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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
23 May 2019 (23.05.2019)

WIPO | PCT

(10) **International Publication Number**
WO 2019/099292 A1

(51) International Patent Classification:
B01J 37/08 (2006.01) ***B01J 21/08*** (2006.01)
B01J 37/02 (2006.01) ***C08F 10/02*** (2006.01)
B01J 23/26 (2006.01)

(21) International Application Number: PCT/US2018/059953

(22) International Filing Date: 09 November 2018 (09.11.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15/816,131 17 November 2017 (17.11.2017) US

(71) Applicant: CHEVRON PHILLIPS CHEMICAL COMPANY LP [US/US]; 10001 Six Pines Drive, The Woodlands, Texas 77380 (US).

(72) Inventors; and
(71) Applicants: MCDANIEL, Max [US/US]; 1601 Melmart Drive, Bartlesville, Oklahoma 74006 (US). **CLEAR, Kathy S.** [US/US]; 2540 Williamsburg Street, Bartlesville, Texas 74006 (US). **SCHWERDTFEGER, Eric** [US/US]; 3801 E. Mountain Road, Bartlesville, Oklahoma 74003 (US). **PRAETORIUS, Jeremy** [US/US]; 2101 SE Hampden Road, Bartlesville, Oklahoma 74003 (US).

(74) Agent: WALTER, Chad; Chevron Phillips Chemical Company LP, 10001 Six Pines Drive, The Woodlands, Texas 77380 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
- — *with international search report (Art. 21(3))*
- — *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: METHODS OF PREPARING A CATALYST UTILIZING HYDROXYLATED UNSATURATED REAGENTS

(57) Abstract: A method of preparing a catalyst comprising a) contacting a titanium- containing compound, a solvating agent comprising an alpha, beta- unsaturated organic compound with a carbonyl or carboxyl group, and a solvent to form a solution; b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

WO 2019/099292 A1

METHODS OF PREPARING A CATALYST UTILIZING HYDROXYLATED UNSATURATED REAGENTS

TECHNICAL FIELD

[0001] The present disclosure relates to catalyst compositions. More specifically, the present disclosure relates to methods of preparing olefin polymerization catalyst compositions and polymers prepared from same.

BACKGROUND

[0002] An economically important class of olefin polymerization catalysts includes chromium-silica-titanium catalysts. Rigorous drying of the water-sensitive catalyst components is often required but drying processes increase the time and cost of production. Development of an aqueous solution suitable for depositing titanium onto a silica-based catalyst support would reduce the costs of production of olefin polymerization catalysts. Thus, there is an ongoing need to develop new methods of producing olefin polymerization catalysts.

SUMMARY

[0003] Disclosed herein is a method of preparing a catalyst comprising a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0004] Also disclosed herein is a method of preparing a catalyst comprising a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting the solution with a silica-support to form a titanated support; c) contacting the titanated support with a chromium-containing compound to form a pre-catalyst; and d) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0005] Also disclosed herein is a method of preparing a catalyst comprising a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting a silica support, a chromium-containing compound and the solution to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0006] Also disclosed herein is a method of preparing a catalyst comprising a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting a silica-support and a chromium-containing compound to form a chrominated support; c) contacting the solution of step (a) with the chrominated support of step (b) to form a pre-catalyst; and d) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0007] Also disclosed herein is a method of preparing a catalyst comprising a) contacting a silica support, a chromium-containing compound, a titanium-containing compound, a solvating agent, and a solvent to form a pre-catalyst; and b) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

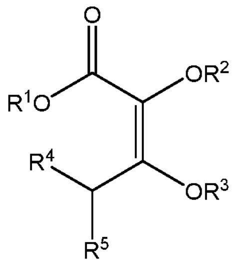
[0008] Also disclosed herein is a method of preparing a catalyst comprising a) contacting $Ti(OiPr)_4$, water, and ascorbic acid to form a solution; b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

DETAILED DESCRIPTION

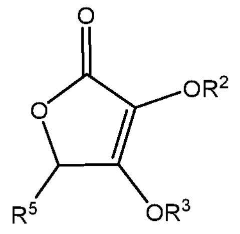
[0009] In an aspect, a method of preparing an olefin polymerization catalyst of the present disclosure comprises contacting an aqueous solution comprising a solvating agent and titanium with a chrominated silica-support under conditions suitable for formation of the olefin polymerization catalyst. In a further aspect, a method of preparing an olefin polymerization catalyst of the present disclosure comprises contacting a solution comprising a solvating agent, titanium and chromium with a silica-support under conditions suitable for formation of the olefin polymerization catalyst.

[0010] While these aspects may be disclosed under a particular heading, the heading does not limit the disclosure found therein. Additionally, the various aspects and embodiments disclosed herein can be combined in any manner.

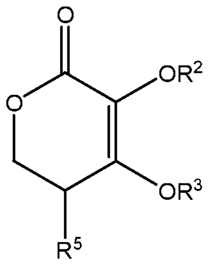
[0011] A method for preparation of an olefin polymerization catalyst as described herein comprises use of a solvating agent to form a titanium solution. In an aspect, the solvating agent used to form titanium solution comprises a β-hydroxy-α,β-unsaturated carbonyl-containing compound, an α,β-dihydroxy-α,β-unsaturated carbonyl-containing compound, or a combination thereof. In a further aspect, the solvating agent comprises a compound having Structure CS 1, Structure CS 2, Structure CS 3, Structure CS 4, Structure CS 5, or Structure CS 6



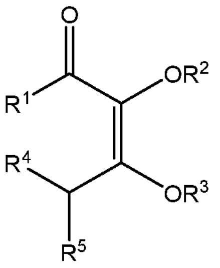
CS 1



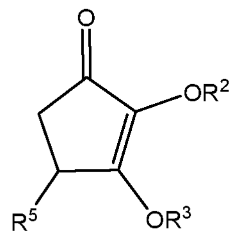
CS 2



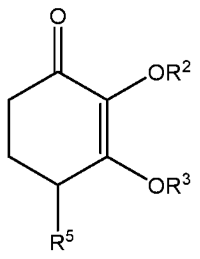
CS 3



CS 4



CS 5



CS 6

where R^1 is a C_1 to C_{12} organyl group or a C_6 to C_{12} aryl group; R^2 and R^3 are each independently hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3; R^4 is -OH, $-OCH_2OCH_3$, $-OCH_2SCH_3$, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group; R^5 is $-CH(OR^6)CH_2OR^7$, -OH, $-OCH_2OCH_3$, -

OCH_2SCH_3, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group; and R^6 and R^7 are each independently hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3; and Y can be methyl (Me), isopropyl (iPr), tert-butyl (t-Bu) or a combination thereof. The term "organyl group" is used herein in accordance with the definition specified by IUPAC: an organic substituent group, regardless of functional type, having one free valence at a carbon atom. The term "aryl group" is used herein in accordance with the definition specified by IUPAC: an organic substituent group regardless of functional type derived from arenes by removal of a hydrogen atom from a ring carbon atom.

[0012] Nonlimiting examples of solvating agents suitable for use in the present disclosure include ascorbic acid, L-ascorbic acid, D-ascorbic acid, L-isoascorbic acid, D-isoascorbic acid, D-erythorbic acid, oxytetronic acid, reductic acid, combinations thereof and derivatives thereof. In a particular aspect, the solvating agent comprises ascorbic acid.

[0013] In an aspect, solvent for use in preparation of an olefin polymerization catalyst comprises an aqueous solution, a nonaqueous solution, an alcohol, or combinations thereof. In an aspect, the solvent comprises an ester, a ketone, an alcohol, or combinations thereof. In an aspect, the solvent comprises a C_1 to C_{20} ester, a C_1 to C_{10} ester or a C_1 to C_5 ester. In another aspect, the solvent comprises a C_1 to C_{20} ketone, a C_1 to C_{10} ketone or a C_1 to C_5 ketone. In another aspect, the solvent comprises a C_1 to C_{20} alcohol, a C_1 to C_{10} alcohol or a C_1 to C_5 alcohol.

[0014] Non-limiting examples of esters suitable for use as solvents of the present disclosure include ethyl acetate, propyl acetate, butyl acetate, isobutyl isobutyrate, methyl lactate, ethyl lactate and combinations thereof. Non-limiting examples of ketones suitable for use as solvents in the present disclosure include acetone, ethyl methyl ketone, methyl isobutyl ketone and combinations thereof. Non-limiting examples of alcohols suitable for use as solvents of the present disclosure include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, pentanol, hexanol, heptanol, octanol, benzyl alcohol, phenol, cyclohexanol and combinations thereof.

[0015] In an aspect, the solvent comprises an aliphatic hydrocarbon, an aromatic hydrocarbon, a halogenated aliphatic hydrocarbon, a halogenated aromatic hydrocarbon, or combinations thereof.

[0016] In an aspect, the solvent comprises a C_3 to C_{20} aliphatic hydrocarbon; alternatively, a C_4 to C_{15} aliphatic hydrocarbon; or alternatively, a C_5 to C_{10} aliphatic hydrocarbon. Aliphatic hydrocarbons which can be utilized as the solvent can be cyclic, acyclic, linear or branched, unless otherwise specified. Non-limiting examples of suitable acyclic aliphatic hydrocarbon solvents that can be utilized singly or in any combination include propane, iso-butane, n-butane, butane (n-butane or a mixture of linear and branched C_4 acyclic aliphatic hydrocarbons), pentane (n-pentane or a mixture of linear and branched C_5 acyclic aliphatic hydrocarbons), hexane (n-hexane or mixture of linear and branched C_6 acyclic aliphatic hydrocarbons), heptane (n-heptane or mixture of linear and branched C_7 acyclic aliphatic hydrocarbons), octane (n-octane or a mixture of linear and branched C_8 acyclic aliphatic hydrocarbons) and combinations thereof.

[0017] In an aspect, the solvent comprises an aromatic hydrocarbon. Aromatic hydrocarbons which can be useful as a solvent a C_6 to C_{20} aromatic hydrocarbon or alternatively, a C_6 to C_{10} aromatic hydrocarbon. Other non-limiting examples of suitable aromatic hydrocarbons that can be utilized singly or in any combination in the present disclosure include benzene, toluene, xylene (including ortho-xylene, meta-xylene, para-xylene, or mixtures thereof), ethylbenzene, and combinations thereof.

[0018] In an aspect, the solvent comprises a halogenated aliphatic hydrocarbon. Halogenated aliphatic hydrocarbons which can be useful as a solvent include C_1 to C_{15} halogenated aliphatic hydrocarbons; alternatively, C_1 to C_{10} halogenated aliphatic hydrocarbons; or alternatively, C_1 to C_5 halogenated aliphatic hydrocarbons. The halogenated aliphatic hydrocarbons can be cyclic, acyclic, linear or branched unless otherwise specified. Non-limiting examples of suitable halogenated aliphatic hydrocarbons which can be utilized include methylene chloride, chloroform, carbon tetrachloride, dichloroethane, trichloroethane, and combinations thereof; alternatively, methylene chloride, chloroform, dichloroethane, trichloroethane and combinations thereof.

[0019] In an aspect, the solvent comprises a halogenated aromatic hydrocarbon. Halogenated aromatic hydrocarbons which can be useful as a solvent include without limitation C_6 to C_{20} halogenated aromatic hydrocarbons; or alternatively, C_6 to C_{10} halogenated aromatic hydrocarbons. Non-limiting examples of suitable halogenated aromatic hydrocarbons include chlorobenzene, dichlorobenzene, and combinations thereof.

[0020] In an aspect, a solvent suitable for use in the present disclosure comprises methanol, ethanol, isopropanol, n-propanol, butanol, acetone, methylethylketone, ethyl acetate, heptane or combinations thereof.

[0021] In an aspect of the present disclosure, the olefin polymerization catalyst comprises titanium. The source of the titanium may be any titanium-containing compound capable of providing effective titanation to the olefin polymerization catalyst. In a further aspect, the titanium-containing compound comprises a tetravalent titanium (Ti^{4+})-containing compound or a trivalent titanium (Ti^{3+})-containing compound. The Ti^{4+}-containing compound may be any compound that comprises tetravalent titanium, alternatively the Ti^{4+}-containing compound may be any compound that is able to release a Ti^{4+} species upon dissolving into solution. The Ti^{3+}-containing compound may be any compound that comprises trivalent titanium, alternatively the Ti^{3+}-containing compound may be any compound that is able to release a Ti^{3+} species upon dissolving into solution. In an aspect, the titanium-containing compound is an organotitanium containing at least one alkoxide group, or alternatively, at least two alkoxide groups. Alternatively, the titanium-containing compound comprises a titanium tetraalkoxide. In an aspect, the titanium tetraalkoxide is titanium ethoxide $Ti(OEt)_4$, titanium isopropoxide $Ti(OiPr)_4$, titanium n-propoxide $Ti(nOPr)_4$, titanium butoxide $Ti(OBu)_4$, titanium 2-ethylhexoxide, or combinations thereof.

[0022] In a still further aspect, the titanium-containing compound may be characterized by the general formula $Ti(OR^1)_2(acac)_2$ wherein R^1 can be ethoxide, isopropoxide, n-propoxide, butoxide, or a combination thereof and "acac" is acetylacetonate. Alternatively, the titanium-containing compound may be characterized by the general formula $Ti(OR^1)_2(oxal)$ wherein R^1 can be ethoxide, isopropoxide, n-propoxide, butoxide, or a combination thereof and "oxal" is oxalate.

[0023] In yet another aspect, titanium-containing compound is a titanium halide such as characterized by the general formula TiX_4 where X is chloride or bromide.

[0024] The amount of titanium present in the olefin polymerization catalyst may range from about 0.01 wt.% to about 10 wt.%; alternatively, from about 0.5 wt.% to about 5 wt.%; alternatively, from about 1 wt.% to about 4 wt.%; or alternatively, from about 2 wt.% to about 4 wt.%. titanium by weight of the olefin polymerization catalyst. In another aspect of the present disclosure, the amount of titanium in the olefin polymerization catalyst may range from about 1 wt.% to about 5 wt.% titanium by weight of the olefin polymerization catalyst. Herein, the percentage of titanium refers to the final weight percent of titanium associated with the olefin polymerization catalyst by total weight of the olefin polymerization catalyst after all processing steps (e.g., after activation via calcination).

[0025] In an aspect, the olefin polymerization catalyst of the present disclosure comprises a silica-support. In an aspect, preparation of an olefin polymerization catalyst of the type disclosed herein excludes thermal treatment of the silica-support prior to contact with any other catalyst component. Consequently, a silica-support suitable for use in the present disclosure may be a termed a hydrated silica-support. Without wishing to be limited by theory, a hydrated silica-support comprises a silica-support wherein water evolution occurs when the silica-support is heated within a range of from about 180 °C to about 200 °C under vacuum conditions for a period of time ranging from about 8 hours to about 20 hours. In a further aspect, the silica-support may contain from about 0.1 wt.% to about 20 wt.% water; or alternatively from about 0.1 wt.% to about 10 wt.% water based upon the total weight of the silica-support.

[0026] A silica-support suitable for use in the present disclosure may have a surface area and pore volume effective to provide for the production of an active olefin polymerization catalyst. In an aspect of the present disclosure, the silica-support possesses a surface area in the range of from about 100

m^2/gram to about 1000 m^2/gram, alternatively from about 250 m^2/gram to about 1000 m^2/gram, alternatively from about 250 m^2/gram to about 700 m^2/gram, alternatively from about 250 m^2/gram to about 600 m^2/gram, or alternatively greater than about 250 m^2/gram. The silica-support may be further characterized by a pore volume of greater than about 0.9 cm^3/gram, alternatively greater than about 1.0 cm^3/gram, or alternatively greater than about 1.5 cm^3/gram. In an aspect of the present disclosure, the silica-support is characterized by a pore volume ranging from about 1.0 cm^3/gram to about 2.5 cm^3/gram. The silica-support may be further characterized by an average particle size of from about 10 microns to about 500 microns, alternatively about 25 microns to about 300 microns, or alternatively about 40 microns to about 150 microns. Generally, the average pore size of the silica-support ranges from about 10 Angstroms to about 1000 Angstroms. In one aspect of the present disclosure, the average pore size of the silica-support is in the range of from about 50 Angstroms to about 500 Angstroms, while in yet another aspect of the present disclosure the average pore size ranges from about 75 Angstroms to about 350 Angstroms.

[0027] The silica-support may contain greater than about 50 wt.% silica; alternatively, greater than about 80 wt.% silica; or alternatively, greater than about 95 wt.% silica based upon the weight of the silica-support. The silica-support may be prepared using any suitable method, for example the silica-support may be prepared synthetically by hydrolyzing tetrachlorosilane ($SiCl_4$) with water or by contacting sodium silicate with a mineral acid. The silica-support may include additional components that do not adversely affect the catalyst, such as zirconia, alumina, thoria, magnesia, fluoride, sulfate, phosphate, or mixtures thereof. Non-limiting examples of silica-supports suitable for use in this disclosure include ES70 which is a silica-support material with a surface area of 300 m^2/gram, and a pore volume of 1.6 cm^3/gram that is commercially available from PQ Corporation; and V398400 which is a silica-support material that is commercially available from Evonik.

[0028] The silica-support may be present in the olefin polymerization catalyst in an amount of from about 50 wt.% to about 99 wt.%; or alternatively, from about 80 wt.% to about 99 wt.%. Herein the percentage of silica-support refers to the final weight percent of silica-support associated with the olefin polymerization catalyst by total weight of the olefin polymerization catalyst after all processing steps (e.g., after activation via calcination).

[0029] In an aspect of the present disclosure, the olefin polymerization catalyst comprises chromium. In a particular aspect, the source of the chromium may be any chromium-containing compound capable of providing a sufficient amount of chromium to the olefin polymerization catalyst. For example, the chromium-containing compound may be a water-soluble compound or a hydrocarbon-soluble compound. Examples of water-soluble chromium compounds include chromium trioxide, chromium acetate, chromium nitrate, or combinations thereof. Examples of hydrocarbon-soluble chromium compounds include tertiary butyl chromate, a diarene chromium (0) compound, biscyclopentadienyl chromium (II), chromium (III) acetylacetonate, or combinations thereof. In one aspect of the present disclosure, the chromium-containing compound may be a chromium (II) compound, a chromium (III) compound, or combinations thereof. Suitable chromium (III) compounds include, but are not limited to, chromium carboxylates, chromium naphthenates, chromium halides, chromium sulfate, chromium nitrate, chromium dionates, or combinations thereof. Specific chromium (III) compounds include, but are not limited to, chromium (III) sulfate, chromium (III) chloride, chromium (III) nitrate, chromic bromide, chromium (III) acetylacetonate, and chromium (III) acetate. Suitable chromium (II) compounds include, but are not limited to, chromous chloride, chromous bromide, chromous iodide, chromium (II) sulfate, chromium (II) acetate, or combinations thereof.

[0030] The amount of chromium present in the olefin polymerization catalyst may range from about 0.01 wt.% to about 10 wt.%; alternatively, from about 0.5 wt.% to about 5 wt.%; alternatively, from about 1 wt.% to about 4 wt.%; or alternatively, from about 2 wt.% to about 4 wt.% chromium by weight of the olefin polymerization catalyst. In another aspect of the present disclosure, the amount of chromium present in the olefin polymerization catalyst may range from about 1 wt.% to about 5 wt.%. Herein, the percentage chromium refers to the final weight percent chromium associated with the olefin polymerization catalyst by total weight of the olefin polymerization catalyst after all processing steps (e.g., after activation via calcination).

[0031] In some aspects of this disclosure, chromium is provided to the olefin polymerization catalyst as a component of the silica support. In such aspects, the olefin polymerization catalyst may be prepared using a chrominated silica-support having the characteristics disclosed herein for a silica support while additionally containing chromium in the amounts also disclosed herein. An example of such material suitable for use in the present disclosure is HW30A which is a chrominated silica-support material that is commercially available from W. R. Grace and Company.

[0032] Disclosed herein are methods of preparing an olefin polymerization catalyst composition comprising contacting the catalyst components disclosed herein. Various sequences for contacting of the catalyst components are also disclosed herein, e.g., forming an aqueous solution comprising titanation followed by contacting the solution with a silica-support. It is contemplated that other sequences for the contacting of the catalyst components may also produce an olefin polymerization catalyst of the type disclosed herein. Consequently, in an aspect of the present disclosure the catalyst components may be contacted in any order or fashion deemed suitable to one of ordinary skill in the art with the aid of the present disclosure to produce a catalyst of the type disclosed herein.

[0033] In the following aspects, a weight ratio of solvating agent to silica may range from about 0.5:1 to about 10:1, alternatively from about 1:1 to about 5:1 or alternatively from about 2:1 to about 5:1. Further, the present disclosure contemplates the formation of a solvating agent-titanium complex/association that results in effective titanation of the support material. In some aspects formation of this solvating agent-titanium complex/association is indicated by the mixture developing a deep red color when both the solvating agent and titanium are present in a mixture.

[0034] In an aspect of the present disclosure, a method for preparation of an olefin polymerization catalyst comprises contacting an aqueous solvent, a solvating agent and a titanium-containing compound, all of the type disclosed herein, to form an aqueous solution comprising titanium.

[0035] The method may further comprise contacting the aqueous solution comprising titanium with a chrominated silica-support to form a mixture comprising a pre-catalyst (e.g., a chrominated, titanated support). In an aspect, preparation of an olefin polymerization catalyst excludes thermal treatment of the chrominated silica-support prior to contact with any other catalyst component.

[0036] In an aspect of the present disclosure, a method for preparation of an olefin polymerization catalyst of the type disclosed herein comprises contacting an aqueous solvent, a solvating agent and a titanium-containing compound, all of the type disclosed herein, to form an aqueous solution comprising titanium. The method may further comprise contacting the aqueous solution comprising titanium with a silica-support to form a first mixture comprising a titanated support. In an aspect, the method further comprises contacting the first mixture comprising the titanated support with a chromium-containing compound to form a second mixture comprising a pre-catalyst (e.g., a chrominated, titanated support).

[0037] In an aspect of the present disclosure, a method for preparation of an olefin polymerization catalyst comprises contacting an aqueous solvent, a solvating agent and a titanium-containing compound, all of the type disclosed herein, to form an aqueous solution comprising titanium. The method may further comprise contacting the aqueous solution comprising titanium with a silica-support and a chromium-containing compound to form a mixture comprising a pre-catalyst (e.g., a chrominated, titanated support).

[0038] In an aspect of the present disclosure, a method for preparation of an olefin polymerization catalyst of the type disclosed herein comprises contacting a silica-support with a chromium-containing compound to form a chrominated support. The method may further comprise contacting an aqueous solvent, a solvating agent and a titanium-containing compound, all of the type disclosed herein, to form an aqueous solution comprising titanium. The chrominated support may then be contacted with the aqueous solution comprising titanium to form a mixture comprising a pre-catalyst (e.g., a chrominated, titanated support).

[0039] In an aspect of the present disclosure, a method for preparation of an olefin polymerization catalyst of the type disclosed herein comprises simultaneously contacting an aqueous solvent, a solvating agent, a titanium-containing compound, a silica-support, and a chromium-containing compound, all of the type disclosed herein, to form an aqueous mixture comprising a pre-catalyst (e.g., a chrominated, titanated support).

[0040] The present disclosure contemplates the use of a hydrated support material in the preparation of the olefin polymerization catalyst. Thus, preparation of an olefin polymerization catalyst of the present disclosure excludes thermal treatment of the support material (e.g., silica-support, chrominated silica support) prior to contact with any other catalyst component. Consequently, the support material may contain from about 0.1 wt.% to about 20 wt.% water.

[0041] In some aspects of the present disclosure, any contacting of the olefin polymerization catalyst components may be carried out in the presence of a reaction media. Specifically, the liquid associated with each component utilized in preparation of the olefin polymerization catalyst (e.g., water associated with the silica support, the titanium-containing compound, the chromium-containing compound, etc.) and optionally an added solvent (e.g., water) may form the reaction media in each contacting step described herein. In an aspect, the reaction media excludes any solid component utilized in the preparation methodology disclosed herein (e.g., excludes the silica-support and any solids associated therewith). In some aspects, the sum of an amount of water present in any reaction media formed during preparation of the olefin polymerization catalyst is from about 1 wt.% to about 99 wt.% based on the total weight of the reaction media (e.g., all liquid components including water and any non-aqueous liquids such as one or more optional organic solvents), alternatively from about 1 wt.% to about 50 wt.%, alternatively from about 1 wt.% to about 20 wt.%, or alternatively from about 1 wt.% to about 10 wt.%. In an aspect of the present disclosure, the reaction media formed during one or more contacting steps performed during preparation of the olefin polymerization catalyst (e.g., the liquid components of a mixture comprising the titanated support, the liquid components of a mixture comprising the chrominated support, the liquid components of a mixture comprising the pre-catalyst, etc.) may contain greater than about 1 wt.% water, alternatively greater than about 5 wt.%, alternatively greater than about 10 wt.%, alternatively greater than about 20 wt.%, alternatively greater than about 30 wt.%, alternatively greater than about 40 wt.%, alternatively greater than about 50 wt.%, alternatively greater than about 60 wt.%, alternatively greater than about 70 wt.%, alternatively greater than about 80 wt.%, or alternatively greater than about 90 wt.% water based on the total weight of the reaction media, where the water may originate from one or more components used to form the mixture.

[0042] In the presently disclosed aspects, the solubility of the titanium may be sufficient to allow the titanium-containing solution to be contacted with the support material (e.g., silica-support, chrominated silica-support) using techniques such as spray drying. Spray drying as used herein refers to a method of producing a dry powder from a liquid or slurry by rapidly drying with a hot gas. Such methodologies may be advantageously utilized in the preparation of catalysts having a consistent particle sized distribution.

[0043] In any aspect of the present disclosure, the pre-catalyst (e.g., a chrominated, titanated support) formed may be dried. For example, the pre-catalyst may be dried at temperatures ranging from about 25 °C to about 300 °C, alternatively from about 50 °C to about 200 °C, or alternatively from about 80 °C to about 150 °C to form a dried pre-catalyst. The dried pre-catalyst may then be activated via a calcination step by heating in an oxidizing environment to produce the olefin polymerization catalyst. For example, the dried pre-catalyst may be calcined in the presence of air at a temperature in the range of from about 400 °C to about 1,000 °C, alternatively from about 500 °C to about 900 °C, or alternatively from about 500 °C to about 850 °C and for a time period of from about 1 min to about 24 hours, alternatively from about 1 minute to about 10 hours, alternatively from about 1 hour to about 24 hours, alternatively from about 1 hour to about 12 hours, alternatively from about 3 hours to about 12 hours, alternatively from about 20 min to about 5 hours, or alternatively from about 1 hour to about 3 hours to produce the olefin polymerization catalyst.

[0044] The olefin polymerization catalysts of the present disclosure are suitable for use in any olefin polymerization method, using various types of polymerization reactors. In an aspect of the present disclosure, a polymer of the present disclosure is produced by any olefin polymerization method, using various types of polymerization reactors. As used herein, “polymerization reactor” includes any reactor capable of polymerizing olefin monomers to produce homopolymers and/or copolymers. Homopolymers and/or copolymers produced in the reactor may be referred to as resin and/or polymers. The various types of reactors include, but are not limited to those that may be referred to as batch, slurry, gas-phase, solution, high pressure, tubular, autoclave, or other reactor and/or reactors. Gas phase reactors may comprise fluidized bed reactors or staged horizontal reactors. Slurry reactors may comprise vertical and/or horizontal loops. High pressure reactors may comprise autoclave and/or tubular reactors. Reactor types may include batch and/or continuous processes. Continuous processes may use intermittent and/or continuous product discharge or transfer. Processes may also include partial or full direct recycle of un-reacted monomer, un-reacted comonomer, catalyst and/or co-catalysts, diluents, and/or other materials of the polymerization process.

[0045] Polymerization reactor systems of the present disclosure may comprise one type of reactor in a system or multiple reactors of the same or different type, operated in any suitable configuration. Production of polymers in multiple reactors may include several stages in at least two separate polymerization reactors interconnected by a transfer system making it possible to transfer the polymers resulting from the first polymerization reactor into the second reactor. Alternatively, polymerization in multiple reactors may include the transfer, either manual or automatic, of polymer from one reactor to subsequent reactor or reactors for additional polymerization. Alternatively, multi-stage or multi-step polymerization may take place in a single reactor, wherein the conditions are changed such that a different polymerization reaction takes place.

[0046] The desired polymerization conditions in one of the reactors may be the same as or different from the operating conditions of any other reactors involved in the overall process of producing the polymer of the present disclosure. Multiple reactor systems may include any combination including, but not limited to multiple loop reactors, multiple gas phase reactors, a combination of loop and gas phase reactors, multiple high pressure reactors or a combination of high pressure with loop and/or gas reactors. The multiple reactors may be operated in series or in parallel. In an aspect of the present disclosure, any arrangement and/or any combination of reactors may be employed to produce the polymer of the present disclosure.

[0047] According to one aspect of the present disclosure, the polymerization reactor system may comprise at least one loop slurry reactor. Such reactors are commonplace, and may comprise vertical or horizontal loops. Monomer, diluent, catalyst system, and optionally any comonomer may be continuously fed to a loop slurry reactor, where polymerization occurs. Generally, continuous processes may comprise the continuous introduction of a monomer, a catalyst, and/or a diluent into a polymerization reactor and the continuous removal from this reactor of a suspension comprising polymer particles and the diluent. Reactor effluent may be flashed to remove the liquids that comprise the diluent from the solid polymer, monomer and/or comonomer. Various technologies may be used for this separation step including but not limited to, flashing that may include any combination of heat addition and pressure reduction; separation by cyclonic action in either a cyclone or hydrocyclone; separation by centrifugation; or other appropriate method of separation.

[0048] Typical slurry polymerization processes (also known as particle-form processes) are disclosed in U.S. Patent Nos. 3,248,179, 4,501,885, 5,565,175, 5,575,979, 6,239,235, 6,262,191 and 6,833,415, for example; each of which are herein incorporated by reference in their entirety.

[0049] Suitable diluents used in slurry polymerization include, but are not limited to, the monomer being polymerized and hydrocarbons that are liquids under reaction conditions. Examples of suitable diluents include, but are not limited to, hydrocarbons such as propane, cyclohexane, isobutane, n-butane, n-pentane, isopentane, neopentane, and n-hexane. Some loop polymerization reactions can occur under bulk conditions where no diluent is used. An example is polymerization of propylene monomer as disclosed in U.S. Patent No. 5,455,314, which is incorporated by reference herein in its entirety.

[0050] According to yet another aspect of the present disclosure, the polymerization reactor may comprise at least one gas phase reactor. Such systems may employ a continuous recycle stream containing one or more monomers continuously cycled through a fluidized bed in the presence of the catalyst under polymerization conditions. A recycle stream may be withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product may be withdrawn from the reactor and new or fresh monomer may be added to replace the polymerized monomer. Such gas phase reactors may comprise a process for multi-step gas-phase polymerization of olefins, in which olefins are polymerized in the gaseous phase in at least two independent gas-phase polymerization zones while feeding a catalyst-containing polymer formed in a first polymerization zone to a second polymerization zone. One type of gas phase reactor is disclosed in U.S. Patent Nos. 4,588,790, 5,352,749, and 5,436,304, each of which is incorporated by reference in its entirety herein.

[0051] According to still another aspect of the present disclosure, a high pressure polymerization reactor may comprise a tubular reactor or an autoclave reactor. Tubular reactors may have several zones where fresh monomer, initiators, or catalysts are added. Monomer may be entrained in an inert gaseous stream and introduced at one zone of the reactor. Initiators, catalysts, and/or catalyst components may be entrained in a gaseous stream and introduced at another zone of the reactor. The gas streams may be intermixed for polymerization. Heat and pressure may be employed appropriately to obtain optimal polymerization reaction conditions.

[0052] According to yet another aspect of the present disclosure, the polymerization reactor may comprise a solution polymerization reactor wherein the monomer is contacted with the catalyst composition by suitable stirring or other means. A carrier comprising an organic diluent or excess monomer may be employed. If desired, the monomer may be brought in the vapor phase into contact with the catalytic reaction product, in the presence or absence of liquid material. The polymerization zone is maintained at temperatures and pressures that will result in the formation of a solution of the polymer in a reaction medium. Agitation may be employed to obtain better temperature control and to maintain uniform polymerization mixtures throughout the polymerization zone. Adequate means are utilized for dissipating the exothermic heat of polymerization.

[0053] Polymerization reactors suitable for the present disclosure may further comprise any combination of at least one raw material feed system, at least one feed system for catalyst or catalyst components, and/or at least one polymer recovery system. Suitable reactor systems for the present invention may further comprise systems for feedstock purification, catalyst storage and preparation, extrusion, reactor cooling, polymer recovery, fractionation, recycle, storage, loadout, laboratory analysis, and process control.

[0054] Conditions that are controlled for polymerization efficiency and to provide polymer properties include, but are not limited to temperature, pressure, type and quantity of catalyst or co-catalyst, and the concentrations of various reactants. Polymerization temperature can affect catalyst productivity, polymer molecular weight and molecular weight distribution. Suitable polymerization temperatures may be any temperature below the de-polymerization temperature, according to the Gibbs Free Energy Equation. Typically, this includes from about 60 °C to about 280° C, for example, and/or from about 70 °C to about 110 °C, depending upon the type of polymerization reactor and/or polymerization process.

[0055] Suitable pressures will also vary according to the reactor and polymerization process. The pressure for liquid phase polymerization in a loop reactor is typically less than 1000 psig (6.9 MPa). Pressure for gas phase polymerization is usually at about 200 psig (1.4 MPa) – 500 psig (3.45 MPa). High pressure polymerization in tubular or autoclave reactors is generally run at about 20,000 psig (138 MPa); to 75,000 psig (518 MPa). Polymerization reactors can also be operated in a supercritical region occurring at generally higher temperatures and pressures. Operation above the critical point of a pressure/temperature diagram (supercritical phase) may offer advantages.

[0056] The concentration of various reactants can be controlled to produce polymers with certain physical and mechanical properties. The proposed end-use product that will be formed by the polymer and the method of forming that product may be varied to determine the desired final product properties. Mechanical properties include, but are not limited to tensile strength, flexural modulus, impact resistance, creep, stress relaxation and hardness tests. Physical properties include, but are not limited to density, molecular weight, molecular weight distribution, melting temperature, glass transition temperature, temperature melt of crystallization, density, stereoregularity, crack growth, short chain branching, long chain branching and rheological measurements.

[0057] The concentrations of monomer, comonomer, hydrogen, co-catalyst, modifiers, and electron donors are generally important in producing specific polymer properties. Comonomer may be used to control product density. Hydrogen may be used to control product molecular weight. Co-catalysts may be used to alkylate, scavenge poisons and/or control molecular weight. The concentration of poisons may be minimized, as poisons may impact the reactions and/or otherwise affect polymer product properties. Modifiers may be used to control product properties and electron donors may affect stereoregularity.

[0058] Polymers such as polyethylene homopolymers and copolymers of ethylene with other mono-olefins may be produced in the manner described above using the polymerization catalysts prepared as described herein. Polymers produced as disclosed herein may be formed into articles of manufacture or end use articles using techniques known in the art such as extrusion, blow molding, injection molding, fiber spinning, thermoforming, and casting. For example, a polymer resin may be extruded into a sheet, which is then thermoformed into an end use article such as a container, a cup, a tray, a pallet, a toy, or a component of another product. Examples of other end use articles into which the polymer resins may be formed include pipes, films, and bottles.

[0059] A method of the present disclosure comprises contacting an olefin polymerization catalyst of the type described with an olefin under conditions suitable for the formation of a polyolefin and recovering the polyolefin. In an aspect the olefin is ethylene and the polyolefin is polyethylene.

[0060] Polyethylene prepared as described herein may be characterized by a high load melt index (HLMI), ranging from about 1 g/10 min. to about 1000 g/10 min.; alternatively, from about 3 g/10 min. to about 300 g/10 min.; alternatively, from about 6 g/10 min. to about 20 g/10 min.; or alternatively, from about 9 g/10 min to about 14 g/10 min. In a further aspect, the polyethylene prepared as described herein may be characterized by a high load melt index that is from about 1.5 to about 2.5 times greater than the high load melt index of a polymer produced by utilizing an otherwise similar catalyst produced in the absence of a titanium ligand. The HLMI represents the rate of flow of a molten polymer through an orifice of 0.0825 inch diameter when subjected to a force of 21,600 grams at 190 °C as determined in accordance with ASTM D1238-82 condition F.

EXAMPLES

[0061] The following examples are given as particular aspects of the present disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

Example 1

[0062] In the following experiments, the solvating agents listed in Table 1 were investigated by dissolving in the solvent system as listed to form a solution. $Ti(OiPr)_4$ was then added and dissolution was attempted in order to form a titanium solution. A pre-catalyst was prepared by depositing the titanium-cation solution onto a chrominated silica-support (HW30A, W. R. Grace and Company). The pre-catalyst was then dried and calcined in air for three hours at 650 °C prior to use in polymerization experiments. HW30A, the solvating agents and solvents were used as received and were not dried prior to use.

[0063] Polymerization tests were conducted in a 2.2 liter stainless-steel reactor equipped with a marine stirrer rotating at 500 rpm. The reactor was surrounded by a steel jacket, through which a mixture of cold water and steam was passed to precisely control the temperature to within half a degree centigrade, with the aid of electronic control instruments.

[0064] Unless otherwise stated, a small amount (0.01 to 0.10 grams normally) of the solid catalyst prepared as described herein was first charged under nitrogen to the dry reactor. Next 1.2 liter of isobutane liquid was charged and the reactor and heated to 105 °C. Finally ethylene was added to the reactor to maintain a fixed pressure, 550 psig (3.8 MPa), during the experiment. The mixture was stirred continuously for the specified time, usually around one hour, and the activity was noted by recording the flow of ethylene into the reactor to maintain the set pressure.

[0065] After the allotted time, the ethylene flow was stopped and the reactor slowly depressurized and opened to recover a granular polymer powder. In all cases the reactor was clean with no indication of any wall scale, coating or other forms of fouling. The polymer powder was then removed and weighed. Activity was specified as grams of polymer produced per gram of solid catalyst charged per hour.

[0066] The results of polymerization runs are shown in Table 1. The table lists each solvating agent and solvent system along with various polymer properties including high load melt index and I_{10} melt index. I_{10} melt index (g/10 min) is the polymer flow rate using a 10 kg weight and was determined in accordance with ASTM D1238 at 190 °C with a 10 kg weight. The high load melt index (HLMI) represents the rate of flow of a molten resin through an orifice of 0.0825 inch diameter when subjected to a force of 21,600 grams at 190 °C. The HLMI values were determined in accordance with ASTM D1238-82 condition F.

[0067] Comparative run CM-1 used no titanium and provided baseline levels for the catalyst productivity, activity, and melt index values for the resultant polymer. The melt index values I_{10} and HLMI indicate the extent of titanation upon the silica-support where higher melt index values indicate more effective (i.e., greater), titanation. Comparative runs CM-2 and CM-3 used no solvating agent: the lack of improvement in HLMI and/or I_{10} indicate that effective titanation was not achieved with an alcohol solvent or a water solvent. Comparative runs CM-4, CM-5, CM-6, CM-7, & CM-12 used a water solvent and none of the potential solvating agents tested displayed effective titanation. Comparative runs CM-8 - CM-11 used a water solvent and none of the potential solvating agents tested were capable of dissolving the Ti(IV) reagent. Comparative runs CM-13 & CM-14 used a mixed solvent system with 2 equivalents ascorbic acid but did not provide effective titanation. The polymers produced using the catalysts of the present disclosure, runs IN-1 & IN-2, displayed highly effective titanation using 4 equivalents ascorbic acid as the solvating agent in either a water solvent or an alcohol solvent.

Table 1

Run No.	**Wt.% Ti**	**Solvating Agent (SA)**	**Molar Equiv. SA/ Ti**	**Solvent**	**Productivity g PE/g catalyst**	**Activity g PE/g-h**	**HLMI g/10 min**	**I_{10} g/10 min**
CM-1	0	None	-	None	2973	2973	5.5	0.87
CM-2	3.5*	None	-	Water	2488	2650	5.2	0.80
CM-3	3.5	None	-	n-PrOH	2765	2614	6.1	0.98
CM-4	3.5	Glycolic acid	4	Water	3098	3320	5.7	0.97
CM-5	3.5	Glyoxilic acid	2	Water	2186	2851	2.9	0.37
CM-6	3.5	HNO_3	1	Water	2846	2339	1.1	0.08
CM-7	3.5	Phosphono-acetic acid	2	Water	867	627	6.0	1.14
CM-8	3.5	Malic acid	4	Water	Ti would not dissolve		-	-
CM-9	3.5	Malonic acid	4	Water	Ti would not dissolve		-	-
CM-10	3.5	Maleic acid	4	Water	Ti would not dissolve		-	-
CM-11	3.5	Aspartic acid	3	Water	Ti would not dissolve		-	-
CM-12	3.5	Citric acid	3	Water	2303	2607	3.9	0.48
CM-13	3.5	Ascorbic acid	2	9/1 nPrOH/ water (v/v)	3236	3034	4.6	0.76
CM-14	3.5	Ascorbic acid	2	2/1 nPrOH/ water (v/v)	3258	2874	6.2	1.07
IN-1	3.5	Ascorbic acid	4	Water	2927	3444	12.8	2.53
IN-2	3.5	Ascorbic acid	4	MeOH	3635	2167	9.6	1.84

* indicates TiO_2 precipitated out of solution

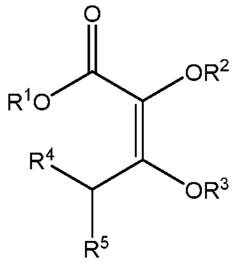
ADDITIONAL DISCLOSURE

[0068] The following enumerated aspects of the present disclosures are provided as non-limiting examples.

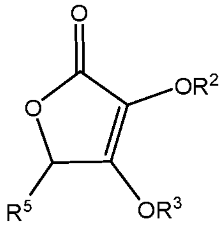
[0069] A first aspect which is a method of preparing a catalyst comprising: a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0070] A second aspect which is the method of the first aspect, wherein the solvating agent comprises a β-hydroxy-α,β-unsaturated carbonyl-containing compound, an α,β-dihydroxy-α,β-unsaturated carbonyl-containing compound, or a combination thereof.

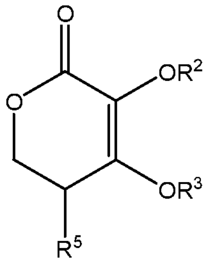
[0071] A third aspect which is the method of any of the first through second aspects wherein the solvating agent has Structure CS 1, Structure CS 2, Structure CS 3, Structure CS 4, Structure CS 5, or Structure CS 6



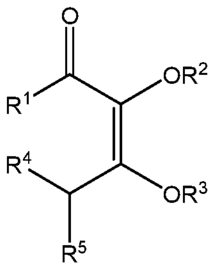
CS 1

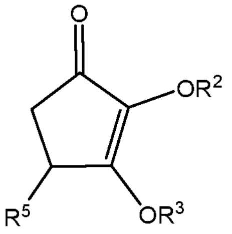


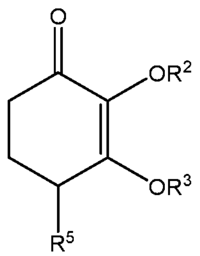
CS 2



CS 3







CS 4 CS 5 CS 6

wherein R^1 is a C_1 to C_{12} organyl group or a C_6 to C_{12} aryl group, R^2 and R^3 are each independently hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3, R^4 is $-OH$, $-OCH_2OCH_3$, $-OCH_2SCH_3$, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group, R^5 is $-CH(OR^6)CH_2OR^7$, $-OH$, $-OCH_2OCH_3$, $-OCH_2SCH_3$, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group, R^6 and R^7 are each independently hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3, and Y is methyl, isopropyl, tert-butyl or a combination thereof.

[0072] A fourth aspect which is the method of the third aspect wherein the solvating agent comprises ascorbic acid, L-ascorbic acid, D-ascorbic acid, L-isoascorbic acid, D-isoascorbic acid, D-erythorbic acid, oxytetronic acid, reductic acid or a combination thereof.

[0073] A fifth aspect which is the method of any of the first through fourth aspects wherein the titanium-containing compound comprises a titanium tetraalkoxide.

[0074] A sixth aspect which is the method of the fifth aspect wherein the titanium tetraalkoxide comprises titanium *n*-propoxide, titanium *n*-butoxide, titanium isopropoxide or a combination thereof.

[0075] A seventh aspect which is the method of any of the first through sixth aspects wherein a weight ratio of solvating agent to silica comprising the chrominated silica-support is from about 0.5:1 to about 10:1.

[0076] An eighth aspect which is the method of any of the first through seventh aspects wherein the solvent is an aqueous solvent, a nonaqueous solvent, an alcohol or a combination thereof.

[0077] An ninth aspect which is the method of any of the first through eighth aspects wherein the chrominated silica-support is characterized by a surface area of from about 100 m^2/gram to about 1000 m^2/gram and a pore volume of from about 1.0 cm^3/gram to about 2.5 cm^3/gram.

[0078] An tenth aspect which is the method of any of the first through ninth aspects wherein an amount of chromium present in the catalyst may range from about 0.01% to about 10% by weight of the catalyst and an amount of titanium present in the catalyst may range from about 0.01% to about 10% by weight of the catalyst.

[0079] An eleventh aspect which is the method of any of the first through tenth aspects wherein the chrominated silica-support is a not thermally treated prior to contacting with the solution.

[0080] A twelfth aspect which is a method of forming a polymer comprising contacting the catalyst of the first aspect with a monomer under conditions suitable for formation of a polymer and recovering the polymer.

[0081] A thirteenth aspect which is the method of the twelfth aspect wherein the monomer comprises an ethylene monomer and the polymer comprises an ethylene polymer.

[0082] A fourteenth aspect which is the method of any of the twelfth through thirteenth aspects wherein the polymer has a high load melt index that is from about 1.5 to about 2.5 times greater than the high load melt index of a polymer produced by utilizing an otherwise similar catalyst produced in the absence of a solvating agent.

[0083] A fifteenth aspect which is the a method of preparing a catalyst comprising: a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting the solution with a silica-support to form a titanated support; c) contacting the titanated support with a chromium-containing compound to form a pre-catalyst; and d) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0084] A sixteenth aspect which is the method of the fifteenth aspect wherein the solvating agent comprises ascorbic acid, L-ascorbic acid, D-ascorbic acid, L-isoascorbic acid, D-isoascorbic acid, D-erythorbic acid, oxytetronic acid, reductic acid or a combination thereof.

[0085] A seventeenth aspect which is the method of any of the fifteenth through sixteenth aspects wherein the titanium-containing compound comprises a titanium tetraalkoxide.

[0086] An eighteenth aspect which is the method of any of the fifteenth through seventeenth aspects wherein a weight ratio of solvating agent to silica comprising the silica-support is from about 0.5:1 to about 10:1.

[0087] A nineteenth aspect which is the method of any of the fifteenth through eighteenth aspects wherein the solvent is an aqueous solvent, a nonaqueous solvent, an alcohol or a combination thereof.

[0088] A twentieth aspect which is the method of any of the fifteenth through nineteenth aspects wherein the chromium-containing compound comprises chromium trioxide, chromium acetate, chromium nitrate, tertiary butyl chromate, a diarene chromium (0) compound, biscyclopentadienyl chromium(II), chromium (III) acetylacetonate, or a combination thereof.

[0089] A twenty-first aspect which is the method of any of the fifteenth through twentieth aspects wherein the silica-support is not thermally treated prior to contacting with the solution.

[0090] A twenty-second aspect which is a method of preparing a catalyst comprising: a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting a silica-support, a chromium-containing compound and the solution to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0091] A twenty-third aspect which is a method of preparing a catalyst comprising: a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution; b) contacting a silica-support and a chromium-containing compound to form a chrominated support; c) contacting the solution of step (a) with the chrominated support of step (b) to form a pre-catalyst; and d) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0092] A twenty-fourth aspect which is a method of preparing a catalyst comprising: a) contacting a silica-support, a chromium-containing compound, a titanium-containing compound, a solvating agent, and a solvent to form a pre-catalyst; and b) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0093] A twenty-fifth aspect which is a method of preparing a catalyst comprising: a) contacting $Ti(OiPr)_4$, water, and ascorbic acid to form a solution; b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

[0094] While various aspects of the present disclosures have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The aspects of the present disclosures described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0095] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an aspect of the present disclosure of the present invention. Thus, the claims are a further description and are an addition to the aspect of the present disclosures of the present disclosure. The discussion of a reference in the present disclosure is not an admission that it is prior art to the present disclosure, especially any reference that may have a publication date after the priority date of this application. The present disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A method of preparing a catalyst comprising:

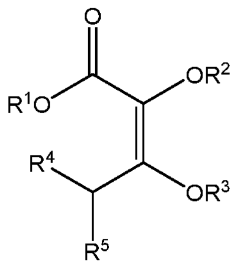
a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution;

b) contacting the solution with a chrominated silica-support to form a pre-catalyst; and

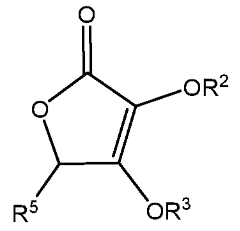
c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

2. The method of claim 1 wherein the solvating agent comprises a β-hydroxy-α,β-unsaturated carbonyl-containing compound, an α,β-dihydroxy-α,β-unsaturated carbonyl-containing compound, or a combination thereof.

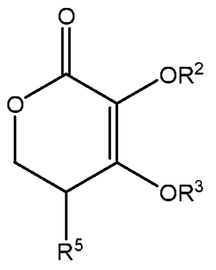
3. The method of claim 1 wherein the solvating agent has Structure CS 1, Structure CS 2, Structure CS 3, Structure CS 4, Structure CS 5, or Structure CS 6



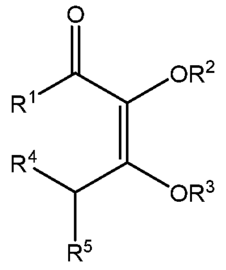
CS 1



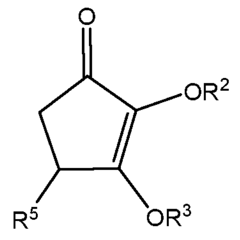
CS 2



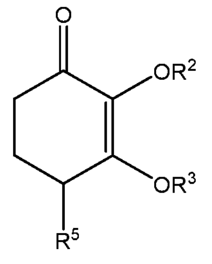
CS 3



CS 4



CS 5



CS 6

wherein

R^1 is a C_1 to C_{12} organyl group or a C_6 to C_{12} aryl group,

R^2 and R^3 are each independently be hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3,

R^4 is -OH, $-OCH_2OCH_3$, $-OCH_2SCH_3$, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group,

R^5 is $-CH(OR^6)CH_2OR^7$, -OH, $-OCH_2OCH_3$, $-OCH_2SCH_3$, $-OSiY_3$, hydrogen, a C_2 to C_{12} organyl group, or a C_6 to C_{12} aryl group,

R^6 and R^7 are each independently be hydrogen, $-CH_2OCH_3$, $-CH_2SCH_3$, or SiY_3, and

Y is methyl, isopropyl, t-butyl or a combination thereof.

4. The method of claim 3 wherein the solvating agent comprises ascorbic acid, L-ascorbic acid, D-ascorbic acid, L-isoascorbic acid, D-isoascorbic acid, D-erythorbic acid, oxytetronic acid, reductic acid or a combination thereof.

5. The method of claim 1 wherein the titanium-containing compound comprises a titanium tetraalkoxide.

6. The method of claim 5 wherein the titanium tetraalkoxide comprises titanium *n*-propoxide, titanium *n*-butoxide, titanium isopropoxide or a combination thereof.

7. The method of claim 1 wherein a weight ratio of solvating agent to silica comprising the chrominated silica-support is from about 0.5:1 to about 10:1.

8. The method of claim 1 wherein the solvent is an aqueous solvent, a nonaqueous solvent, an alcohol or a combination thereof.

9. The method of claim 1 wherein the chrominated silica-support is characterized by a surface area of from about 100 m^2/gram to about 1000 m^2/gram and a pore volume of from about 1.0 cm^3/gram to about 2.5 cm^3/gram.

10. The method of claim 1 wherein an amount of chromium present in the catalyst may range from about 0.01% to about 10% by weight of the catalyst and an amount of titanium present in the catalyst may range from about 0.01% to about 10% by weight of the catalyst.

11. The method of claim 1 wherein the chrominated silica-support is a not thermally treated prior to contacting with the solution.

12. A method of forming a polymer comprising contacting the catalyst of claim 1 with a monomer under conditions suitable for formation of a polymer and recovering the polymer.

13. The method of claim 12 wherein the monomer comprises an ethylene monomer and the polymer comprises an ethylene polymer.

14. The method of claim 13 wherein the polymer has a high load melt index that is from about 1.5 to about 2.5 times greater than the high load melt index of a polymer produced by utilizing an otherwise similar catalyst produced in the absence of a solvating agent.

15. A method of preparing a catalyst comprising:

a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution;

b) contacting the solution with a silica-support to form a titanated support;

c) contacting the titanated support with a chromium-containing compound to form a pre-catalyst; and

d) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

16. The method of claim 15 wherein the solvating agent comprises ascorbic acid, L-ascorbic acid, D-ascorbic acid, L-isoascorbic acid, D-isoascorbic acid, D-erythorbic acid, oxytetronic acid, reductic acid or a combination thereof.

17. The method of claim 15 wherein the titanium-containing compound comprises a titanium tetraalkoxide.

18. The method of claim 15 wherein a weight ratio of solvating agent to silica comprising the silica-support is from about 0.5:1 to about 10:1.

19. The method of claim 15 wherein the solvent is an aqueous solvent, a nonaqueous solvent, an alcohol or a combination thereof.

20. The method of claim 15 wherein the chromium-containing compound comprises chromium trioxide, chromium acetate, chromium nitrate, tertiary butyl chromate, a diarene chromium (0) compound, biscyclopentadienyl chromium(II), chromium (III) acetylacetonate, or a combination thereof.

21. The method of claim 15 wherein the silica-support is not thermally treated prior to contacting with the solution.

22. A method of preparing a catalyst comprising:

a) contacting a titanium-containing compound, a solvating agent, and a solvent to form a solution;

b) contacting a silica support, a chromium-containing compound and the solution to form a pre-catalyst; and

c) thermally treating the pre-catalyst by heating to a temperature of from about 400 °C to about 1000 °C for a time period of from about 1 minute to about 24 hours to form the catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/059953

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/08 B01J37/02 B01J23/26 B01J21/08 C08F10/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2017/080406 A1 (PRAETORIUS JEREMY M [US] ET AL) 23 March 2017 (2017-03-23) paragraph [0050]; claims 2,15,18,21; examples 1-5	1,5-10 2-4,11
X A	US 2017/015764 A1 (PRAETORIUS JEREMY M [US] ET AL) 19 January 2017 (2017-01-19) paragraphs [0016] - [0021], [0083]; claim 10; table 1	1,5-10 2-4,11
X A	WO 2017/032535 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 2 March 2017 (2017-03-02) page 2, lines 9-32; claim 10; examples I,II	1,5-10 2-4,11

-/--

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 22 February 2019	Date of mailing of the international search report 10/05/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Goebel, Matthias

1

International application No
PCT/US2018/059953

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PAUL J. DESLAURIERS ET AL: "Short chain branching profiles in polyethylene from the Phillips Cr/silica catalyst", JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY, vol. 45, no. 15, 11 June 2007 (2007-06-11), pages 3135-3149, XP055124768, ISSN: 0887-624X, DOI: 10.1002/pola.22174	1,5-10
A	abstract see surface titania layer embodiment; page 3136; table 3 -----	2-4,11
A	MAX MCDANIEL: "Some reflections on the current state of Cr-based polymerization catalysts", M R S BULLETIN, vol. 38, no. 03, 1 March 2013 (2013-03-01), pages 234-238, XP055558412, US ISSN: 0883-7694, DOI: 10.1557/mrs.2013.48 the whole document page 235, paragraph 2 -----	1-11

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/059953

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-11

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11

   drawn to the preparation method (I) for a catalyst comprising Ti, SiO_2 and Cr.

   ---

2. claims: 12-14

   drawn to a polymerization method using the catalyst obtainable by preparation method (I).

   ---

3. claims: 15-21

   drawn to the preparation method (II) for a catalyst comprising Ti, SiO_2 and Cr.

   ---

4. claim: 22

   drawn to the preparation method (III) for a catalyst comprising Ti, SiO_2 and Cr.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2018/059953

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017080406 A1	23-03-2017	BR 112018005406 A2	09-10-2018
		CA 2996317 A1	23-03-2017
		CN 108026207 A	11-05-2018
		EP 3350234 A1	25-07-2018
		KR 20180055804 A	25-05-2018
		US 2017080406 A1	23-03-2017
		WO 2017048930 A1	23-03-2017
US 2017015764 A1	19-01-2017	BR 112017023285 A2	04-09-2018
		CA 2984239 A1	03-11-2016
		CN 107683294 A	09-02-2018
		EP 3288985 A1	07-03-2018
		KR 20180002693 A	08-01-2018
		US 2016319052 A1	03-11-2016
		US 2017015764 A1	19-01-2017
		WO 2016176189 A1	03-11-2016
WO 2017032535 A1	02-03-2017	CN 107922541 A	17-04-2018
		EP 3341427 A1	04-07-2018
		US 2018194868 A1	12-07-2018
		WO 2017032535 A1	02-03-2017