Claims

1. A process for producing a metallocene catalyst support-activator for olefin polymerization catalyst compositions, said support-activator comprising:

an intercalated smectite clay having pillars comprising at least one of aluminum, zirconium or chromium and:

(i) at least one rare earth or lanthanum group metal selected from lanthanum and cerium; or

(ii) at least one rare earth or lanthanide group metal as in (i) and gallium;

said clay comprising at least one ion-exchanged metal ion selected from magnesium or zinc comprising steps:

(A) contacting an aqueous slurry comprising a smectite clay with an aqueous pillaring agent comprising at least one of aluminum, zirconium or chromium and: (i) at least one rare earth or lanthanide group metal selected from lanthanum and cerium; or (ii) at least one rare earth or lanthanide group metal as in (i) and gallium; to form a solids-containing phase and an aqueous phase;

(B) separating the solids-containing phase from the aqueous phase formed in (A);

(C) following separation of the solids-containing phase in (B), the solids-containing phase is extracted at least once with water until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the aqueous pillaring agent; or (ii) unconsumed pillaring agent or byproduct thereof; or (iii) both (i) and (ii);

(D) contacting the separated solids obtained in (C) at least once with an aqueous Met_mX_n composition, comprising at least one Met_mX_n wherein Met_m is at least one metal ion selected from magnesiumor zinc, and X_n comprises at least one anionic species; and m and n = numerals that together satisfy the valence requirement for the combination of Met_m and X_n, to form a mixture comprising a solids-containing phase and an aqueous phase;

(E) separating the aqueous phase formed in (D) in order to form a new solids-containing phase;

(F) wherein following separation of the solids-containing phase in (E), the new solids-containing phase is extracted at least once with water, wherein water extraction is repeated until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the Met_mX_n composition; or (ii) unconsumed Met_mX_n composition or byproduct thereof; or (iii) both (i) and (ii) and separating the extracted water from the solids;

wherein in water extraction steps (C) and (F) free or substantially free is confirmed by a conductance value of less than 20,000 µS/cm or a negative $AgNO_3$ test result, or both;

(G) drying the separated, solids-containing phase from (F) in order to obtain dry solids and reducing said dry solids to a dry, particulate form; and

(H) calcining the dry, particulate from (G) to form a dry, pillared, solid catalyst support-activator in particulate form;

wherein said catalyst support-activator is characterized by a basal spacing equal to or greater than about 18.5 angstroms and equal to or less than about 100 angstroms;

said support-activator providing activation of olefin polymerization metallocene catalyst compositions in the absence of aluminoxane or borate activator.

2. The process of claim 1, wherein X_n comprises at least one anionic species independently selected from the group consisting of a halide selected from the group consisting of chloride, iodide, fluoride and bromide; bromate; chlorate; perchlorate; sulfate; sulfamate; carbonate; hydrogen-carbonate; carbamate; nitrite; nitrate; oxalate; phosphate; selenate; sulfamate; azide; alkoxide; amide, including NR_2 or $R[CON(R)]_a$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and a=1-4; and carboxylate, including $R[CO_2]_b$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and b=1-4; or wherein $MetX_n$ is selected from the group consisting of MgF_2, $MgCl_2$, $Mg(OAc)_2$, $Mg(NO_3)_2$, $ZnCl_2$, $ZnSO_4$, and mixtures thereof.

3. The process of claim 1 wherein contacting with Met_mX_n is carried out from 2 to 10 times, and wherein Met_mX_n used in more than one contacting step is the same or different as Met_mX_n used in a prior contacting step, and including a separating step as in (E) between one or more contacting step.

4. The process of any one of claims 1 to 3, wherein the pillaring agent is selected from the group consisting of a basic aluminum complex, a basic zirconium complex, a basic chromium complex and mixtures thereof.

5. A process to produce an olefin polymerization catalyst composition, said process comprising contacting:

(1) at least one organometal compound or procatalyst compound, and

(2) at least one organoaluminum compound, and

(3) at least one catalyst support-activator,

the catalyst composition having catalytic activity for the polymerization of at least one olefin in the absence or substantial absence of organoborates and aluminoxanes,

wherein:

(I) the organometal compound has the following general formula:

$$(X^1)(X^2)(X^3)(X^4)M^1$$

wherein:

M^1 is selected from the group consisting of titanium, zirconium, or hafnium;

(X^1) is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls;

substituents on the substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls of (X^1) are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, silyl groups, alkyl halide groups, halides, organometallic groups, phosphorus groups, nitrogen groups, silicon, phosphorus, boron, or germanium;

at least one substituent on (X^1) can be a bridging group which connects (X^1) and (X^2);

(X^3) and (X^4) are independently selected from the group consisting of halides, aliphatic groups, substituted aliphatic groups, cyclic groups, substituted cyclic groups, combinations of aliphatic groups and cyclic groups, combinations of substituted aliphatic groups and cyclic groups, combinations of aliphatic groups and substituted cyclic groups, combinations of substituted aliphatic groups and substituted cyclic groups, amido groups, substituted amido groups, phosphido groups, substituted phosphido groups, alkyloxide groups, substituted alkyloxide groups, aryloxide groups, substituted aryloxide groups, organometallic groups, and substituted organometallic groups; and (X^3) and (X^4) together may form a diene or polyene moiety or a metallocycle, or may be linked to form a ring;

(X^2) is selected from cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, substituted fluorenyls, halides, aliphatic groups, substituted aliphatic groups, cyclic groups, substituted cyclic groups, combinations of aliphatic groups and cyclic groups, combinations of substituted aliphatic groups and cyclic groups, combinations of aliphatic groups and substituted cyclic groups, combinations of substituted aliphatic groups and substituted cyclic groups, amido groups, substituted amido groups, phosphido groups, substituted phosphido groups, alkyloxide groups, substituted alkyloxide groups, aryloxide groups, substituted aryloxide groups, organometallic groups, and substituted organometallic groups;

substituents on (X^2) are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic groups and cyclic groups, silyl groups, alkyl halide groups, halides, organometallic groups, phosphorus groups, nitrogen groups, silicon, phosphorus, boron, and germanium;

at least one substituent on (X^2) can be a bridging group which connects (X^1) and (X^2);

(II) the organoaluminum compound has the general formula:

$$Al(X^5)_n(X^6)_{3-n}$$

wherein:

(X^5) is a hydride or hydrocarbyl having from 1 to about 20 carbon atoms;

(X^6) is an anionic species independently selected from the group consisting of a halide selected from the group consisting of chloride, iodide, fluoride and bromide; bromate; chlorate; perchlorate; sulfate; sulfamate; carbonate; hydrogen-carbonate; carbamate; nitrite; nitrate; oxalate; phosphate; selenate; sulfamate; azide; alkoxide; amide, including NR_2 or $R[CON(R)]_a$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and a=1-4; and carboxylate, including $R[CO_2]_b$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and b=1-4; and

n is a number from 1 to 3 inclusive; and

(III) the catalyst support-activator is obtainable by a process comprising:

(A) contacting an aqueous slurry comprising a smectite clay with an aqueous pillaring agent comprising at least one of aluminum, zirconium or chromium and: (i) at least one rare earth or lanthanide group metal selected from lanthanum and cerium; or (ii) at least one rare earth or lanthanide group metal as in (i) and gallium; to form a solids-containing phase and an aqueous phase;

(B) separating the solids-containing phase from the aqueous phase formed in (A);

(C) following separation of the solids-containing phase in (B), the solids-containing phase is extracted at least once with water until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the aqueous pillaring agent; or (ii) unconsumed pillaring agent or byproduct thereof; or (iii) both (i) and (ii);

(D) contacting the solids obtained in (C) at least once with an aqueous Met_mX_n composition, wherein Met_m is at least one metal ion selected from magnesium or zinc and X_n comprises at least one anionic species; and m and n = numerals that together satisfy the valence requirement for the combination of Met_m and X_n, in order to form a mixture comprising a solids-containing phase and an aqueous phase;

(E) wherein following separation of the solids-containing phase in (D), the solids-containing phase is extracted at least once with water, wherein water extraction is repeated until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the Met_mX_n composition; or (ii) unconsumed Met_mX_n composition or byproduct thereof; or (iii) both (i) and (ii);

(F) separating the aqueous phase formed in (E) in order to form a new solids-containing phase;

(G) wherein following separation of the solids-containing phase in (F), the new solids-containing phase is extracted at least once with water, wherein water extraction is repeated until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the Met_mX_n composition; or (ii) unconsumed Met_mX_n composition or byproduct thereof; or (iii) both (i) and (ii);

wherein in water extraction steps (E) and (G) free or substantially free is confirmed by a conductance value of less than 20,000 μS/cm or a negative $AgNO_3$ test result, or both;

(H) drying the separated, solids-containing phase from (G) in order to obtain dry solids and reducing said dry solids to a dry, particulate form; and

(I) calcining the dry, particulate from (H) and optionally removing entrapped air, to form a dry, solid catalyst support-activator in particulate form;

wherein said catalyst support-activator is characterized by a basal spacing equal to or greater than about 18.5 angstroms and equal to or less than about 100 angstroms;

said support-activator providing activation of olefin polymerization metallocene catalyst compositions in the absence of aluminoxane or borate activator.

6. The process of claim 5, wherein X_n comprises at least one anionic species independently selected from the group consisting of a halide selected from the group consisting of chloride, iodide, fluoride and bromide; bromate; chlorate; perchlorate; sulfate; sulfamate; carbonate; hydrogen-carbonate; carbamate; nitrite; nitrate; oxalate; phosphate; selenate; sulfamate; azide; alkoxide; amide, including NR_2 or $R[CON(R)]_a$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and a=1-4; and carboxylate, including $R[CO_2]_b$, wherein R is independently H or a C_1-C_{20} unsubstituted or substituted hydrocarbyl group and b=1-4; or wherein Met_mX_n is selected from MgF_2, $MgCl_2$, $Mg(OAc)_2$, $Mg(NO_3)_2$, $ZnCl_2$, $ZnSO_4$, and mixtures thereof.

7. The process of claim 5 wherein contacting with Met_mX_n is carried out from 2 to 10 times, and wherein Met_mX_n used in more than one contacting step is the same or

different as Met_mX_n used in a prior contacting step, and including a separating step as in (F) between one or more contacting step.

8. The process of any one of claims 5, 6 or 7, wherein the pillaring agent is selected from the group consisting of a basic aluminum complex, a basic zirconium complex, a basic chromium complex and mixtures thereof.

9. An olefin polymerization metallocene catalyst composition produced by the process of any one of claims 5, 6, 7 or 8, comprising an organometal compound or procatalyst compound, an organoaluminum compound and a catalyst support-activator comprising an intercalated calcined smectite clay having pillars comprising aluminum and: (i) at least one rare earth or lanthanide group metal selected from lanthanum, cerium and mixtures thereof; or (ii) at least one rare earth or lanthanide group metal as in (i) and gallium; said clay comprising at least one ion-exchanged metal ion selected from the group consisting of magnesiumand zinc; said catalyst composition in the absence of an aluminoxane or borate activator.

10. The catalyst composition of claim 9 wherein the catalyst support-activator comprises (i) or (ii) and is characterized by a basal spacing equal to or greater than about 18.5 angstroms and equal to or less than about 100 angstroms.

11. A process for producing a metallocene catalyst support-activator for olefin polymerization catalyst compositions, said support-activator comprising:

an intercalated smectite clay having pillars comprising at least one of aluminum, zirconium or chromium and:

(i) at least one rare earth or lanthanum group metal selected from lanthanum and cerium; or

(ii) at least one rare earth or lanthanide group metal as in (i) and gallium;

said clay comprising at least one ion-exchanged metal ion selected from the group consisting of aluminum, barium, calcium, cerium, cesium, copper, chromium, gadolinium, gallium, germanium, hafnium, holmium, iron (II and III), lanthanum, lithium, magnesium, manganese, neodymium, potassium, praseodymium, rubidium, samarium, silver, selenium, sodium, strontium, tellurium, terbium, thallium, thorium, tin, titanium, uranium, ytterbium, yttrium, zinc and zirconium comprising steps:

(A) contacting an aqueous slurry comprising a smectite clay with an aqueous pillaring agent comprising at least one of aluminum, zirconium or chromium, and: (i) at least one rare earth or lanthanide group metal selected from lanthanum and cerium; or (ii) at least one rare earth or lanthanide group metal as in (i) and gallium; to form a solids-containing phase and an aqueous phase;

(B) separating the solids-containing phase from the aqueous phase formed in (A);

(C) following separation of the solids-containing phase in (B), the solids-containing phase is extracted at least once with water until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the aqueous pillaring agent; or (ii) unconsumed pillaring agent or byproduct thereof; or (iii) both (i) and (ii);

(D) contacting the separated solids obtained in (C) at least once with an aqueous Met_mX_n composition, comprising at least one Met_mX_n wherein Met_m is at least one metal ion selected from the group consisting of aluminum, barium, calcium, cerium, cesium, chromium, cobalt, copper, chromium, gadolinium, gallium, germanium, hafnium, holmium, iron (II and III), lanthanum, lithium, magnesium, manganese, neodymium, nickel, potassium, praseodymium, rubidium, samarium, silver, selenium, sodium, strontium, tellurium, terbium, thallium, thorium, tin, titanium, uranium, ytterbium, yttrium, zinc and zirconium, and X_n comprises at least one anionic species; and m and n = numerals that together satisfy the valence requirement for the combination of Met_m and X_n, to form a mixture comprising a solids-containing phase and an aqueous phase;

(E) separating the aqueous phase formed in (D) in order to form a new solids-containing phase;

(F) wherein following separation of the solids-containing phase in (E), the new solids-containing phase is extracted at least once with water, wherein water extraction is repeated until upon separation from the solids, the separated water is free or substantially free of: (i) residual anions originally present in the Met_mX_n composition; or (ii) unconsumed Met_mX_n composition or byproduct thereof; or (iii) both (i) and (ii) and separating the extracted water from the solids;

wherein in water extraction steps (C) and (F) free or substantially free is confirmed by a conductance value of less than 20,000 μS/cm or a negative $AgNO_3$ test result, or both;

(G) drying the separated, solids-containing phase from (F) in order to obtain dry solids and reducing said dry solids to a dry, particulate form; and

(H) calcining the dry, particulate from (G) to form a dry, pillared, solid catalyst support-activator in particulate form;

wherein said catalyst support-activator is characterized by a basal spacing equal to or greater than 30 angstroms and equal to or less than about 100 angstroms;

said support-activator providing activation of olefin polymerization metallocene catalyst compositions in the absence of aluminoxane or borate activator.