 4500 grams polymer/gram catalyst and above, 5000 grams polymer/gram catalyst and above, or even 6000 grams polymer/gram catalyst and above.

[0121] In a particular embodiment, the support useful in the present invention is a Group 13 or 14 inorganic oxide support having a pore volume ranging from 0.8 to 3 cm^3/g and a surface area of from 100 to 500 m^2/g. This support is desirably dehydrated as described herein in one embodiment. A preferred support is an amorphous high surface area silica, such as Davison 952 or Sylopol® 955, sold by Davison Chemical Division of W.R. Grace and Company. Those silicas are in spherical form, prepared by the spray drying process, with a surface area of 300 m^2/g and a pore volume of 1.65 cm^3/g. A procedure for dehydrating the silica at 600 °C is set forth in US 5,525,678.

[0122] The enhanced support is then combined with a non-polar hydrocarbon diluent to form a support slurry, which can be stirred and optionally heated during mixing.

[0123] A variety of non-polar hydrocarbon diluents can be used to form the support slurry, but any non-polar hydrocarbon selected should remain in liquid form at all relevant reaction temperatures, and the ingredients used to form the first catalyst component should be at least partially soluble in the non-polar hydrocarbon. Accordingly, the non-polar hydrocarbon diluent is considered to be a "solvent" herein, even though in certain embodiments the ingredients are only partially soluble in the hydrocarbon.

[0124] Examples of suitable non-polar hydrocarbons include C_4-C_{10} linear or branched alkanes, cycloalkanes and aromatics. More specifically, a non-polar alkane can be isopentane, hexane, isohexane, n-heptane, octane, nonane, or decane; a non-polar cycloalkane such as cyclohexane; or an aromatic such as benzene, toluene, or ethylbenzene. Mixtures of different non-polar hydrocarbons can also be used.

[0125] The support slurry can be heated both during and after mixing of the support particles with the non-polar hydrocarbon solvent, but at the point when either or both of the catalysts are combined with the support slurry, the temperature of the slurry should be sufficiently low so that neither of the catalysts are inadvertently deactivated. Thus, the temperature of the support slurry (*e.g.*, silica slurry) is preferably maintained at a temperature below 90°C, for example, from 25 to 70°C, or from 40 to 60°C in another embodiment.

Gas Phase Polymerization Process

[0126] The bimetallic catalysts, and more particularly, the supported bimetallic catalyst composition, described herein are preferably used to make bimodal polyolefin compositions, that is, compositions having a bimodal molecular weight distribution; in a particular embodiment, the bimetallic catalysts described herein are used in a single polymerization reactor to make the bimodal polyolefin composition. Once the supported bimetallic catalyst composition is prepared, as described above, a variety of processes can be carried out using that composition. Among the varying approaches that can be used include procedures set forth in US 5,525,678 in which those processes are modified in accordance with the inventions claimed herein, for example, involving the high fluidized bulk density as described herein. The equipment, process conditions, reactants, additives and other materials will of course vary in a

given process, depending on the desired composition and properties of the polymer being formed. For example, the processes discussed in any of the following patents can be used: US 6,420,580; 6,388,115; 6,380,328; 6,359,072; 6,346,586; 6,340,730; 6,339,134; 6,300,436; 6,274,684; 6,271,323; 6,248,845; 6,245,868; 6,245,705; 6,242,545; 6,211,105; 6,207,606; 6,180,735; and 6,147,173.

[0127] More particularly, the process of the present invention is directed toward a gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, from 2 to12 carbon atoms in a more particular embodiment, and from 2 to 8 carbon atoms in yet a more particular embodiment. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 4-methyl-1-pentene, 1-isobutene, 1-isobutene and 1-decene.

[0128] Other monomers useful in the process of the invention include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

[0129] In the most preferred embodiment of the process of the invention, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one α-olefin having from 4 to 15 carbon atoms, from 4 to 12 carbon atoms in yet a more particular embodiment, and from 4 to 8 carbon atoms in yet a more particular embodiment, is polymerized in a gas phase process.

[0130] In another embodiment of the process of the invention, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

[0131] Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example US 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228.)

[0132] The reactor pressure in a gas phase process may vary from 100 psig (690 kPa) to 500 psig (3448 kPa) in one embodiment, from 200 psig (1379 kPa) to 400 psig (2759 kPa) in a more particular embodiment, and from 250 psig (1724 kPa) to 350 psig (2414 kPa) in yet a more particular embodiment.

[0133] The reactor temperature in a gas phase process may vary from 30°C to 120°C in one embodiment, from 60°C to 115°C in a more particular embodiment, from 70°C to 110°C in yet a more particular embodiment, and from 70°C to 95°C in yet a more particular embodiment, or as set out further below.

[0134] In an embodiment of the invention, the process is operated by introducing a carboxylate metal salt such as aluminum stearate or other metal-fatty acid compound into the reactor and/or contacting a carboxylate metal salt with the catalyst system of the invention prior to its introduction into the reactor.

[0135] The "catalyst system" useful in the gas phase polymerization process of the invention includes the first and second catalyst components, making up a bimetallic catalyst, and one or more activators. The bimetallic catalyst is activated by any suitable means known in the art, either before introduction into the polymerization reactor or *in situ*. The supported bimetallic catalyst is fed to the reactor in a dry (no diluent) state in a particular embodiment. In

another embodiment, the bimetallic catalyst is suspended in a diluent (*e.g.*, C_5 to C_{15} hydrocarbon) comprising from 5 wt% to 100 wt% mineral oil or silicon oil and fed into the reactor.

[0136] The gas-phase process of the present invention includes contacting the catalyst system (including catalyst components and activators, and optionally, a support) with monomers in a reactor vessel of desirable configuration to form a polyolefin. In one embodiment, the contacting may take place in a first reactor vessel, followed by transfer of the formed polymer into another second, third etc. reactor vessel to allow further polymerization, optionally by adding the same or different monomers and optionally by adding the same or different catalyst components, activators, etc. In a particular embodiment of the present invention, the bimetallic catalyst system is contacted with monomers in a single reactor vessel (or "reactor"), followed by isolation of a finished polyolefin resin.

[0137] For example, a gas phase polymerization process claimed herein may include use of a continuous cycle in which a cycling gas stream (*i.e.*, a recycle stream or fluidizing medium) is heated in the reactor by the heat of polymerization. This heat can be removed from the recycle stream in another part of the cycle by a cooling system that is external to the reactor. In a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers can be continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is preferably withdrawn from the fluidized bed and then recycled back into the reactor. Polymer product can be withdrawn from the reactor and fresh monomer added to replace the polymerized monomer. (See for example US 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228)

[0138] The reactor pressure in a gas phase process may vary from 100 psig (690 kPa) to 500 psig (3448 kPa) in one embodiment, from 200 psig (1379 kPa) to 400 psig (2759 kPa) in a particular embodiment, and from 250 psig (1724 kPa) to 350 psig (2414 kPa) in yet a more particular embodiment.

[0139] In one aspect of the invention, the voidage of the gas phase reactor is desirably controlled. In one embodiment, the polymerization process of the invention is characterized as

a process of polymerization using a bimetallic catalyst wherein the voidage of the fluidized bed gas phase reactor is maintained at less than 40%. This can be accomplished by any suitable means such as by, for example, adjusting the hydrogen level in the reactor or reactors. The voidage of the reactor can be described in the equation below (A):

$$\text{Voidage} = \frac{\text{SBD - FBD}}{\text{SBD - gas density}} \qquad \text{(A)}$$

wherein SBD is the "settled bulk density" of the formed resin granules in the reactor; FBD is the "fluidized bulk density", which is the density of the resin granules in the reactor; and "gas density" is simply the density of the gas in the reactor. The FBD is the ratio of the measured pressure drop upward across a centrally fixed portion of the reactor to the height of the fixed portion. As noted therein, the FBD is a mean value, which may be greater or less than the localized bulk density at any point in the fixed reactor portion. Since the gas density is diminishingly small, the equation describing voidage can be simplified to the following (B):

$$\text{Voidage} = 1 - \frac{\text{FBD}}{\text{SBD}} \qquad \text{(B)}$$

[0140] Certain specific embodiments of the invention are advantageously directed to a process having fluidized bulk density (FBD) that is higher than other bimodal polyolefin polymerization processes. A high FBD (or low voidage) can have benefits in a gas phase polymerization process, since higher FBD generally means higher catalyst productivity due to the higher residence times allowable in such a reactor. A high FBD also provides for advantages for restarting a commercial-scale reactor when a gas phase polymerization cycle is interrupted by extraneous factors. For example, a low FBD corresponds to excessive bed expansion during the restarting process, and can sometimes even make the restart process unsuccessful.

[0141] As used herein, the term "fluidized bulk density" (FBD) has the same meaning given that same term in US 5,436,304, in which the term is defined as the ratio of the measured pressure drop upward across a centrally fixed portion of the reactor to the height of the fixed

portion, for example, a "pressure tap vertical separation." As noted therein, the FBD is a mean value, which may be greater or less than the localized bulk density at any point in the fixed reactor portion.

[0142] All FBD values that are absolute values of fluidized bulk density are expressed in units of lbs/ft^3. The values of FBD of the present invention range from 5 to 50 lbs/ft^3 in one embodiment, from 7 to 40 lbs/ft^3 in a more particular embodiment, and from 8 to 30 lbs/ft^3 in yet a more particular embodiment, and from 10 to 25 lbs/ft^3 in yet another embodiment, wherein a desirable range for FBD may be any combination of any upper limit with any lower limit.

[0143] All SBD values are expressed in units of lbs/ft^3. The values of SBD of the present invention range from 10 to 60 lbs/ft^3 in one embodiment, and from 12 to 50 lbs/ft^3 in a more particular embodiment, and from 14 to 40 lbs/ft^3 in yet another embodiment, and from 15 to 35 lbs/ft^3 in yet another embodiment, wherein a desirable range for SBD may be any combination of any upper limit with any lower limit.

[0144] In one embodiment, the voidage of the reactor is less than 50% (expressing the values above as percentages), and less than 45% in a more particular embodiment, and less than 40% in yet a more particular embodiment, and less than 35% in a particular embodiment, and less than 30% in a more particular embodiment, and less than 20% in a more particular embodiment; and at least 5% in one embodiment, and at least 10% in a more particular embodiment, wherein a desirable range of voidage values may include any combination of any upper voidage limit with any lower voidage limit described herein. Stated another way, the FBD/SBD ratio may have a value of from greater than 0.40 (or 40% when multiplied by 100 as in the data tables) in one embodiment, and greater than 45% in a more particular embodiment, and greater than 50% in yet a more particular embodiment, and greater than 60% in yet a more particular embodiment, and greater than 65% in yet a more particular embodiment; and less than 95% in one embodiment, and less than 90% in yet another embodiment, and less than 85% in yet a more particular embodiment, wherein a desirable range of FBD/SBD values may include any combination of any upper FBD/SBD limit with any lower FBD/SBD limit described herein.

[0145] It has been found that the voidage can be adjusted to a desirable level when using bimetallic catalyst systems comprising at least one metallocene by adjusting the level of hydrogen in the polymerization reactor. The level of hydrogen in the reactor can be adjusted by adjusting the level of hydrogen in the gas stream that is introduced into the reactor, or stated alternately, adjusting the ratio of hydrogen and ethylene.

[0146] In certain specific embodiments, the polymerization reactor temperature is maintained at a certain level to further optimize the voidage at a desirable level. As used herein, the term "reactor temperature" can refer to an actual measured temperature (*i.e.*, at a point in time) of a fluidized bed in a reaction zone of a fluidized bed reactor used to carry out a gas phase polymerization; and can also refer to a calculated number that equals an average of a plurality of actual measured temperatures, measured intermittently over a period of time, for example, an average of ten measured temperatures over a four-hour period. In a particular embodiment, the polymerization reactor temperature ranges from 100°C, or 99°C, or 98°C, or 97°C, or 96°C, or 95°C, or 94°C, or 93°C, or 92°C, or 91°C, or 90°C, to 40°C, 50°C, 60°C, 70°C, or 80°C, or 82°C, or 84°C, or 86°C, or 88°C, or 90°C, wherein the reactor temperature may be in a range from any combination of any upper temperature limit with any lower temperature limit described herein. Thus, for example, a reactor temperature that averages 97°C for at least a one, two, three, four or more-hour period may be utilized during a continuous gas phase polymerization cycle of the invention in one embodiment.

[0147] The voidage (or FBD) may be controlled in one embodiment by adjusting the hydrogen level in the polymerization process. The hydrogen levels (also referred to as hydrogen amounts) are sometimes expressed herein in terms of the molar ratio of H_2 to C_2 (also H_2/C_2 or H_2:C_2), wherein H_2 refers to molecular hydrogen, and C_2 refers to ethylene. Alternatively, the hydrogen levels discussed herein can refer to the ratio of moles H_2 to moles of monomers used in the polymerization reaction, for example, ethylene, propylene and/or butene. Preferably, however, the hydrogen level referenced herein is the molar ratio of hydrogen gas to ethylene monomers. As with reactor temperature, the hydrogen levels referenced herein and in the claims include actual instantaneous measured hydrogen levels, for

example, a molar ratio of hydrogen gas to ethylene, or an average hydrogen level, based on measured hydrogen levels taken intermittently over a period of time.

[0148] The ratio of hydrogen to ethylene has an upper limit of 0.015 in one embodiment, and an upper limit of 0.01 in another embodiment, 0.009 in yet another embodiment, and 0.008 in a more particular embodiment, and 0.007 in yet a more particular embodiment, and 0.006 in yet a more particular embodiment, and 0.005 in yet a more particular embodiment, and 0.004 in yet a more particular embodiment. Thus, for example, the average ratio of a molecular hydrogen to ethylene over a four-hour period is 0.009 or below during a continuous gas phase polymerization cycle in one embodiment. The ratio of hydrogen to ethylene may have a lower limit of 0.0005 in another embodiment, and 0.001 in a more particular embodiment, and 0.002 in yet a more particular embodiment, and 0.003 in yet a more particular embodiment, and 0.004 in yet a more particular embodiment, and 0.005 in yet a more particular embodiment. The range of hydrogen levels (molar ratios of H_2/C_2) may have comprise any combination of any upper ratio limit with any lower ratio limit described herein. For example, in a specific embodiment, the molar ratio of the hydrogen gas in the gaseous stream to ethylene in the gaseous stream is from 0.003 to 0.009.

[0149] An alkylaluminum compound, or mixture of compounds, such as trimethylaluminum or triethylaluminum is feed into the reactor in one embodiment at a rate of from 10 wt. ppm to 500 wt. ppm (weight parts per million alkylaluminum feedrate compared to ethylene feed rate), and from 50 wt. ppm to 400 wt. ppm in a more particular embodiment, and from 60 wt. ppm to 300 wt. ppm in yet a more particular embodiment, and from 80 wt. ppm to 250 wt. ppm in yet a more particular embodiment, and from 75 wt. ppm to 150 wt. ppm in yet another embodiment, wherein a desirable range may comprise any combination of any upper limit with any lower limit. The alkylaluminum can be represented by the general formula AlR_3, wherein each R is the same or different and independently selected from C_1 to C_{10} alkyls and alkoxys.

[0150] Also, water may also be fed into the reactor in another embodiment at a rate of from 0.01 wt. ppm to 200 wt. ppm (weight parts per million water feedrate compared to ethylene feed rate), and from 0.1 wt. ppm to 150 wt. ppm in another embodiment, and from 0.5

wt. ppm to 100 wt. ppm in yet another embodiment, and from 1 wt. ppm to 60 wt. ppm in yet another embodiment, and from 5 wt. ppm to 40 wt. ppm in yet a more particular embodiment, wherein a desirable range may comprise any combination of any upper limit with any lower limit described herein.

Bimodal Polymer Product and Films Made Therefrom

[0151] The polymers produced by the processes described herein, utilizing the bimetallic catalysts described herein, which are preferably bimodal, can be used in a wide variety of products and end-use applications such as films, pipes and tubing, wire coating, and other applications. The polymers produced by the process of the invention include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes, low density polyethylenes, polypropylene and polypropylene copolymers.

[0152] Polymers that can be made using the described processes can have a variety of compositions, characteristics and properties. At least one of the advantages of the bimetallic catalysts is that the process utilized can be tailored to form a polymer composition with a desired set of properties. For example, it is contemplated that the polymers having the same properties as the bimodal polymer compositions in US 5,525,678 can be formed. Accordingly, US 5,525,678. Also, the bimetallic catalysts described herein can be used in polymerization processes to form polymers having the same properties as the polymers in the following patents: US 6,420,580; 6,388,115; 6,380,328; 6,359,072; 6,346,586; 6,340,730; 6,339,134; 6,300,436; 6,274,684; 6,271,323; 6,248,845; 6,245,868; 6,245,705; 6,242,545; 6,211,105; 6,207,606; 6,180,735; and 6,147,173.

[0153] The polymers, typically ethylene based polymers, have a density in the range of from 0.860 g/cm^3 to 0.970 g/cm^3 in one embodiment, from 0.880 g/cm^3 to 0.965 g/cm^3 in a more particular embodiment, from 0.900 g/cm^3 to 0.960 g/cm^3 in yet a more particular embodiment, from 0.905 g/cm^3 to 0.955 g/cm^3 in yet a more particular embodiment, from 0.910 g/cm^3 to 0.955 g/cm^3 in yet a more particular embodiment, greater than 0.915 g/cm^3 in yet a more particular embodiment, greater than 0.920 g/cm^3 in yet a more particular embodiment, and greater than 0.925 g/cm^3 in yet a more particular embodiment.

[0154] The polymers derived from the bimodal catalyst and process of the invention have a bulk density of from 0.400 to 0.900 g/cm^3 in one embodiment, and from 0.420 to 0.800 g/cm^3 in another embodiment, and from 0.430 to 0.500 g/cm^3 in yet another embodiment, and from 0.440 to 0.60 g/cm^3 in yet another embodiment, wherein a desirable range may comprise any upper bulk density limit with any lower bulk density limit described herein.

[0155] The polymers have a molecular weight distribution, a weight average molecular weight to number average molecular weight (M_w/M_n) of from 5 to 80 in one embodiment, of from 10 to 60 in a more particular embodiment, of from 15 to 55 in yet a more particular embodiment, and of from 20 to 50 in yet a more particular embodiment.

[0156] The polymers made by the described processes have a melt index (MI) (I_2, as measured by ASTM D-1238, 190/2.16) in the range from 0.01 dg/min to 100 dg/min in one embodiment, from 0.01 dg/min to 50 dg/min in a more particular embodiment, from 0.02 dg/min to 20 dg/min in yet a more particular embodiment, and from 0.03 dg/min to 2 dg/min in yet a more particular embodiment, and from 0.002 dg/min to 1 dg/min in yet a more particular embodiment, wherein a desirable range may comprise any combination of any upper I_2 limit with any lower I_2 limit.

[0157] Polymers made by the method of the invention have an HLMI (I_{21}, I_{21} is measured by as measured by ASTM-D-1238, 190/21.6) value that ranges from 0.01 to 50 dg/min in one embodiment, and from 0.1 to 30 in another embodiment, and from 0.5 to 20 in yet a more particular embodiment, and from 1 to 10 in yet a more particular embodiment wherein a desirable range is any combination of any upper I_{21} limit with any lower I_{21} limit.

[0158] Polymers made by the described processes have a melt index ratio (MIR, or I_{21}/I_2) of from 20 to 500 in one embodiment, from 30 to 300 in a more particular embodiment, and from 60 to 200 in yet a more particular embodiment. Expressed differently, polymers made by the described processes have a melt index ratio of from greater than 40 in one embodiment, greater than 50 in a more particular embodiment, greater that 60 in yet a more particular embodiment, greater than 65 in yet a more particular embodiment, and greater than 70 in yet a more particular embodiment.

[0159] The bimodal polymers produced by the present invention may have a certain average particle size, or APS, ranging from greater than 150 microns in one embodiment, and from 150 to 2000 microns in a more particular embodiment, and from 150 to 1000 microns in yet another embodiment, and from 300 to 800 microns in yet a more particular embodiment. This was determined by using standard sieves. Fines (particles of less than 125 μm) are typically present to less than 5 wt%, or less than 4 wt%, or less than 3 wt%.

[0160] In certain embodiments, propylene based polymers can be produced using the processes described herein. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example US 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117.

[0161] The polymers of the invention may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes produced via conventional Ziegler-Natta and/or metallocene-type catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

[0162] Polymers produced by the process of the invention and blends thereof are useful in such forming operations as film, sheet, pipe and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, cable and wire sheathing, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include single and

multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

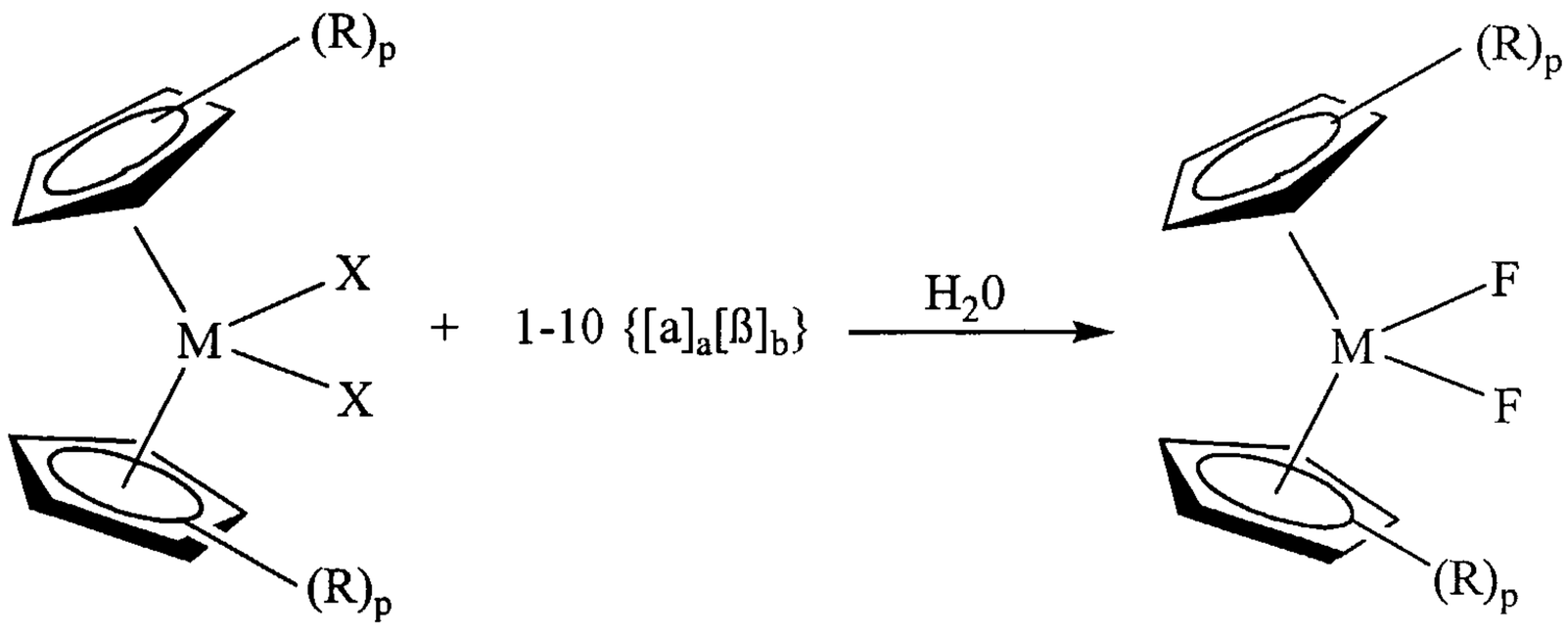
[0163] More particularly, the polymers made by the method of the invention are useful in making films. The films may be of any desirable thickness or composition, in one embodiment from 1 to 100 microns, and from 2 to 50 microns in a more particular embodiment, and from 10 to 30 microns in yet a more particular embodiment; and comprise copolymers of ethylene with a C_3 to C_{10} olefin in one embodiment, ethylene with C_3 to C_8 α-olefins in a particular embodiment, and ethylene with C_4 to C_6 α-olefins in yet a more particular embodiment. The resins used to make the films may be blended with other additives such as pigments, antioxidants, fillers, etc, as is known in the art, as long as they do not interfere with the desired film properties.

[0164] In one embodiment, a film made from one or more of the bimodal polyolefin compositions disclosed herein has a Dart Drop Impact F50 Value of at least 100 [g] on 25.4 micron film and 50 [g] on 12.5 micron film; and in a more particular embodiment, the bimodal compositions have a Dart Drop Impact of at least 100 [g] on 25.4 micron film and 75 [g] on 12.5 micron film; and in yet a more particular embodiment, the bimodal compositions have a Dart Drop Impact of at least 200 [g] on 25.4 micron film and 100 [g] on 12.5 micron film.

[0165] In one embodiment, a film made from one or more of the bimodal polyolefin compositions disclosed herein has an MD Tear value of at least 0.8 g/micron on a 25.4 micron film in one embodiment; of at least 0.6 g/micron on a 25.4 micron film in a more particular embodiment; and of at least 0.4 g/micron on a 25.4 micron film in yet a more particular embodiment; and less than 5 g/microgram on a 25.4 micron film in yet a more particular embodiment; and less than 5 g/micron on a 25.4 micron film in yet a more particular embodiment; and at least 0.2 g/micron on 12.5 micron film in one embodiment; at least 0.4 g/micron on 12.5 micron film in a more particular embodiment; and at least 0.8 g/micron on 12.5 micron film in yet a more particular embodiment; and less than 10 g/micron on 12.5 micron film in one embodiment; and less than 5 g/micron on 12.5 micron film a more particular embodiment; wherein a desirable range of MD Tear values may comprise any upper limit (corresponding to a given gauge) with any lower limit described herein.

[0166] In one embodiment, a film made from one or more of the bimodal polyolefin compositions disclosed herein has a TD Tear value of at least 1.5 g/micron on 24.5 micron film in one embodiment; at least 3 g/micron on 24.5 micron film in a more particular embodiment; and at least 5 g/micron on 24.5 micron film in yet a more particular embodiment; and at least 9 g/micron on 24.5 micron film in one embodiment; and less than 40 g/micron on a 24.5 micron film in yet a more particular embodiment, and less than 20 g/micron on a 24.5 micron film in yet a more particular embodiment; and 1.0 g/micron on 12.5 micron film in yet another embodiment; 2.0 g/micron on 12.5 micron film in yet a more particular embodiment; 3.0 g/micron on 12.5 micron film in yet a more particular embodiment; and less than 20 g/micron on a 12.5 micron film in yet a more particular embodiment; and less than 15 g/micron on a 12.5 micron film in yet a more particular embodiment; wherein a desirable range of TD Tear values may comprise any upper limit (corresponding to a given gauge) with any lower limit described herein.

[0167] The invention can thus be described by any combination of the various embodiments described above. For example, the method of producing a fluorided metallocene catalyst component can be described by the reaction scheme (VI):



(VI)

wherein M is a Group 4, 5 or 6 metal in one embodiment; and zirconium or hafnium in a particular embodiment;

each X is independently selected from the group consisting of chloride, bromide, C_1 to C_{20} carboxylates, C_2 to C_{20} acetylacetonates, hydroxide and C_1 to C_{10} alkoxides in one embodiment, and more particularly selected from the group consisting of chloride, bromide, C_1 to C_{20} carboxylates, C_2 to C_{20} acetylacetonates;

R are groups that may replace hydrides on the Cp rings and are independently selected from groups as defined above; and in a particular embodiment, selected from the group consisting of C_1 to C_6 alkyls;

p is an integer from 0 to 5 in one embodiment, and from 1 to 5 in a particular embodiment; wherein when p is 2 on any given Cp ring, adjacent R groups may form ring systems;

$[a]_a[ß]_b$ is as defined above; and

the reaction conditions are as defined above in one embodiment, and more particularly, comprise a two phase system, wherein one phase is an aqueous phase comprising at least 50 wt% water, at least 80% water in a particular embodiment; and the other phase comprising a hydrocarbon or halogenated hydrocarbon diluent.

[0168] The present invention also includes a bimetallic catalyst composition comprising at least one fluorided metallocene catalyst component as described herein, a non-metallocene catalyst component, and an activator, the catalyst components and activator supported on an inorganic oxide dehydrated at a temperature of greater than 800°C. The non-metallocene component, or "first catalyst component" is desirably a Ziegler-Natta catalyst component. The composition is formed in one embodiment by first synthesizing the fluorided metallocene as described above, followed by combining with the non-metallocene catalyst component, activator and support in any order. In one embodiment, the non-metallocene component is first combined with the support followed by an activator, followed then by combining with the fluorided metallocene catalyst produced by the method described herein.

[0169] The present invention also includes a process for producing a bimodal polyolefin composition comprising the steps of: (a) contacting a metallocene catalyst

compound with an fluorinated inorganic salt for a time sufficient to form a fluorinated metallocene catalyst compound; next, (b) isolating the fluorided metallocene catalyst compound; followed by (c) combining the fluorided metallocene catalyst compound with an activator and ethylene monomers and optionally a support at from 50°C to 120°C; and (d) isolating polyethylene. The catalyst may be combined with other monomer such as 1-butene, 1-hexene, etc.

[0170] In one embodiment, the fluorided metallocene, activator and support are also combined with a Ziegler-Natta catalyst comprising titanium halide. This can be done in any desirable order to produce a bimetallic catalyst. In a particular embodiment, the fluorided metallocene, activator and support are combined and isolated prior to combining with ethylene monomers. In another embodiment, the combined fluorided metallocene, activator and support are suspended in a diluent comprising from 5 wt% to 100 wt% mineral oil or silicon oil. In a particular embodiment, the fluorinated inorganic salt is characterized in that it generates fluoride ions when contacted with a diluent that is at least 50 wt% water.

[0171] These embodiments of the present invention are exemplified by the following examples.

EXAMPLES

Example 1

[0172] In the following example, five samples of supported bimetallic catalysts were prepared. Each sample differed primarily in whether a fluorinated or chlorinated metallocene was used and the dehydration temperature for the silica support. Specifically, Samples 1 and 4 had the same dehydration temperature (760 °C), but differed in whether fluorinated or chlorinated metallocene was used, demonstrating a slight increase in polymer productivity at that temperature (760°C) due to use of a fluoride leaving group rather than a chloride leaving group. Samples 3 and 5 demonstrate that the fluorinated metallocene samples that included silica dehydrated at temperatures above 800°C provided surprisingly higher catalyst productivity than either chlorinated metallocene samples having silica dehydrated at similar temperatures (Sample 3) or fluorinated metallocene samples having silica dehydrated at lower temperatures. Specific properties of the samples are displayed in Table 1.

[0173] *Catalyst Preparation.* In all the samples, Davidson Sylopol® 955 Silica was used. Samples 1 and 4 were dehydrated at a temperature of 760°C; Sample 2 was dehydrated at 830°C; and Samples 3 and 5 were dehydrated at 875°C. Then, for each sample, a non-metallocene catalyst was combined with the dehydrated silica. That is, for each sample, 500 grams of the respective dehydrated silica was added into a 5-liter, 3-neck round bottom flask enclosed in an N_2 glove box. Anhydrous hexane (2500 ml) was then added into the flask, making a silica/hexane slurry. The slurry was heated to a temperature of 54°C while under constant stirring, and 380 grams of a 15 wt.% solution of dibutyl magnesium was added to the slurry over a period of 20 minutes. The slurry was then allowed to stand for an additional 30 minutes. Butanol (27.4 grams) was diluted to volume with hexane in a 125 ml volumetric flask. The entire 125 ml of diluted butanol solution was added dropwise into the flask containing the slurry, and then the slurry was held at a temperature of 54°C for 30 minutes while under constant agitation. Titanium tetrachloride (41.0 grams) was diluted to volume with hexane in a 125 ml volumetric flask. The entire 125 ml of diluted titanium tetrachloride solution was then added dropwise into the flask containing the slurry. Following the addition of the solution, the slurry was allowed to stand for 30 minutes at a temperature of 54°C. The slurry was then allowed to cool to ambient temperature to form the "ZN" supported catalyst.

[0174] The respective metallocene catalyst compound was then added to each sample from the above slurry. First, 673 grams of a 30 wt.% solution of methylaluminoxane (MAO) in toluene was added to a new flask in an N_2 glove box. For Samples 1, 2, and the metallocene bis-n-butyl-cyclopentadienyl zirconium dichloride (13.72 grams) was added into the MAO solution and the mixture was stirred until all of the solids had been dissolved. For Samples 4 and 5, 13.72 grams of the metallocene bis-n-butyl-cyclopentadienyl zirconium difluoride was added into the MAO solution, and the mixture was stirred until all of the solids had been dissolved. Next, the MAO/Metallocene mixture was slowly added into the flask containing the previously prepared titanium reaction slurry over a period of one hour. Toluene (50 ml) was used to wash the residual MAO/Metallocene mixture remaining in the flask into the flask containing the reaction slurry. Each resulting mixture that included the respective bimetallic catalyst sample was then held at ambient temperature for a period of one hour. Afterward, each mixture was dried using a rotary vaporizer, followed by removing most of the hexanes using a

vacuum pressure of 21 mmHg at a temperature of 52°C. The high boiling point toluene was subsequently removed using a vacuum pressure of 28 mmHg at a temperature of 70°C. The final dried bimetallic catalyst appeared brown in color as a free flowing solid. Each sample of "ZN/MN" supported catalyst was used in a separate polymerization run in a gas phase reactor, under the conditions identified in Table 1 to form a polyethylene polymer composition.

[0175] *Fluid-Bed Polymerization.* The polymerizations were conducted in a continuous gas phase fluidized bed reactor. The fluidized bed is made up of polymer granules. The gaseous feed streams of ethylene and hydrogen together with liquid comonomer were mixed together in a mixing tee arrangement and introduced below the reactor bed into the recycle gas line. Monomers of 1-hexene were used as the comonomer. The individual flow rates of ethylene, hydrogen and comonomer were controlled to maintain fixed composition targets. The ethylene concentration was controlled to maintain a constant ethylene partial pressure. The hydrogen was controlled to maintain a constant hydrogen to ethylene mole ratio. The concentration of all the gases were measured by an on-line gas chromatograph to ensure relatively constant composition in the recycle gas stream.

[0176] The solid catalyst was injected directly into the fluidized bed using purified nitrogen as a carrier. Trimethylaluminum (TMA) was added as a cocatalyst for the ZN catalyst. Its rate was adjusted to maintain a constant production rate. The reacting bed of growing polymer particles is maintained in a fluidized state by the continuous flow of the make up feed and recycle gas through the reaction zone. A superficial gas velocity of 1-3 ft/sec was used to achieve this. The reactor was operated at a total pressure of 300 psig. To maintain a constant reactor temperature, the temperature of the recycle gas is continuously adjusted up or down to accommodate any changes in the rate of heat generation due to the polymerization.

[0177] The fluidized bed was maintained at a constant height by withdrawing a portion of the bed at a rate equal to the rate of formation of particulate product. The product is removed semi-continuously via a series of valves into a fixed volume chamber, which is simultaneously vented back to the reactor. This allows for highly efficient removal of the product, while at the same time recycling a large portion of the unreacted gases back to the

reactor. This product is purged to remove entrained hydrocarbons and treated with a small steam of humidified nitrogen to deactivate any trace quantities of residual catalyst.

[0178] *Resin Properties*. The properties of the polymer was determined by the following test methods:

1. Melt Index: ASTM D-1238-Condition E,
2. Density: ASTM D-105,
3. Bulk Density: The resin is poured via a 7/8 inch diameter funnel into a fixed volume cylinder of 400 cc. The bulk density is measured as the weight of resin divided by 400 cc to give a value in g/cc,
4. Particle Size: The particle size is measured by determining the weight of material collected on a series of U.S. Standard sieves and determining the weight average particle size based on the sieve series used.

The fines are defined as the percentage of the total distribution passing through a 120 mesh standard sieve. This has a particle size equivalent of 120 microns. Fines are important since high levels can lead to sheeting and fouling of the reaction cycle gas system. This results in heat exchanger distributor plate fouling requiring a reactor shut down to clean out.

[0179] Each run was operated over a period of 24 hours, as indicated in Tables 1 and 3. Each run was conducted using the same continuous gas phase fluidized bed reactor. The fluidized bed of that reactor was made up of polymer granules. During each run, the gaseous feed streams of ethylene and hydrogen were introduced below the reactor bed into a recycle gas line. Hexene comonomer was introduced below the reactor bed. The individual flows of ethylene, hydrogen and hexene comonomer were controlled to maintain fixed composition targets, identified in Tables 1 and 3. The concentrations of gases were measured by an on-line chromatograph.

Example 2

[0180] Resins produced from the catalysts in Example 1 were compounded on a ZSK-30 compounder with an additive package of 1500 ppm Irganox 1010, 1500 ppm Irgafos 168 and 1500 ppm zinc stearate. The compounding operation was conducted under a nitrogen blanket, and conditions were adjusted to maintain the melt temperature below 230°C. Films made from the polymers were formed for purposes of assessing polymer properties. The

following example describes the fabricating conditions for the film fabrication process. Films were fabricated on an Alpine blown film line with a single 50 mm grooved extruder. The die was 100 mm in diameter and had a 1 mm die gap. Extrusion was conducted at a rate of 45.4 kg/hr, while maintaining a temperature profile of 201/204°C on the extruder and a flat temperature profile of 210°C on the die. The film was blown at a 4:1 blow up ratio (BUR), with an initial gauge of 25 microns and a frost line height of 90 cm using chilled air without using an internal bubble stabilizer bar or an internal bubble cooling. The take-up speed was gradually increased until either the maximum take-up speed of the winder was reached or the onset of the bubble instability was noted. Physical properties, reported in Table 2 were measured on stable bubbles of gauges 25 and 12 microns using standard ASTM techniques. Elmendorf Tear Strength values were measured in the MD and TD direction in accordance with ASTM D1922-00. Dart Drop Impact F50 values were measured using the procedures in ASTM D1709-00.

[0181] The present invention offers many advantages over the prior art. One advantage is that the catalyst system offers improved catalyst productivity in polyethylene production. More particularly, the silica supported titanium-based Ziegler Natta/fluorided metallocene catalyst has an activity of from greater than 4500 g/g in one embodiment, and greater than 5000 g/g in a more particular embodiment, and greater than 5400 g/g in yet a more particular embodiment at a polymerization temperature of from 90 to 100°C in one embodiment, and from 93 to 98°C in a more particular embodiment. This is a higher activity than for the corresponding chlorided metallocene (Samples 1-3) and even the chlorided metallocenes with the enhanced silica support (Samples 2-3).

[0182] The catalyst and method of the present invention also offers the advantage of producing polyethylene polymers having bulk densities ranging from 0.420 to 0.500 g/ml in one embodiment, and ranging from 0.440 to 0.490 g/ml in another embodiment, and ranging from 0.450 to 0.480 g/ml in yet a more particular embodiment; and particularly when an silica support is used that has been dehydrated at from 830°C or more in particular embodiments.

[0183] These results are accomplished using a molar ratio of hydrogen to ethylene as described herein, and more particularly of from 0.001 to 0.015 in one embodiment, and from

0.002 to 0.010 in another embodiment, and from 0.003 to 0.009 in yet another embodiment, and from 0.004 to 0.008 in yet another embodiment, wherein a desirable range may comprise any combination of any upper mole ratio limit with any lower mole ratio limit described herein.

[0184] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to many different variations not illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the scope of the present invention. Further, certain features of the present invention are described in terms of a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges formed by any combination of these limits are within the scope of the invention unless otherwise indicated.

[0185] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties, reaction conditions, and so forth, used in the specification and claims are to be understood as approximations based on the desired properties sought to be obtained by the present invention, and the error of measurement, etc., and should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and values setting forth the broad scope of the invention are approximations, the numerical values set forth are reported as precisely as possible.

All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

TABLE 1. Reaction Conditions and Resin Properties

Parameter	**1**	**2**	**3**	**4**	**5**
Catalyst Description	ZN/MN-dichloride	ZN/MN-dichloride	ZN/MN-dichloride	ZN/MN-difluoride	ZN/MN-difluoride
Catalyst Dehydration Temp. (°C)	760	830	875	760	875
Residence Time (hrs)	3.9	3.1	2.8	3.3	3.3
C_2 Partial Pressure (psia)	157.1	157.1	157.3	156.5	155.7
H_2/C_2 anz ratio (ppm/%)	110.5	108.0	110.0	112.2	107.3
C_6/C_2 anz ratio (%/%)	0.010	0.010	0.010	0.011	0.010
Bed Temperature (°C)	95	95	95	95	95
Production Rate (lb/hr)	55.8	69.4	75.7	69.8	70.2
Catalyst Productivity (g/g)	2594	3603	4000	2881	5564
TMA/ C_2 Flow Ratio (wt ppm)	121.4	122.0	124.7	124.9	124.9
H_2O/C_2 Flow Ratio (wt ppm)	20.1	24.7	27.0	13.0	23.6
Resin Properties					
I_2 [g/10 min]	0.051	0.061	0.055	0.064	0.061
I_{21} [g/10 min]	5.58	5.32	5.58	7.73	6.92
I_{21}/I_2	110.0	87.2	97.5	120.7	118.4
Density (g/cm^3)	0.9507	0.9518	0.9538	0.9528	0.9506
Bulk Density (g/cm^3)	0.4005	0.4168	0.4533	0.4160	0.4715
APS [microns]	630	653	609	579	661
Fines (<125 μm) (%)	3.1	2.0	1.9	3.8	3.3

TABLE 2. Film Properties

Property	Units	1		2		3		4		5	
Amperage	amps	59.4		60.1		59.9		59.9		60.4	
Pressure	MPa	50.2		49.5		50.8		46.4		46.4	
Max Draw Down	m/min	54.9		51.8		57.9		51.8		51.8	
Gauge	microns	25.4	12.7	25.4	12.7	25.4	12.7	25.4	12.7	25.4	13
Dart Drop Impact F50	g	344	344	335	296	317	266	287	269	341	326
MD Tear	g/micron	1.01	0.97	1.18	0.76	1.38	1.02	0.92	0.84	1.05	1.00
TD Tear	g/micron	9.40	1.91	9.38	2.91	7.66	2.49	10.69	3.64	11.97	3.80

CLAIMS

What is claimed is:

1. A bimetallic catalyst composition comprising a fluorided metallocene catalyst component, a non-metallocene catalyst component, and an activator, the catalyst components and activator supported on an inorganic oxide dehydrated at a temperature of greater than 800°C.

2. The bimetallic catalyst composition of Claim 1, wherein the fluorided metallocene compound is described by the formulas:

$Cp^ACp^BMX_n$, Cp^AMX_n or $Cp^A(A)Cp^BMX_n$

wherein M is a Group 4, 5 or 6 atom;

Cp^A and Cp^B are each bound to M and are independently selected from the group consisting of cyclopentadienyl ligands, substituted cyclopentadienyl ligands, ligands isolobal to cyclopentadienyl and substituted ligands isolobal to cyclopentadienyl;

(A) is a divalent bridging group bound to both Cp^A and Cp^B selected from the group consisting of divalent C_1 to C_{20} hydrocarbyls and C_1 to C_{20} heteroatom containing hydrocarbonyls; wherein the heteroatom containing hydrocarbonyls comprise from one to three heteroatoms;

at least one X is a fluoride ion; and

n is an integer from 1 to 3.

3. The bimetallic catalyst composition of Claim 1, wherein the metallocene compound is described by the formulas:

$Cp^ACp^BMX_n$ or $Cp^A(A)Cp^BMX_n$

wherein M is zirconium or hafnium;

Cp^A and Cp^B are each bound to M and are independently selected from the group consisting of substituted cyclopentadienyl ligands, substituted indenyl ligands, substituted tetrahydroindenyl ligands, substituted fluorenyl ligands, and heteroatom derivatives of each; wherein the substituent groups are selected from the group consisting of C_1 to C_{10} alkyls and halogens;

(A) is a divalent bridging group bound to both Cp^A and Cp^B selected from the group consisting of divalent C_1 to C_{20} hydrocarbyls and C_1 to C_{20} heteroatom containing hydrocarbonyls; wherein the heteroatom containing hydrocarbonyls comprise from one to three heteroatoms;

at least one X is a fluoride ion; and

n is an integer from 1 to 3.

4. The bimetallic catalyst composition of Claim 1, wherein at least one Cp is substituted.

5. The bimetallic catalyst composition of Claim 1, wherein at least one Cp is disubstituted.

6. The bimetallic catalyst composition of Claim 1, wherein at least one Cp has from 2 to 5 substitutions.

7. The bimetallic catalyst composition of Claim 1, wherein the substituent groups are selected from the group consisting of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, and tert-butyl.

8. The bimetallic catalyst composition of Claim 1, wherein the bimetallic catalyst also includes a Ziegler-Natta catalyst component.

9. The bimetallic catalyst composition of Claim 8, wherein the Ziegler-Natta catalyst component comprises a compound selected from the group consisting of Group 4 and Group 5 halides, oxides, oxyhalides, alkoxides, and mixtures thereof.

10. The bimetallic catalyst composition of Claim 1, wherein the inorganic oxide is dehydrated at a temperature of greater than 830°C.

11. The process of Claim 1, wherein the support material comprises silica dehydrated at a temperature of 870 °C or more.

12. The bimetallic catalyst composition of Claim 1, wherein the inorganic oxide is silica.

13. A process for producing a bimodal polyolefin composition comprising: contacting hydrogen and ethylene monomers with the supported bimetallic catalyst composition of Claim 1 to form a bimodal polyolefin composition.

14. The process of Claim 13, wherein the bimetallic catalyst has a productivity of at least 3000 grams polymer/gram catalyst.

15. The process of Claim 13, wherein the bimetallic catalyst has a productivity of at least 3500 grams polymer/gram catalyst.

16. The process of Claim 13, wherein from 0.01 wt. ppm to 200 wt. ppm of water is also contacted.

17. The process of Claim 13, wherein the first catalyst component is a Ziegler-Natta catalyst.

18. The process of Claim 17, wherein the Ziegler-Natta catalyst component comprises a compound selected from the group consisting of Group 4 and Group 5 halides, oxides, oxyhalides, alkoxides, and mixtures thereof.

19. The process of Claim 13, wherein the supported bimetallic catalyst composition includes a support material comprising a Group 13 or 14 inorganic oxide dehydrated at a temperature of from 800°C to 1000°C.

20. The process of Claim 13, wherein Cp^A and Cp^B are selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, and substituted versions thereof.

21. The process of Claim 13, wherein Cp^A and Cp^B are selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, and substituted versions thereof; characterized in that at least one of either Cp^A or Cp^B has at least one R group selected from C_1 to C_{10} alkyls.

22. The process of Claim 13, further comprising combining a comonomer selected from C_3 to C_{12} olefins.

23. The process of Claim 13, further comprising combining a comonomer selected from the group consisting of 1-propene, 1-butene, 1-hexene and 1-octene.

24. The process of Claim 13, wherein the monomers are contacted with the supported bimetallic catalyst in a single reactor vessel and form the bimodal polyolefin composition in the same reactor vessel.

25. The process of Claim 13, wherein the bimetallic catalyst composition further comprises alumoxane.

26. The process of Claim 13, wherein the molar ratio of hydrogen to ethylene ranges from 0.001 to 0.015.

27. The process of Claim 13, further comprising the steps of:

(a) providing a particulate support material comprising silica;

(b) heating the particulate support material to a temperature of 800 °C or more for a time sufficient to form a dehydrated support material comprising dehydrated silica;

(c) combining the dehydrated support material with a non-polar hydrocarbon to provide a support slurry;

(d) providing a first catalyst component that includes a non-metallocene catalyst;

(e) providing a second catalyst component that includes a metallocene catalyst compound having at least one fluoride or fluorine containing leaving group;

(f) combining the support slurry with the first and second catalyst components to form a supported bimetallic catalyst composition;

(g) contacting monomers with the bimetallic catalyst composition for a time sufficient to form a bimodal polyolefin composition;

wherein the bimodal polyolefin composition has a density of from 0.86 g/cm^3 to 0.97 g/cm^3, a molecular weight distribution of from 5 to 80, a I_2 of from 0.01 dg/min to 50 dg/min, and a I_{21}/I_2 of from 40 to 500.

28. A bimodal polyolefin composition of Claim 27, wherein the bimodal polyolefin composition has a density of from 0.86 g/cm^3 to 0.97 g/cm^3, a molecular weight distribution of from 5 to 80, a I_2 of from 0.01 dg/min to 50 dg/min, and a I_{21}/I_2 of from 40 to 500.

29. A film made from the composition of Claim 28, wherein the film has a Dart Drop Impact F50 Value of at least 100 [g] on 25.4 micron film and 75 [g] on 12.5 micron film.

30. The film of Claim 29, wherein the film has an MD Tear value of at least 0.4 g/micron on 25.4 micron film and at least 0.2 g/micron on 12.5 micron film.

31. The film of Claim 29, wherein the film has a TD Tear value of at least 1.5 g/micron on 24.5 micron film and 1.0 g/micron on 12.5 micron film.

32. The film of Claim 29, wherein the polyolefin comprises ethylene derived units.

33. The film of Claim 29, wherein the polyolefin comprises ethylene derived units and units derived from the group consisting of C_3 to C_{10} olefins.

34. The film of Claim 29, wherein the polyolefin comprises ethylene derived units and units derived from the group consisting of C_4 to C_8 α-olefins.

35. The film of Claim 29, wherein the polyolefin has a molecular weight distribution of from 10 to 60.

36. The film of Claim 29, wherein the polyolefin has a I_2 of from 0.002 to 2 dg/min.

37. The film of Claim 29, wherein the polyolefin has a I_{21} of from 1 to 10 dg/min.

38. The film of Claim 29, wherein the polyolefin has a bulk density of from 0.420 to 0.600 g/cm^3.

39. A process for producing the bimodal polyolefin composition comprising the steps of:

(a) contacting the catalyst composition of Claim 1, the fluorinated metallocene catalyst compound produced by contacting a metallocene catalyst compound with an fluorinated inorganic salt for a time sufficient to form a fluorinated metallocene catalyst compound;

(b) isolating the fluorided metallocene catalyst compound;

(c) combining the fluorided metallocene catalyst compound with an activator and ethylene monomers and optionally a support at from 50°C to 120°C; and

(d) isolating polyethylene.

40. The process of Claim 39, wherein the fluorided metallocene, activator and support are also combined with a Ziegler-Natta catalyst comprising titanium halide.

41. The process of Claim 39, wherein the fluorided metallocene, activator and support are combined and isolated prior to combining with ethylene monomers.

42. The process of Claim 39, wherein the fluorinated inorganic salt is characterized by generating fluoride ions when contacted with a diluent that is at least 50 wt% water.

43. The process of Claim 39, wherein the fluorinated inorganic salt is described by the general formula:

$[\alpha]_a[\beta]_b$,

wherein α is a cationic species selected from the group consisting of Group 1 and 2 cations, anilinium and substituted versions thereof, and NH_4^+, NH_3R, NH_2R_2, and NHR_3^+ wherein R is selected from the group consisting of hydride, chloride, C_1 to C_{10} alkyl and C_6 to C_{12} aryls;

β is an anionic species selected from the group consisting of fluorine ions and moieties comprising fluorine and one or more elements selected from the group consisting of hydrogen, silicon, carbon, phosphorous, oxygen, aluminum and boron; and

a and b are integers from 1 to 10.

44. The process of Claim 39, wherein the inorganic salt is selected from the group consisting of $(NH_4)_3AlF_6$, NH_4HF_2, NaF, KF, NH_4F, $(NH_4)_2SiF_6$ and combinations thereof.