COMPOSITIONS INCLUDING GERMANIUM BRIDGED GROUP IV METALLOCENE DICHLORIDES

Field of Disclosure

[0001] Embodiments of the present disclosure are directed towards compositions including unsupported Ge bridged Group IV metallocene dichlorides, supported catalyst systems, and methods utilizing the metallocene dichlorides to make activated supported catalyst systems without a drying process, which are then used to make polyolefin polymers.

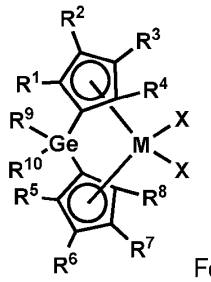
Background

[0002] Polymers may be utilized for a number of products including pipes, films, fibers, nonwoven and/or woven fabrics, extruded articles, and/or molded articles, among others. Polymers can be formed by reacting one or more types of monomer in a polymerization reaction. There is continued focus in the industry on developing new and improved materials and/or processes that may be utilized to form polymers.

Summary

[0003] The present disclosure provides various embodiments, including: a composition for making a polyolefin polymer including:

[0004] an unsupported Ge bridged Group IV metallocene represented by Formula I:



Formula I

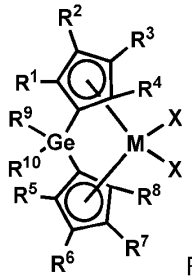
[0005] wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 heteroaryl or aryl, M is a Group IV atom, and each X is independently a leaving group; an activator; a support; and a solvent.

Detailed Description

[0006] Compositions including the treatment of Ge bridged Group IV metallocene complexes with a support and activator, or supported activator, and the mixtures are used directly, without a drying step, as heterogeneous activated supported catalyst systems to

make polyolefin polymers are discussed herein. Surprisingly, undried supported catalyst compositions including the Ge bridged Group IV metallocenes, which can be made *in situ* by mixing the initially unsupported metallocenes represented by Formula (I) and a supported activator in an alkane hydrocarbon solvent, without a drying step, can be utilized to provide increased productivity and/or increased polymerization efficiency as compared to making polymers with other supported metallocene compositions using similar polymerization conditions. The dichloride complexes, i.e. the unsupported Ge bridged Group IV metallocene dichlorides (Formula I), where X = Cl, in an alkane hydrocarbon solvent are first mixed with a heterogeneous support and activator, and are used without a drying step to render a highly active heterogeneous supported catalyst system, which are then used in the polymerizations. This is surprising because typically Group IV metallocene dichloride complexes have poor solubility in alkane hydrocarbon solvents, and therefore typically have poor activation with typical activators, including supported activators, in hydrocarbon solvents rendering them as poor catalysts, either supported or unsupported, and therefore are not useful as catalyst systems. Also, advantageously, compositions including the undried supported Ge bridged Group IV metallocene heterogeneous catalyst systems can provide increased C_6 consumption, as compared to making polymers with other types of supported metallocene compositions using similar polymerization conditions. The compositions including these *in situ* prepared, undried supported Ge bridged Group IV metallocene heterogeneous catalyst systems can be utilized to provide polymers with a range of weight average molecular weights (Mw), including polymers with fractional melt indices ($I_2 \leq 0.5$), narrow molecular weight distributions as well as melt flow ratios (MFR, $I_{21}/I_2 \leq 20$), and/or polymers with high comonomer incorporation.

[0007] The Ge bridged Group IV metallocenes can be represented by Formula I



Formula I.

[0008] Embodiments provide that R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each

independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group.

[0009] One or more embodiments provide that M is Ti. One or more embodiments provide that M is selected from Zr and Hf. One or more embodiments provide that M is Zr. One or more embodiments provide that M is Hf.

[0010] One or more embodiments provide that each X is independently a halogen. One of more embodiments provide that X is Cl.

[0011] One or more embodiments provide that only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C8 alkyl while three of R^5-R^8 are H. One or more embodiments provide that only one of R^1-R^4 is a C1 to C3 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C3 alkyl while three of R^5-R^8 are H. One or more embodiments provide that only one of R^1-R^4 is a C3 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C3 alkyl while three of R^5-R^8 are H.

[0012] Embodiments provide that R^9-R^{10} are each independently hydrogen, a C1 to C6 alkyl, or a C3 to C30 aryl or heteroaryl. One or more embodiments provide that R^9-R^{10} are each independently a C1 to C3 alkyl. One or more embodiments provide that R^9-R^{10} are each independently a C1 to C2 alkyl. One or more embodiments provide that R^9-R^{10} are each independently a C1 alkyl.

[0013] One or more embodiments provide that the dichloride complexes of Formula I, wherein X is Cl, are soluble in hydrocarbon solvents.

[0014] As used herein, all reference to the Periodic Table of the Elements and groups thereof is to the NEW NOTATION published in HAWLEY'S CONDENSED CHEMICAL DICTIONARY, Thirteenth Edition, John Wiley & Sons, Inc., (1997) (reproduced there with permission from IUPAC), unless reference is made to the Previous IUPAC form noted with Roman numerals (also appearing in the same), or unless otherwise noted.

[0015] As used herein, an "alkyl" includes linear and branched radicals that are deficient by one hydrogen. Thus, for example, CH_3 ("methyl"), CH_2CH_3 ("ethyl"), and $CH_2CH_3CH_3$ ("propyl") are examples of alkyls.

[0016] As used herein, an "alkenyl" includes linear and branched radicals that are deficient by one hydrogen; alkynyl radicals include linear and branched radicals deficient by one hydrogen radical.

[0017] As used herein, "aryl" groups include phenyl, naphthyl, pyridyl and other radicals whose molecules have the ring structure characteristic of benzene, naphthylene, phenanthrene, anthracene, etc. It is understood that an "aryl' group can be a C_5 to C_{20} aryl group. 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. It is understood that an "aralkyl" group can be a C_7 to C_{20} aralkyl group. An "alkylaryl" is an aryl group having one or more alkyl groups pendant therefrom.

[0018] 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".

[0019] The Ge bridged Group IV metallocene dichlorides discussed herein can be made by processes by those skilled in the art, i.e. with conventional solvents, reaction conditions, reaction times, and isolation procedures, utilized for making known metallocenes.

[0020] As mentioned, the Ge bridged Group IV metallocenes can be utilized as unsupported complexes to make active supported catalyst systems or compositions. One or more embodiments provide that the composition includes a number of components that have undergone a conventional drying, or spray-drying process. Various conventional drying or spray-drying process are known in the art and are suitable for forming the compositions disclosed herein.

[0021] As mentioned, the Ge bridged Group IV metallocenes can be utilized to make supported catalyst systems or compositions. In some embodiments the Ge bridged Group IV metallocene and support material are contacted together in an inert hydrocarbon liquid to give a suspension in the inert hydrocarbon liquid, then the suspension is contacted with the activator to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0022] In some embodiments the Ge bridged Group IV metallocene and activator are contacted together in an inert hydrocarbon liquid to give a solution of a catalyst in the

inert hydrocarbon liquid, then the solution is contacted with the support material to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0023] In some embodiments the activator and the support material are contacted together in an inert hydrocarbon liquid to give a suspension of a supported activator in the inert hydrocarbon liquid, then the suspension is contacted with the Ge bridged Group IV metallocene to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0024] In some embodiments the Ge bridged Group IV metallocene and supported activator are contacted together in an inert hydrocarbon liquid to give a suspension of the supported catalyst.

[0025] In some embodiments the Ge bridged Group IV metallocene, activator, and support material are contacted together simultaneously in an inert hydrocarbon liquid to give a suspension of the supported catalyst, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0026] In some embodiments the inert hydrocarbon liquid is not removed from the supported catalyst system, and the supported catalyst system is used as a suspension.

[0027] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may include a step of decanting some of the inert hydrocarbon liquid from the suspension. In some embodiments the decanting method comprises pouring off excess inert hydrocarbon liquid from the suspension to give a concentrated suspension of the supported catalyst system.

[0028] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may include a step of drying the supported catalyst system. The drying step may comprise a conventional drying method or a spray-drying method.

[0029] In one or more embodiments, the spray-drying process may comprise atomizing a composition including an activator. A number of other known components may be utilized in the spray-drying process. An atomizer, such as an atomizing nozzle or a centrifugal high-speed disc, for example, may be used to create a spray or dispersion of droplets of the composition. The droplets of the composition may then be rapidly dried by contact with an inert drying gas. The inert drying gas may be any gas that is non-reactive under the conditions employed during atomization, such as nitrogen, for example. The inert drying gas may meet the composition at the atomizer, which produces a droplet

stream on a continuous basis. Dried particles of the composition may be trapped out of the process in a separator, such as a cyclone, for example, which can separate solids formed from a gaseous mixture of the drying gas, solvent, and other volatile components.

[0030] A conventionally dried or spray-dried composition may have the form of a free-flowing powder, for instance. After the conventional or spray-drying process, the conventional or spray-dried composition and a number of known components may be utilized to form a slurry. The conventional or spray-dried composition may be utilized with a diluent to form a slurry suitable for use in olefin polymerization, for example. In one or more embodiments, the slurry may be combined with the unsupported Ge bridged Group IV dichloride metallocene prior to delivery into a polymerization reactor.

[0031] In one or more embodiments, a composition may be formed by contacting a conventionally dried or spray dried activator particle, such as spray dried fumed silica, e.g. CABOSIL, and methylaluminoxane(MAO), with a solution of the unsupported Ge bridged Group IV metallocene dichloride in an alkane hydrocarbon solvent. Such a solution of the unsupported Ge bridged Group IV metallocene dichlorides may be made in an inert hydrocarbon solvent, for instance, and can be referred to as a trim solution. Such a composition comprised of contacting a trim solution of the unsupported Ge bridged Group IV metallocene complex with a conventionally dried or spray dried activator particle, such as spray-dried MAO, may be made *in situ* in a feed line prior to entry or injection into a slurry or gas phase polymerization reactor by contacting the trim solution with a slurry, typically in mineral oil and/or alkane hydrocarbon solvent, of the conventionally dried or spray-dried activator particle.

[0032] As an example, various spray-drying conditions may be utilized for different applications. For instance, the spray-drying process may utilize a drying temperature from 115 to 185 °C. Various orifice sizes of the atomizing nozzle employed during the spray-drying process may be utilized to obtain different particle sizes. Alternatively, for other types of atomizers such as discs, rotational speed, disc size, and number/size of holes may be adjusted to obtain different particle sizes. One or more embodiments provide that a filler may be utilized in the spray-drying process. Different fillers and amounts thereof may be utilized for various applications.

[0033] The compositions disclosed herein, i.e. including using the unsupported Ge bridged Group IV metallocene dichloride complex, may be utilized to make a polymer. For instance, the unsupported Ge bridged Group IV metallocene dichloride complex may be activated, i.e. with an activator, to make a metallocene catalyst. One or more

embodiments provide that the conventionally dried or spray-dried compositions include an activator. As used herein, "activator" refers to any compound or combination of compounds, supported, or unsupported, which can activate a complex or a catalyst component, such as by creating a cationic species of the catalyst component, e.g., to provide the catalyst. The activator may also be referred to as a "co-catalyst". The activator can include a Lewis acid or a non-coordinating ionic activator or ionizing activator, or any other compound including Lewis bases, aluminum alkyls, and/or conventional-type co-catalysts. Activators include methylaluminoxane (MAO) and modified methylaluminoxane (MMAO), among others. One or more embodiments provide that the activator is methylaluminoxane. Activating conditions are well known in the art. Known activating conditions may be utilized.

[0034] The activator used in the heterogenization method may be any compound capable of reacting with the precatalyst of formula (I) to yield an active olefin polymerization catalyst. The activator may be a Lewis acid, a non-coordinating ionic activator, or an ionizing activator, or a Lewis base.

[0035] A molar ratio of metal, e.g., aluminum, in the activator to Group IV metal in the unsupported Ge bridged Group IV metallocene dichloride may be 10,000:1 to 0.5:1, 7,500:1 to 0.5:1, 5,000:1 to 0.5:1, 3500: 1 to 0.5: 1, 1500 : 1 to 0.5: 1, 750 : 1 to 0.5 : 1, 300 : 1 to 0.5 : 1, or 150: 1 to 1 : 1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the unsupported Ge bridged Group IV dichloride metallocene is at least 75:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the unsupported Ge bridged Group IV dichloride metallocene is at least 100:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the unsupported Ge bridged Group IV dichloride metallocene is at least 150:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the unsupported Ge bridged Group IV dichloride metallocene is at least 300:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the unsupported Ge bridged Group IV dichloride metallocene is at least 750:1. Suitable activators are commercially available. In some embodiments the aluminum based activator is an alkylaluminum or an alkylaluminoxane (alkylalumoxane). Any alkyl group may be utilized. In some embodiments, each alkyl of the alkylaluminum or alkylaluminoxane independently may be a $(C_1\text{-}C_8)$alkyl, alternatively a $(C_1\text{-}C_7)$alkyl, alternatively a $(C_1\text{-}C_6)$alkyl, alternatively a $(C_1\text{-}C_4)$alkyl.

[0036] The alkylaluminum may be a trialkylaluminum, alkylaluminum halide, or alkylaluminum alkoxide (diethylaluminum ethoxide). The trialkylaluminum may be trimethylaluminum, triethylaluminum ("TEAl"), tripropylaluminum, or tris(2-methylpropyl)aluminum. The alkylaluminum halide may be diethylaluminum chloride. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

[0037] A number of components discussed herein can be supported on the same or on separate supports, or one or more of the components, e.g., the unsupported Ge bridged Group IV metallocene dichloride, may be used in an unsupported form. Utilizing the support may be accomplished by any technique used in the art. One or more embodiments provide that the conventional drying process or spray-dry process is utilized. The support may be functionalized. One or more embodiments provide that the spray-dried compositions include a support.

[0038] A "support", which may also be referred to as a "carrier", refers to any support material, including a porous support material, such as talc, inorganic oxides, and inorganic chlorides. Other support materials include resinous support materials, e.g., polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

[0039] Support materials include inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 metal oxides. The terms "support", "solid support", "support material", and "solid support material" may be used interchangeably, and herein refer to a porous inorganic substance or organic substance. Some preferred supports include silica, fumed silica, alumina, silica-alumina, and mixtures thereof. Some other supports include magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays, 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 porous acrylic polymers, nanocomposites, aerogels, spherulites, and polymeric beads. An example of a support is fumed silica available under the trade name CABOSIL TS- 610, or other TS- or TG-series supports, available from Cabot Corporation. Fumed silica is typically a silica with particles 7 to 30 nanometers in size that has been treated with dimethylsilyldichloride such that a majority of the surface hydroxyl groups are capped.

[0040] Embodiments provide that the inorganic oxide support material is porous and has variable surface area, pore volume, and average particle size. In some embodiments, the surface area is from 50 to 1000 square meter per gram (m^2/g) and the

average particle size is from 1 to 300 micrometers (μm), alternatively 20 to 300 μm. Alternatively, the pore volume is from 0.5 to 6.0 cubic centimeters per gram (cm^3/g) and the surface area is from 200 to 600 m^2/g. Alternatively, the pore volume is from 1.1 to 1.8 cm^3/g and the surface area is from 245 to 375 m^2/g. Alternatively, the pore volume is from 2.4 to 3.7 cm^3/g and the surface area is from 410 to 620 m^2/g. Alternatively, the pore volume is from 0.9 to 1.4 cm^3/g and the surface area is from 390 to 590 m^2/g. Each of the above properties are measured using conventional techniques known in the art.

[0041] The support material may comprise silica, alternatively amorphous silica (not quartz), alternatively a high surface area amorphous silica, e.g., from 500 to 1000 m^2/g. Such silicas are commercially available from several sources including the Davison Chemical Division of W.R. Grace and Company, e.g., Davison 952 and Davison 955 products, and PQ Corporation, e.g., ES70 product. The silica may be in the form of spherical particles, which may be obtained by a spray-drying process. Alternatively, MS3050 product is a silica from PQ Corporation that is not spray-dried. As procured, these silicas are not calcined (i.e., not dehydrated). Silica that is calcined prior to purchase may also be used as the support material.

[0042] In some embodiments the solid support is a hydrophobic fumed silica. The hydrophobic fumed silica is made by contacting an untreated fumed silica, having surfaces containing silicon-bonded hydroxyl groups (Si-OH groups), with a hydrophobing agent, described later. In some embodiments the hydrophobing agent is a silicon-based hydrophobing agent, containing on average per molecule one or more functional groups reactive with a Si-OH group, to give the hydrophobic fumed silica. The silicon-based hydrophobing agent may be selected from $(CH_3)_2SiCl_2$, a polydimethylsiloxane, hexamethyldisilazane (HMDZ), and a $(C_1\text{-}C_{10})$alkylSi$((C_1\text{-}C_{10})$alkoxy$)_3$ (e.g., an octyltrialkoxysilane such as octyltriethoxysilane, i.e., $CH_3(CH_2)_7Si(OCH_2CH_3)_3$). In some embodiments the silicon-based hydrophobing agent is dimethyldichlorosilane, i.e., $(CH_3)_2SiCl_2$. In some embodiments the support material is a dimethyldichlorosilane-treated fumed silica, such as that sold as product TS-610 from Cabot Corporation.

[0043] The support material may be uncalcined or calcined. The calcined support material is made prior to being contacted with a precatalyst, activator, and/or hydrophobing agent, by heating the support material in air to give a calcined support material. The calcining comprises heating the support material at a peak temperature from

350 °C to 850 °C, alternatively from 400 °C to 800 °C, alternatively from 400 °C to 700 °C, alternatively from 500° to 650° C and for a time period from 2 to 24 hours, alternatively from 4 to 16 hours, alternatively from 8 to 12 hours, alternatively from 1 to 4 hours, thereby making the calcined support material. If the support material has not been heated in this way it is an uncalcined support material.

[0044] Embodiments provide that the compositions including unsupported Ge bridged Group IV metallocenes include the unsupported Ge bridged Group IV metallocene complex, an activator, a support, and a solvent.

[0045] As mentioned, the solvent can be a hydrocarbon solvent. Different solvents can be utilized for various applications. Examples of the solvent can include toluene, hexanes, methylcyclohexane, mineral oil, and combinations thereof.

[0046] Embodiments provide that the initially used unsupported Ge bridged Group IV metallocene can be from 0.000001 to 35 weight percent of the final supported composition based upon a total weight of the Ge bridged Group IV metallocene, the activator, the support, and the solvent. All individual values and subranges from 0.000001 to 35 weight percent are included; for example, the Ge bridged Group IV metallocene can be from a lower limit of 0.000001, 0.00001, 0.0001, 0.001, 0.01, 0.1, 1, 2, 3, or 5 weight percent to an upper limit of 35, 30, or 25 weight percent based on the total weight of the final combined Ge bridged Group IV metallocene, the activator, the support, and the solvent.

[0047] Embodiments provide that the activator can be from 0.00001 to 35 weight percent of the composition based upon a total weight of the initially used unsupported Ge bridged Group IV metallocene, the activator, the support, and the solvent. All individual values and subranges from 0.00001 to 35 weight percent are included; for example, the activator can be from a lower limit of 0.00001, 0.0001, 0.001, 0.01, 0.1, 1, 2, 3, or 5 weight percent to an upper limit of 35, 30, or 25 weight percent based on the total weight of the final combined Ge bridged Group IV metallocene, the activator, the support, and the solvent.

[0048] Embodiments provide that the support can be from 0.00001 to 35 weight percent of the composition based upon a total weight of the initially used unsupported Ge bridged Group IV metallocene, the activator, the support, and the solvent. All individual values and subranges from 0.00001 to 35 weight percent are included; for example, the support can be from a lower limit of 0.00001, 0.0001, 0.001, 0.01, 0.1, 1, 2, 3, or 5 weight percent to an upper limit of 35, 30, or 25 weight percent based on the total weight of the

final combined Ge bridged Group IV metallocene, the activator, the support, and the solvent.

[0049] Embodiments provide that the solvent can be from 5 to 99.99998 weight percent of the composition based upon a total weight of the initially used unsupported Ge bridged Group IV metallocene, the activator, the support, and the solvent. All individual values and subranges from 5 to 99.99998 weight percent are included; for example, the solvent can be from a lower limit of 5, 10, 15, 20, 30, or 50 weight percent to an upper limit of 99.99998, 99.9, 99, 95, 90, 85, or 80 weight percent based on the total weight of the final combined Ge bridged Group IV metallocene, the activator, the support, and the solvent.

[0050] As discussed herein, one or more embodiments provide that the activator and the support are spray-dried, while the Ge bridged Group IV metallocene is not spray-dried, e.g., the Ge bridged Group IV metallocene is unsupported.

[0051] In one or more embodiments, the spray-drying process may comprise atomizing a composition optionally one or more activators, optionally one or more support material, and optionally including the Ge bridged Group IV metallocene. A number of other known components may be utilized in the spray-drying process. An atomizer, such as an atomizing nozzle or a centrifugal high-speed disc, for example, may be used to create a spray or dispersion of droplets of the composition. The droplets of the composition may then be rapidly dried by contact with an inert drying gas. The inert drying gas may be any gas that is non-reactive under the conditions employed during atomization, such as nitrogen, for example. The inert drying gas may meet the composition at the atomizer, which produces a droplet stream on a continuous basis. Dried particles of the composition may be trapped out of the process in a separator, such as a cyclone, for example, which can separate solids formed from a gaseous mixture of the drying gas, solvent, and other volatile components.

[0052] A spray-dried composition may have the form of a free-flowing powder, for instance. After the spray-drying process, the spray-dried composition and a number of known components may be utilized to form a slurry. The spray-dried composition may be utilized with a diluent to form a slurry suitable for use in olefin polymerization, for example. In one or more embodiments, the slurry may be combined with one or more additional catalysts or other known components prior to delivery into a polymerization reactor.

[0053] As discussed herein, one or more embodiments provide that the activator and the support are conventionally dried, while the Ge bridged Group IV dichloride

metallocene is not spray-dried, e.g., the Ge bridged Group IV dichloride metallocene is unsupported.

[0054] A conventional drying method can include slowly increasing the mass or molar amount of less volatile chemical constituent(s) per unit volume of a continuous mixture comprising more volatile and less volatile chemical constituent(s) by gradually removing the more volatile chemical constituent(s) from the less volatile constituent(s) of the continuous mixture to give a concentrate having a higher mass or molar amount of the less volatile chemical constituent(s) per unit volume than did the continuous mixture, wherein the rate of gradual removing is limited by a relatively small evaporative surface area to mass ratio (compared to spray-drying). The concentrate may be a precipitated solid.

[0055] The compositions disclosed herein and an olefin can be contacted under polymerization conditions to make a polymer, e.g., a polyolefin polymer. This can include the use of an initially unsupported germanium bridged Group IV metallocene dichloride complex in an alkane hydrocarbon solvent; an activator; and a support, wherein the activator is supported. The polymerization process may be a suspension polymerization process, a slurry polymerization process, and/or a gas phase polymerization process. The polymerization process may utilize using known equipment and reaction conditions, e.g., known polymerization conditions. The polymerization process is not limited to any specific type of polymerization system. The polymer can be utilized for a number of articles such as films, fibers, pipes, nonwoven and/or woven fabrics, extruded articles, and/or molded articles.

[0056] One or more embodiments provide that the polymers are made utilizing a gas-phase reactor system. One or more embodiments provide that a single gas-phase reactor is utilized. In other words, polymerization reaction can occur in only one reactor. For instance, the polymers can be made utilizing a fluidized bed reactor. Gas-phase reactors are known and known components may be utilized for the fluidized bed reactor.

[0057] As used herein an “olefin,” which may be referred to as an “alkene,” refers to a linear, branched, or cyclic compound including carbon and hydrogen and having at least one double bond. As used herein, when a polyolefin, polymer, and/or copolymer is referred to as comprising, e.g., being made from, an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an ethylene content of 75 wt% to 95 wt%, it is understood that the polymer unit in the copolymer is derived from ethylene in the polymerization reaction(s)

and the derived units are present at 75 wt% to 95 wt%, based upon the total weight of the polymer. A higher α-olefin refers to an α-olefin having 3 or more carbon atoms.

[0058] Polyolefins made with the compositions disclosed herein can made from olefin monomers such as ethylene, i.e., polyethylene, and linear or branched higher alpha-olefin monomers containing 3 to 20 carbon atoms. Examples of higher alpha-olefin monomers include, but are not limited to, propylene, butene, pentene, 1-hexene (which can be referred to more simply as hexene), and 1-octene. One or more embodiments provide that the olefin includes ethylene, 1-butene, 1-hexene, or combinations thereof. Examples of polyolefins include ethylene-based polymers, having at least 50 wt % ethylene, including ethylene-1-butene, ethylene-1-hexene, and ethylene-1-octene copolymers, among others. One or more embodiments provide that the polymer can include from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polymer. All individual values and subranges from 50 to 99.9 wt % are included; for example, the polymer can include from a lower limit of 50, 60, 70, 80, or 90 wt % of units derived from ethylene to an upper limit of 99.9, 99.7, 99.4, 99, 96, 93, 90, or 85 wt % of units derived from ethylene based on the total weight of the polymer. The polymer can include from 0.1 to 50 wt % of units derived from comonomer based on the total weight of the polymer. One or more embodiments provide that ethylene is utilized as a monomer and 1-hexene is utilized as a comonomer.

[0059] As mentioned, the polymers made with the compositions disclosed herein can be made in a fluidized bed reactor. The fluidized bed reactor can have a reaction temperature from 10 to 130 °C. All individual values and subranges from 10 to 130 °C are included; for example, the fluidized bed reactor can have a reaction temperature from a lower limit of 10, 20, 30, 40, 50, or 55 °C to an upper limit of 130, 120, 110, 100, 90, 80, 70, or 60 °C.

[0060] The fluidized bed reactor can have an ethylene partial pressure from 30 to 350 pounds per square inch (psi). All individual values and subranges from 30 to 350 are included; for example, the fluidized bed reactor can have an ethylene partial pressure from a lower limit of 30, 45, 60, 75, 85, 90, or 95 psi to an upper limit of 350, 300, 240, 220, 200, 150, or 125 psi.

[0061] One or more embodiments provide that ethylene is utilized as a monomer and hexene is utilized as a comonomer. The fluidized bed reactor can have a comonomer to ethylene mole ratio, e.g., C_6/C_2, from 0.0001 to 0.100. All individual values and subranges from 0.0001 to 0.100 are included; for example, the fluidized bed reactor can

have a comonomer to ethylene mole ratio from a lower limit of 0.0001, 0.0005, 0.0007, 0.001, 0.0015, 0.002, 0.007, or 0.010 to an upper limit of 0.100, 0.080, or 0.050.

[0062] When hydrogen is utilized for a polymerization process, the fluidized bed reactor can have a hydrogen to ethylene mole ratio (H_2/C_2) from 0.00001 to 0.90000, for instance. All individual values and subranges from 0.00001 to 0.90000 are included; for example, the fluidized bed reactor can have a H_2/C_2 from a lower limit of 0.00001, 0.00005, or 0.00008 to an upper limit of 0.90000, 0.500000, 0.10000, 0.01500, 0.00700, or 0.00500. One or more embodiments provide that hydrogen is not utilized.

[0063] The polymers made with the compositions disclosed herein can have a density from 0.8700 to 0.9700 g/cm^3. All individual values and subranges from 0.8700 to 0.9700 g/cm^3 are included; for example, the polymer can have a density from a lower limit of 0.8700, 0.9000, 0.9100, 0.9150, 0.9200, or 0.9250 g/cm^3 to an upper limit of 0.9700, 0.9600, 0.9500, 0.9450, 0.9350, or 0.9300 g/cm^3. Density can be determined by according to ASTM D792.

[0064] The polymers made with the compositions disclosed herein can have a melt index (I_2) from 0 to 400 dg/min. I_2 can be determined according to ASTM-1238, Condition B (190 °C, 2.16 kg). All individual values and subranges from 0.05 to 400 dg/min are included; for example, the polymer can have an I_2 from a lower limit of 0, 0.05, 0.07 or 0.10 dg/min to an upper limit of 400, 375, or 350 dg/min.

[0065] The polymers made with the compositions disclosed herein can have a weight average molecular weight (Mw) from 10,000 to 1,000,000 g/mol. All individual values and subranges from 10,000 to 1,000,000 g/mol are included; for example, the polymers can have an Mw from a lower limit of 10,000, 15,000, or 20,000 g/mol to an upper limit of 1,000,000, 800,000, 600,000, or 350,000 g/mol. Mw can be determined by gel permeation chromatography (GPC), as is known in the art. GPC is discussed herein.

[0066] The polymers made with the compositions disclosed herein can have a weight average molecular weight to number average molecular weight ratio (Mw/Mn), which may be referred to as polydispersity index or molecular weight distribution, from 2.0 to 30.0. All individual values and subranges from 2.0 to 30.0 are included; for example, the polymers can have an Mw/Mn from a lower limit of 2.0, 2.2, or 2.3 to an upper limit of 30.0, 28.0, or 26.0.

[0067] Advantageously, utilizing the heterogeneous supported catalyst compositions made from the homogeneous solutions of the unsupported Ge bridged

Group IV metallocene dichlorides, in alkane hydrocarbon solvents, to make polymers can provide improved, i.e. increased, productivity as compared to making polymers with other metallocene compositions, including other methods of supporting metallocenes, using similar polymerization conditions. Productivity (grams polymer/grams catalyst-hour) can be determined as a calculated ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst added to the reactor.

[0068] Advantageously, utilizing the heterogeneous supported catalyst compositions made from the homogeneous solutions of the unsupported Ge bridged Group IV metallocene dichlorides, in alkane hydrocarbon solvents, to make polymers can provide improved, i.e. increased, polymerization efficiency as compared to making polymers with other metallocene compositions, including other methods of supporting metallocenes, using similar polymerization conditions. Efficiency (grams polymer/grams catalyst metal) can be determined as a ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst metal added to the reactor.

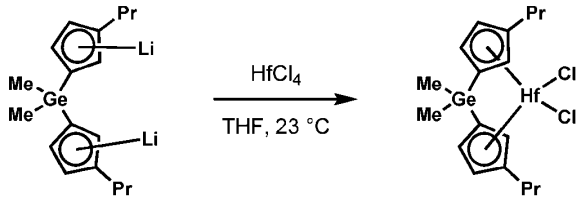
[0069] Advantageously, utilizing the heterogeneous supported catalyst compositions made from the homogeneous solutions of the unsupported Ge bridged Group IV metallocene dichlorides, in alkane hydrocarbon solvents, to make polymers can provide improved, i.e. increased, comonomer, i.e., 1-hexene, or C_6, consumption and incorporation, as compared to making polymers with other metallocene compositions, including other methods of supporting metallocenes, using similar polymerization conditions. Increased C_6 consumption and incorporation can be desirable due to increasing the degrees of freedom in the design of catalyst system(s) and/or resin(s) to unlock improved product performance.

[0070] Advantageously, utilizing the heterogeneous supported catalyst compositions made from the homogeneous solutions of the unsupported Ge bridged Group IV metallocene dichlorides, in alkane hydrocarbon solvents, to make polymers can provide improved, i.e. lesser or narrower, molecular weight distribution or polydispersity index (Mw/Mn or PDI, respectively), as compared to making polymers with other metallocene compositions, including other methods of supporting metallocenes, using similar polymerization conditions. Narrower molecular weight distributions can be desirable for improving product performance, and it can also increase the degrees of freedom in the design of catalyst system(s) and/or resin(s) to further unlock improved product attributes.

EXAMPLES

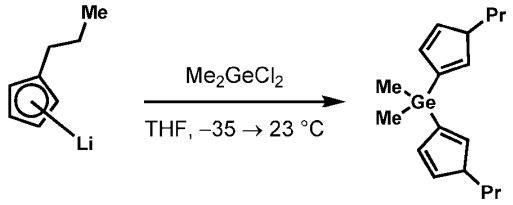
[0071] All solvents and reagents were obtained from commercial sources and used as received unless otherwise noted. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purified via passage through activated alumina and, in some cases, Q-5 reactant. Solvents used for experiments performed in a nitrogen-filled glovebox were further dried by storage over activated 3Å molecular sieves. Glassware for moisture-sensitive reactions was dried in an oven overnight prior to use. NMR spectra were recorded on Varian 400-MR and VNMRS-500 spectrometers. LC-MS analyses were performed using a Waters e2695 Separations Module coupled with a Waters 2424 ELS detector, a Waters 2998 PDA detector, and a Waters 3100 ESI mass detector. LC-MS separations were performed on an XBridge C18 3.5 µm 2.1x50 mm column using a 5:95 to 100:0 acetonitrile to water gradient with 0.1% formic acid as the ionizing agent. HRMS analyses were performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8µm 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization. 1H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for 1H NMR data are reported in ppm downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. 13C NMR data were determined with 1H decoupling, and the chemical shifts are reported downfield from tetramethylsilane (TMS, δ scale) in ppm versus the using residual carbons in the deuterated solvent as references.

[0072] Metallocene 1, a Ge bridged Group IV dichloride metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Cl, was made as follows.



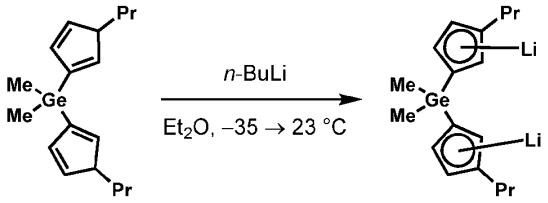
[0073] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (92.8 mg, 0.2896 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.3040 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The

resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to provide Metallocene 1, a dichloride complex, observed as a clear pale-yellow oil (95.4 mg, 0.1686 mmol, 58%). NMR indicated product exists as a mixture of *rac*- and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. **^{1}H NMR** (500 MHz, C_6D_6) δ 6.59 – 6.56 (m, 2H), *6.53– 6.49 (m, 2H), *5.57 (t, J = 2.7 Hz, 2H), 5.43 (t, J = 2.7 Hz, 2H), 5.25 (t, J = 2.4 Hz, 2H), *5.16 (t, J = 2.3 Hz, 2H), 2.88 – 2.70 (m, 4H), 1.61 – 1.47 (m, 4H), 0.87 (td, J = 7.4, 5.5 Hz, 6H), *0.33 (s, 3H), 0.29 (s, 6H), 0.26 (s, 3H). **^{13}C NMR** (126 MHz, C_6D_6) δ *140.01, 139.99, *125.30, 124.83, *111.29, 111.22, *110.74, 110.43, *107.83, 107.70, 32.25, *23.67, 23.62, 13.85, *13.83, *-6.18, -6.22, *-6.24.



[0074] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) in anhydrous deoxygenated THF (15 mL) was placed in a freezer (-35 °C) for 12 hrs, and then neat Me_2GeCl_2 (0.11 mL, 0.9738 mmol, 1.00 eq) was added. The red-orange mixture was allowed to sit in the freezer for 30 mins, removed, and the red-orange solution was stirred (500 rpm) at 23 °C for 4 hrs. The solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed to be a clear golden yellow oil (0.303 g, 0.9524 mmol, 98%). NMR indicated product exists as

a mixture of isomers. ^{1}H NMR (400 MHz, C_6D_6) δ 6.82 – 5.91 (m, 6H), 4.31 – 2.83 (m, 2H), 2.39 (t, *J* = 7.6 Hz, 4H), 1.57 (h, *J* = 7.4 Hz, 4H), 0.92 (t, *J* = 7.4 Hz, 6H), -0.08 (s, 6H).



[0075] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.303 g, 0.9524 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (0.86 mL, 2.143 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, removed from the freezer, and stirred (500 rpm) at 23 °C for 2 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried *in vacuo* to provide the dilithio salt, which was observed to be a white solid (0.273 g, 0.8269 mmol, 87%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6 with THF) δ 6.05 – 6.02 (m, 2H), 5.94 (t, *J* = 2.1 Hz, 2H), 5.91 (t, *J* = 2.6 Hz, 2H), 2.69 – 2.60 (m, 4H), 1.75 – 1.66 (m, 4H), 1.05 – 0.99 (m, 6H), 0.63 (s, 6H).

[0076] A spray-dried Ge bridged Group IV metallocene composition of metallocene 1 was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CAB-O-SIL TS-610; 0.583 grams) and toluene (37.5 grams) were added to a container and mixed, followed by addition of a 4.60 grams of a 10 % solution by weight of methylaluminoxane (MAO) in toluene. Then, the contents of the container were stirred for approximately 15 minutes. Then, metallocene 1 (0.018 grams) was added to the container and the contents of the container were stirred for approximately 45 minutes. Then, the contents of the container were spray-dried utilizing a Buchi Mini Spray Drier B-290 (140 °C set temperature; 75 °C outlet temperature; aspirator setting of 95 rotations per minute (rpm) and 150 rpm pump speed) to provide the comparative spray dried composition 1.

[0077] Example 1, a composition including an unsupported Ge bridged Group IV dichloride metallocene 1, which may also be referred to as a Trim Composition, was made as follows. In a nitrogen-purged glove box, supported MAO (SMAO) was added into a 10 mL Parr Bomb, and then an anhydrous deoxygenated hydrocarbon solvent, either toluene or hexanes (3.0 mL), was added to create a slurry. Then, a hexanes solution of the

unsupported Metallocene 1(0.0005 M) was then added to that slurry and mixed to make the trim composition Example 1.

[0078] Examples 2-5 were made as Example 1 with any changes shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Solution of Metallocene 1 (mL)	0.10	0.10	0.31	0.34	0.11
Amount of Metallocene 1 (mg)	0.029	0.028	0.091	0.096	0.031
SMAO (mg)	3.1	3.0	3.1	3.4	3.4
Solvent (mg)	Toluene (3,460)	Hexanes (4,539)	Toluene (3,460)	Toluene (3,460)	Toluene (3,460)
Metallocene 1	0.0008 wt%	0.0006 wt%	0.0026 wt%	0.0028 wt%	0.0009 wt%
SMAO	0.0895 wt%	0.0661 wt%	0.0895 wt%	0.0982 wt%	0.0982 wt%
Solvent	99.9 wt%	99.9 wt%	99.9 wt%	99.9 wt%	99.9 wt%
Total	100 wt%	100 wt%	100 wt%	100 wt%	100 wt%
Amount of Metallocene 1 on SMAO	0.93 wt%	0.92 wt%	2.9 wt%	2.7 wt%	0.90 wt%
Mixing Time	22 min.	23 min.	22 min.	23 min.	20 min.

[0079] After Example 1 was mixed for 22 minutes, then Example 1 was ready for polymerizations in a gas-phase in a 2-liter polymerization reactor.

[0080] Gas-phase reactor catalyst testing procedure: The gas phase reactor utilized is a 2-liter, stainless steel autoclave equipped with a mechanical agitator. For the polymerizations, the reactor was first dried for 1 hour by charging the reactor with NaCl (400 g) and maintaining a reactor temperature of 105 °C under nitrogen for 60 minutes. After drying the reactor, SMAO (5 g) was added to the reactor as a scavenger under nitrogen pressure. After adding SMAO, the reactor was sealed, and components were stirred. The reactor was then charged with hydrogen and 1-hexene pressurized with ethylene. Once the

system reached a steady state, a respective catalyst system was charged into the reactor at 80 °C to start polymerization. The reactor was brought to the desired reaction temperature and maintained at this temperature, while keeping the ethylene, 1-hexene, and hydrogen feed ratios consistent throughout the 1 hour run. At the end of the run, the reactor was cooled down, vented, and opened. The resulting product mixture was washed with water and methanol, then dried. Polymerization activity or productivity (grams polymer/gram catalyst-hour) and polymerization efficiency (grams polymer / gram metal (Hf)) was determined as the ratio of the calculated polymer produced, based on ethylene and hexene uptake/consumption, compared to the amount of catalyst added to the reactor. Conditions and results are reported in the following Tables.

Table 2

	Polymerization 1	Polymerization 2
Catalyst system	Example 1	Spray-dried Composition 1
Reaction Temp. (°C)	100	100
C_6/C_2	0.004	0.004
H_2/C_2	0.002	0.002
Charge (mg)	3.1	3.2
Productivity (gPE/gCat/hr)	15,500	23,400
Efficiency (gPE/gHf)	5,171,300	4,369,700
C_6 Consumption (%)	4.0	2.9
I_2 (dg/min)	5.1	5.2
I_{21} (dg/min)	76.9	183.0
I_{21} / I_2	15	35
Mw (g/mol)	78,500	79,800
Mp (g/mol)	55,300	41,900
PDI (Mw/Mn)	2.7	4.3
C6 Wt% (corrected)	3.3	4.3
Melt Temp. (°C)	122	122
ΔH (J/g)	134	154

Table 3

	Polymerization 3	Polymerization 4	Polymerization 5
Catalyst system	Example 2	Example 3	Spray-dried Composition 1
Reaction Temp. (°C)	100	100	100
C_6/C_2	0.004	0.004	0.004
H_2/C_2	0.0005	0.0005	0.0005
Charge (mg)	3.0	3.1	2.7
Productivity (gPE/gCat/hr)	21,100	32,400	17,200
Efficiency (gPE/gHf)	7,081,200	3,515,400	3,212,000
C_6 Consumption (%)	N.D.	2.8	1.9
I_2 (dg/min)	2.7	0.8	0.3
I_{21} (dg/min)	38.3	13.0	11.3
I_{21} / I_2	14	16	38
Mw (g/mol)	96,100	117,800	142,400
Mp (g/mol)	65,500	83,200	74,400
PDI (Mw/Mn)	2.8	2.6	3.8
C6 Wt% (corrected)	1.9	4.0	3.2
Melt Temp. (°C)	129	121	123
ΔH (J/g)	138	128	124

Table 4

.....	Polymerization 6	Polymerization 7
Catalyst system	Example 4	Spray-dried Composition 1
Reaction Temp. (°C)	80	80
C_6/C_2	0.004	0.004
H_2/C_2	0.0005	0.0005
Charge (mg)	3.4	3.0
Productivity (gPE/gCat/hr)	12,200	6,500

Efficiency (gPE/gHf)	1,370,900	1,213,800
C_6 Consumption (%)	2.5	1.6
I_2 (dg/min)	0.6	No flow
I_{21} (dg/min)	9.8	3.1
I_{21} / I_2	16	-
Mw (g/mol)	133,900	227,100
Mp (g/mol)	80,200	71,300
PDI (Mw/Mn)	3.1	6.7
C6 Wt% (corrected)	3.8	2.4
Melt Temp. (°C)	123	125
ΔH (J/g)	119	121

Table 5

	Polymerization 8	Polymerization 9
Catalyst system	Example 5	Spray-dried Composition 1
Reaction Temp. (°C)	80	80
C_6/C_2	0.016	0.016
H_2/C_2	0.0005	0.0005
Charge (mg)	3.4	3.3
Productivity (gPE/gCat/hr)	11,600	6,900
Efficiency (gPE/gHf)	4,033,600	1,288,500
C_6 Consumption (%)	21.6	16.2
I_2 (dg/min)	No flow	0.1
I_{21} (dg/min)	1.4	3.5
I_{21} / I_2	-	35
Mw (g/mol)	220,800	205,700
Mp (g/mol)	157,400	99,600
PDI (Mw/Mn)	2.8	4.4

C6 Wt% (corrected)	22.4	17.9
Melt Temp. (°C)	83	87
ΔH (J/g)	27	62

[0081] The data of Tables 2-5 show that utilizing Examples 1-5 provided improved, i.e., increased, productivity, as compared to utilizing Spray-dried Composition 1.

[0082] The data of Tables 2-5 show that utilizing Examples 1-5 provided improved, i.e., increased, efficiency, as compared to utilizing Spray-dried Composition 1.

[0083] The data of Tables 2-5 show that utilizing Examples 1-5 provided improved, i.e., increased, C_6 Consumption, as compared to utilizing Spray-dried Composition 1.

[0084] The data of Tables 2-5 show that utilizing Examples 1-5 provided lesser, i.e. narrower, melt flow ratios (MFR, I21/I2) as compared to utilizing Spray-dried composition 1.

[0085] The data of Tables 2-5 show that utilizing Examples 1, and 3-5 provided higher polymer peak maxima molecular weight (Mp) as compared to utilizing Spray-dried composition 1.

[0086] The data of Tables 5 show that utilizing Example 5 provided higher polymer weight average molecular weight (Mw) as compared to utilizing Spray-dried composition 1.

[0087] The data of Tables 2-5 show that utilizing Examples 1-5 provided lesser, i.e. narrower, polydispersity index (PDI) or molecular weight distribution (Mw/Mn) as compared to utilizing Spray-dried composition 1.

[0088] The data of Tables 3-5 show that utilizing Examples 3-5 provided polymer compositions with higher incorporation of hexene wt% (C6 wt%) as compared to utilizing Spray-dried composition 1.

[0089] Productivity (grams polymer/grams catalyst-hour) was determined as a calculated ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst added to the reactor.

[0090] Efficiency (grams polymer/grams catalyst metal) was determined as a ratio of polymer produced, based upon C2 and C6 uptake/consumption, as a ratio to an amount of catalyst metal, i.e. Hf, added to the reactor.

[0091] Melt index (I_2) was determined according to ASTM-1238, Condition B (190 °C, 2.16 kg). Flow index (I_{21}) was determined according to ASTM-1238, Condition B (190 °C, 21.6 kg).

[0092] Melt temperature (Tm) was determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample (10 mg) was used, and the second heating cycle was used to determine Tm.

[0093] Change of enthalpy (ΔH) was determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample (10 mg) was used, and the second heating cycle was used to determine ΔH.

[0094] C6 consumption (%) was determined for the trim composition examples 1 – 5 and the comparative spray dried composition 1 using the ratio of the amount of hexene consumed (grams) to amount of ethylene consumed (grams) in the gas phase reactor over the course of the 1 hour experiment, and then multiplying that ratio by 100.

[0095] Mw, Mn, Mp, and Polydispersity Index (Mw/Mn) were determined by GPC. Mp is reported as the molecular weight of the peak maxima.

[0096] GPC was determined as follows.

[0097] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 165 ºC and the column compartment was set at 155 ºC. The columns used were 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0098] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 g/mol and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 ºC with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160 ºC for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

[0099] $$M_{polyethylene} = A \times \left(M_{polystyrene}\right)^{B} \quad \text{(EQ1)}$$

[00100] where M is the molecular weight, A has a value of 0.3992 and B is equal to 1.0.

[00101] A third order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[00102] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 12,000 for the 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size columns.

[00103] Samples were prepared in a semi-automatic manner with the PolymerChar Instrument Control Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 3 hours at 165 ºC under low speed shaking.

[00104] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCONE software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

[00105]
$$Mn_{(GPC)} = \frac{\sum^{i} IR_i}{\sum^{i} \left(IR_i / M_{polyethylene_i} \right)} \quad \text{(EQ 2)}$$

[00106]
$$Mw_{(GPC)} = \frac{\sum^{i} \left(IR_i * M_{polyethylene_i} \right)}{\sum^{i} IR_i} \quad \text{(EQ 3)}$$

[00107] $$Mz_{(GPC)} = \frac{\sum_{i}^{i}\left(IR_i * M_{polyethylene_i}{}^{2}\right)}{\sum_{i}^{i}\left(IR_i * M_{polyethylene_i}\right)} \quad \text{(EQ 4)}$$

[00108] To monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate ($Flowrate_{(nominal)}$) for each sample by RV alignment of the respective decane peak within the sample ($RV_{(FM\ Sample)}$) to that of the decane peak within the narrow standards calibration ($RV_{(FM\ Calibrated)}$). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate ($Flowrate_{(effective)}$) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCONE Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

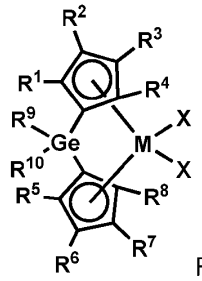
[00109] Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample)) (EQ5).

[00110] The comonomer content (C6 wt%), e.g., 1-hexene, incorporated in the polymers was determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement. Comonomer content was determined with respect to polymer molecular weight by use of an infrared detector (an IR5 detector) in a gel permeation chromatography measurement, as described in Analytical Chemistry 2014, 86(17), 8649-8656. "Toward Absolute Chemical Composition Distribution Measurement of Polyolefins by High-Temperature Liquid Chromatography Hyphenated with Infrared Absorbance and Light Scattering Detectors" by Dean Lee, Colin Li Pi Shan, David M. Meunier, John W. Lyons, Rongjuan Cong, and A. Willem deGroot. *Analytical Chemistry* 2014 *86* (17), 8649-8656.

What is claimed is:

1. A composition for making a polyolefin polymer comprising:

an unsupported Ge bridged Group IV metallocene complex represented by Formula I:



Formula I

wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group;

an activator;

a support; and

an inert hydrocarbon liquid.

2. The composition of claim 1, wherein M is selected from Hf and Zr.

3. The composition of any one of claims 1-2, wherein X is Cl or methyl.

4. The composition of any one of claims 1-3, wherein only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H and only one of R^5-R^8 is a C1 to C8 alkyl while three of R^5-R^8 are H.

5. The composition of any one of claims 1-3, wherein only one of R^1-R^4 is a C1 to C8 alkyl while three of R^1-R^4 are H, and R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl.

6. The composition of any one of claims 1-3, wherein two of R^1-R^4 is a C1 to C8 alkyl while two of R^1-R^4 are H, and R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl.

7. The composition of any one of claims 1-6, wherein the activator is a supported activator.

8. The composition of any one of claims 1-4, wherein:

a) the activator is added to the support in the inert hydrocarbon liquid, and then the complex represented by Formula I is added to make an activated supported catalyst system; or

b) the support is added to the activator in the inert hydrocarbon liquid, and then the complex represented by Formula I is added to make an activated supported catalyst system; or

c) the complex represented by Formula I is added to the activator in the inert hydrocarbon liquid, and then the support is added to make an activated supported catalyst system; or

d) the complex represented by Formula I is added to the support in the inert hydrocarbon liquid, and then the activator is added to make an activated supported catalyst system; or

e) the activator is added to the support in the hydrocarbon liquid, then dried by spray drying, decanting, or application of reduced pressure, and then the complex represented by Formula (I) is added to make an activated supported catalyst system; or

f) the support is added to the activator in the inert hydrocarbon liquid, then dried by spray drying, decanting, or application of reduced pressure, and then the complex represented by Formula I is added to make an activated supported catalyst system; or

e) the complex represented by Formula I is added to a mixture of supported activator in the inert hydrocarbon liquid to make an activated supported catalyst system; or

h) the complex of formula (I) is added to a mixture of a supported activator in the inert hydrocarbon liquid, and dried to make a dried activated supported catalyst system; or

i) the complex of formula (I) is added to a mixture of supported activator in the inert hydrocarbon liquid to make an activated supported catalyst system, which is then fed in line into a polymerization reactor without a drying step.

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9. The composition of any one of claims 1-4, wherein a mixture of the complex of Formula I, the support, and the activator in the invert hydrocarbon liquid are used without drying.

10. The composition of any one of claims 1-9, wherein the activator and the support are spray dried.

11. The composition of any one of claims 1-10, wherein the activator is methylaluminoxane.

12. The composition of any one of claims 1-11, wherein the support comprises silica or fumed silica.

13. The composition of any one of claims 1-12, wherein:

the complex represented by Formula I is from 0.000001 to 35 weight percent of the composition based upon a total weight of the complex represented by Formula I, the activator, the support, and the inert hydrocarbon liquid;

the activator is from 0.00001 to 35 weight percent of the composition based upon the total weight of the complex represented by Formula I, the activator, the support, and the inert hydrocarbon liquid;

the support is from 0.00001 to 35 weight percent of the composition based upon the total weight of the complex represented by Formula I, the activator, the support, and the inert hydrocarbon liquid; and

the inert hydrocarbon liquid is from 5 to 99.99998 weight percent of the composition based upon the total weight of the final combined Ge bridged Group IV dichloride metallocene, the activator, the support, and the inert hydrocarbon liquid.

14. The composition of any one of claims 1-13, wherein the inert hydrocarbon liquid comprises mineral oil, a hydrocarbon solvent, or a combination thereof.

15. The composition of any one of claims 1-14, wherein a supported catalyst system in the inert hydrocarbon liquid, is made in line prior to entry or injection into a slurry or gas phase polymerization reactor and is utilized for a polymerization reaction in the reactor directly without a drying or decanting step.

16. A method of making a catalyst system, the method comprising:
contacting the complex represented by Formula (I) of claim 1 in an inert hydrocarbon with a supported or spray dried activator particle, wherein the contacting step is performed in-line to a polymerization reactor.

17. A method of making a polyolefin polymer, the method comprising:
contacting, under polymerization conditions, an olefin with the composition of any one of claims 1-15 so as to polymerize the olefin, thereby making a polyolefin polymer.

18. The method of claim 17, wherein contacting, under polymerization conditions, the olefin with the composition of any one of claims 1-15 occurs in a gas phase polymerization process.

19. The method of any one of claims 17-18, wherein the olefin comprises ethylene, or a combination of ethylene and propylene, or a combination of ethylene and a (C_4-C_{20})alpha-olefin, and wherein the polyolefin polymer is an ethylene homopolymer, or an ethylene/propylene copolymer, or an ethylene/(C_4-C_{20})alpha-olefin copolymer.

20. The method of any one of claims 17-19, wherein the olefin comprises 1-butene.

21.. The method of claims 17-19, wherein the olefin comprises 1-hexene.