

A SUPPORTED NONMETALLOCENE CATALYST, PREPARATION AND USE THEREOF

Technical Field

The present invention relates to a nonmetallocene catalyst. Specifically, this invention relates to a supported nonmetallocene catalyst, preparation thereof and use thereof in olefin homopolymerization/copolymerization. The present invention further relates to an ethylene polymer produced by this olefin homopolymerization/copolymerization, and use of said ethylene polymer in production of a chlorinated polyethylene.

Background Art

A chlorinated polyethylene (CPE) is a random polymer produced by a replacement reaction between polyethylene and chlorine gas. CPEs may perform like soft plastics, elastic plastics, rubber-like elastics, leather-like rigid plastics or fire resisting brittle resins, depending on the chlorine content in the molecular thereof. This specific molecular structure provides CPE with superior performances in flexibility, weather resistance, ozone resistance, chemical resistance, cold resistance and fire resistance, and makes it find wide use in such industrial fields like plastic doors/windows, PVC tubes and sheets, water-proofing rolls, anti-corrosion coatings, wires/cables, rubber-plastic composites and so on.

Generally, a chlorinated polyethylene is produced by using a polyethylene powder as the starting material. The polyethylene powder can be readily obtained by a polymerization process, or can be obtained by milling polyethylene pellets. The polymerization process can be conducted at an industrial scale with an acceptable cost, and progressively represents the dominant process for producing the starting material of the chlorinated polyethylene.

Chinese patent Nos. 200910180602.9 and 200910180605.2 disclose a polyethylene respectively, which has been produced by homopolymerization of ethylene or copolymerization of ethylene with an alpha-olefin in the presence of a supported nonmetallocene catalyst. The polyethylene suffers from inferior performances in particle morphology, specific surface area, pore volume and pore size, and for this reason, is not suitable for use in production of a chlorinated polyethylene as the starting material.

The Chinese patent No. 200710162667.1 discloses a magnesium compound supported nonmetallocene catalyst and preparation thereof, wherein a magnesium compound containing a nonmetallocene ligand directly contacts with a compound containing a catalytically active metal by an in-situ supporting process. The magnesium compound to be used herein may be an alkoxy magnesium, however, said prior art fails to identify if the shape of the alkoxy magnesium shows some influence on the polymerization activity of the resultant catalyst or the bulk density of

the resultant polymer, and further fails to suggest if the polymer produced herein can be used for direct production of a chlorinated polyethylene as the starting material.

Therefore, in the prior art, there still exists a need for a polyethylene, which is especially suitable for use in direct production of a chlorinated polyethylene as the starting material. Any other polyolefin, which shows characteristics suitable for use in direct production of the corresponding chlorinated polyolefin, is needed by the prior art as well.

Summary of the Invention

Upon in-depth study of the prior art, the present inventors found that the supported nonmetallocene catalyst conventionally used by the prior art results in a polyolefin showing characteristics quite unsuitable for use in direct production of a chlorinated polyolefin, and on the basis of this fact, further found that if the polyolefin is to be produced by using a supported nonmetallocene catalyst produced in accordance with the present specified process, the problems identified as aforesaid can be solved, whereby achieving this invention.

According to this invention, the present process for producing a supported nonmetallocene catalyst can be conducted in the absence of any proton donor (for example, those conventionally used in this field). Further, the present process for producing a supported nonmetallocene catalyst can be conducted in the absence of any electron donor (for example, compounds like mono-esters, di-esters, di-ethers, di-ketones and glycol esters, conventionally used in production of a Ziegler-Natta catalyst or a Ziegler catalyst). Still further, the present process for producing a supported nonmetallocene catalyst can be conducted without the need of severe reaction requirements and reaction conditions. For these reasons, the present process is simple and suitable for industrial application.

Specifically, this invention relates to the following aspects.

1. A process for producing a supported nonmetallocene catalyst, comprising the step of: contacting a nonmetallocene ligand with a chemical treating agent selected from a Group IVB metal compound in the presence of an alkoxy magnesium spherical carrier, preferably comprising the step of contacting the nonmetallocene ligand, the chemical treating agent and the alkoxy magnesium spherical carrier in the presence of a solvent.

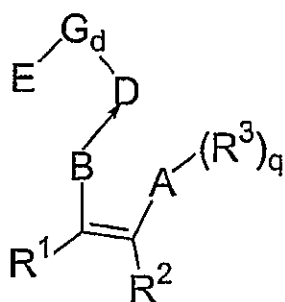
2. The process according to any of the aforesaid aspects, wherein in the presence of the solvent, the nonmetallocene ligand contacts the alkoxy magnesium spherical carrier, and then the chemical treating agent is added for a further contact.

3. The process according to any of the aforesaid aspects, wherein the alkoxy magnesium spherical carrier is represented by the formula $Mg(OR_a)(OR_b)$, wherein R_a and R_b are the same as or different from each other, and each independently selected from a C_1 - C_{18} straight-chain or branched alkyl, preferably each

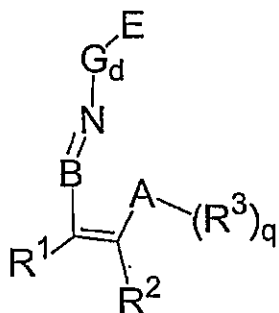
independently selected from a C₁-C₁₀ straight-chain or branched alkyl, more preferably each independently selected from a C₁-C₆ straight-chain or branched alkyl, further preferably each independently selected from a C₁-C₄ straight-chain or branched alkyl, more preferably each independently selected from a C₂-C₄ straight-chain or branched alkyl, most preferably both ethyl.

4. The process according to any of the aforesaid aspects, wherein the alkoxy magnesium spherical carrier has a sphericity of 1 to 3, preferably 1 to 1.5, a bulk density of 0.2 to 1.0 g/cm³, preferably 0.25 to 0.7 g/cm³, more preferably 0.3 to 0.5 g/cm³, and an average particle size of 5 to 2000 μm, preferably 50 to 1500 μm, more preferably 100 to 1000 μm.

5. The process according to any of the aforesaid aspects, wherein the nonmetallocene ligand is one or more selected from the group consisting of the compounds having the following structure,

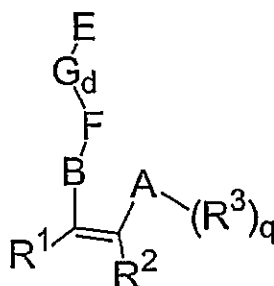


preferably one or more selected from the group consisting of the following compound (A) and the following compound (B),



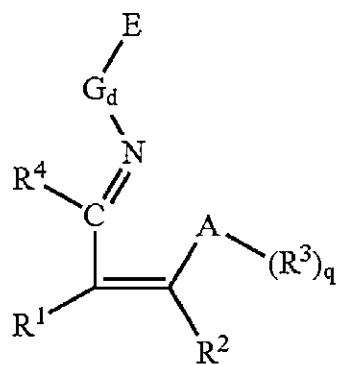
(A)

and

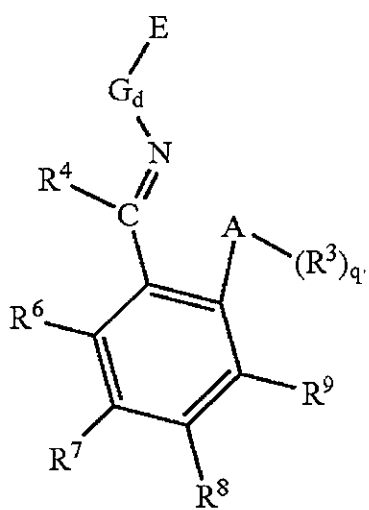


(B)

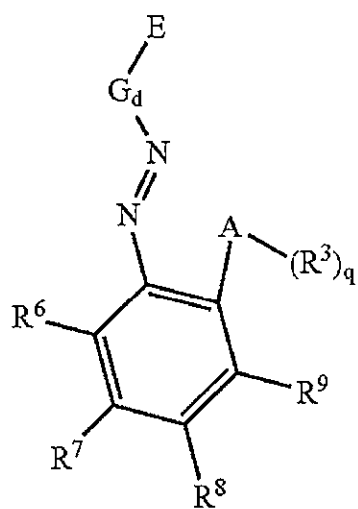
more preferably one or more selected from the group consisting of the following compound (A-1), the following compound (A-2), the following compound (A-3), the following compound (A-4), the following compound (B-1), the following compound (B-2), the following compound (B-3), and the following compound (B-4),



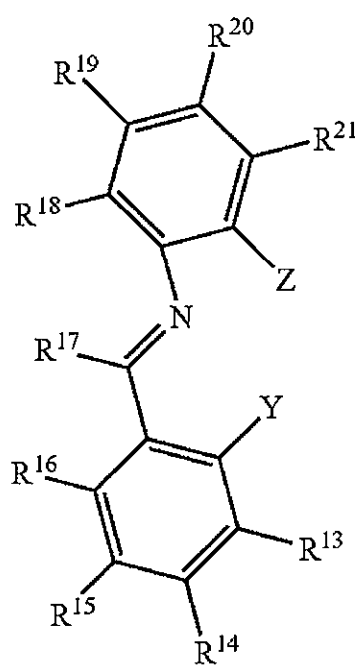
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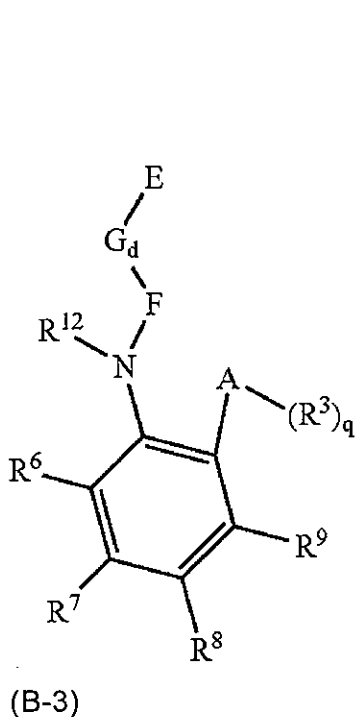
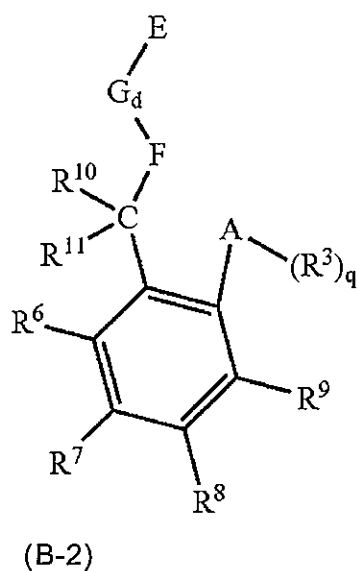
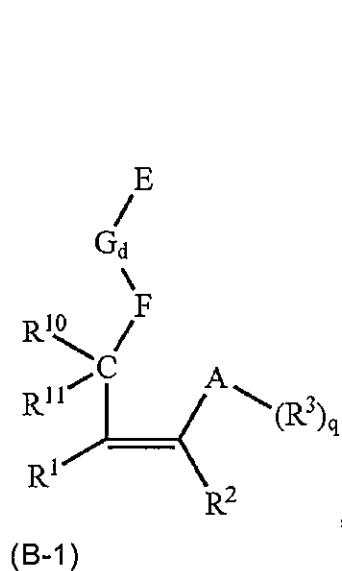
(A-2)



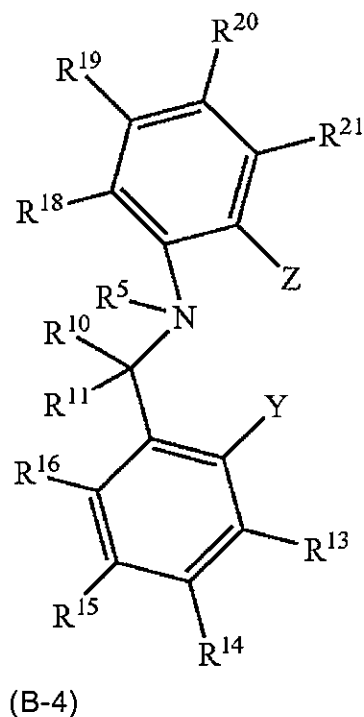
(A-3)



(A-4)



and



in all of the aforesaid formulae,

q is 0 or 1;

d is 0 or 1;

A is selected from the group consisting of an oxygen atom, a sulfur atom, a selenium atom, NR^{22} , $\text{-NR}^{23}\text{R}^{24}$, $\text{-N(O)R}^{25}\text{R}^{26}$, PR^{27} , $\text{-PR}^{28}\text{R}^{29}$, $\text{-P(O)R}^{30}\text{OR}^{31}$, a sulfone group, a sulfoxide group and -Se(O)R^{39} , wherein N, O, S, Se and P each represents a coordination atom;

B is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, a phosphor-containing group and a $\text{C}_1\text{-C}_{30}$ hydrocarbyl;

D is selected from the group consisting of a nitrogen atom, an oxygen atom, a

sulfur atom, a selenium atom, a phosphor atom, a nitrogen-containing group, a phosphor-containing group, a C₁-C₃₀ hydrocarbyl, a sulfone group or a sulfoxide group, wherein N, O, S, Se and P each represents a coordination atom;

E is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group, wherein N, O, S, Se and P each represents a coordination atom;

F is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

G is selected from the group consisting of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group;

Y is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

Z is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group, wherein N, O, S, Se and P each represents a coordination atom;

→ represents a single bond or a double bond;

— represents a covalent bond or an ionic bond;

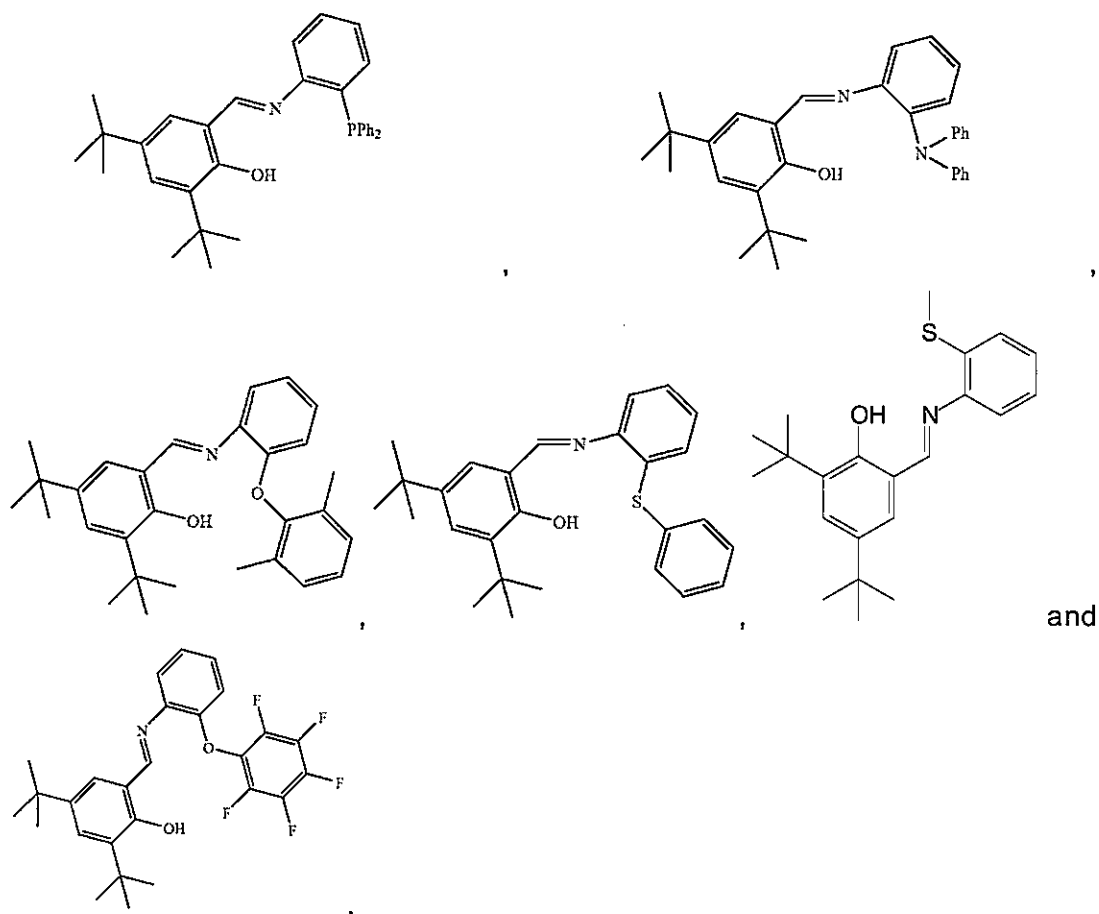
R¹ to R⁴, R⁶ to R²¹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group, R²² to R³⁶, R³⁸ and R³⁹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl and a substituted C₁-C₃₀ hydrocarbyl, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring (preferably an aromatic ring) with one another;

the inert functional group is selected from the group consisting of a halogen atom, an oxygen-containing group, a nitrogen-containing group, a silicon-containing group, a germanium-containing group, a sulfur-containing group, a tin-containing group, a C₁-C₁₀ ester group and a nitro group,

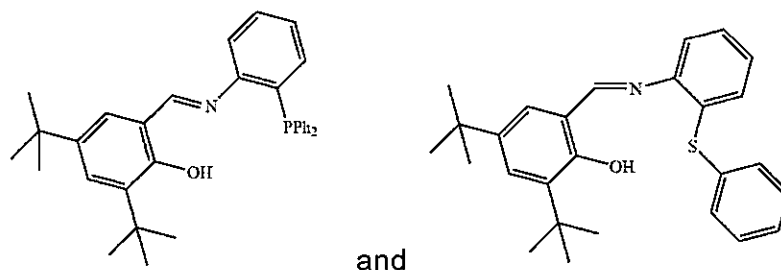
R⁵ is selected from the group consisting of the lone pair electron on the nitrogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a selenium-containing group, and a phosphor-containing group, with the proviso that when R⁵ is the oxygen-containing group, the sulfur-containing group, the nitrogen-containing group, the selenium-containing group or the phosphor-containing group, N, O, S, P and Se in the group R⁵ each can act as a coordination atom; and

the substituted C₁-C₃₀ hydrocarbyl is selected from a C₁-C₃₀ hydrocarbyl having

one or more substituent(s) selected from a halogen atom and a C₁-C₃₀ alkyl group,
the nonmetallocene ligand is more preferably one or more selected from the group consisting of the following compounds,



more preferably one or more selected from the group consisting of the following compounds,



6. The process according to any of the aforesaid aspects, wherein,
the halogen atom is selected from the group consisting of F, Cl, Br and I,

the nitrogen-containing group is selected from the group consisting of NR^{22} , $\text{-NR}^{23}\text{R}^{24}$, $\text{-T-NR}^{23}\text{R}^{24}$ and $\text{-N(O)R}^{25}\text{R}^{26}$,

the phosphor-containing group is selected from the group consisting of PR^{27} , $\text{-PR}^{28}\text{R}^{29}$, $\text{-P(O)R}^{30}\text{R}^{31}$ and $\text{-P(O)R}^{32}(\text{OR}^{33})$,

the oxygen-containing group is selected from the group consisting of hydroxy, -OR^{34} and -T-OR^{34} ,

the sulfur-containing group is selected from the group consisting of $-SR^{35}$, $-T-SR^{35}$, $-S(O)R^{36}$ and $-T-SO_2R^{37}$,

the selenium-containing group is selected from the group consisting of $-SeR^{38}$, $-T-SeR^{38}$, $-Se(O)R^{39}$ and $-T-Se(O)R^{39}$,

the group T is selected from the group consisting of a C_1-C_{30} hydrocarbonyl and a substituted C_1-C_{30} hydrocarbonyl,

R^{37} is selected from the group consisting of a hydrogen atom, a C_1-C_{30} hydrocarbonyl, and a substituted C_1-C_{30} hydrocarbonyl,

the C_1-C_{30} hydrocarbonyl is selected from the group consisting of a C_1-C_{30} alkyl group, a C_7-C_{30} alkylaryl group, a C_7-C_{30} aralkyl group, a C_3-C_{30} cyclic alkyl group, a C_2-C_{30} alkenyl group, a C_2-C_{30} alkynyl group, a C_6-C_{30} aryl group, a C_8-C_{30} fused-ring group and a C_4-C_{30} heterocycle group, wherein the heterocycle group contains 1 to 3 hetero atom(s) selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom,

the silicon-containing group is selected from the group consisting of $-SiR^{42}R^{43}R^{44}$, and $-T-SiR^{45}$,

the germanium-containing group is selected from the group consisting of $-GeR^{46}R^{47}R^{48}$, and $-T-GeR^{49}$,

the tin-containing group is selected from the group consisting of $-SnR^{50}R^{51}R^{52}$, $-T-SnR^{53}$ and $-T-Sn(O)R^{54}$,

R^{42} to R^{54} are each independently selected from the group consisting of a hydrogen atom, the C_1-C_{30} hydrocarbonyl and the substituted C_1-C_{30} hydrocarbonyl, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another, and

the group T is defined as aforesaid.

7. The process according to any of the aforesaid aspects, wherein ratio by molar of the alkoxy magnesium spherical carrier (based on Mg) to the nonmetallocene ligand is 1:0.001-0.08, preferably 1:0.005-0.06, more preferably 1:0.01-0.04, and ratio by molar of the alkoxy magnesium spherical carrier (based on Mg) to the chemical treating agent (based on the Group IVB metal) is 1:1-30, preferably 1:2-20, more preferably 1:4-10.

8. The process according to any of the aforesaid aspects, wherein the Group IVB metal compound is one or more selected from the group consisting of a Group IVB metal halide, a Group IVB metal alkyl halide, and a Group IVB metal alkoxy halide, preferably one or more of the Group IVB metal halide, more preferably one or more selected from the group consisting of $TiCl_4$, $TiBr_4$, $ZrCl_4$, $ZrBr_4$, $HfCl_4$ and $HfBr_4$, more preferably one or more selected from the group consisting of $TiCl_4$ and $ZrCl_4$.

9. A supported nonmetallocene catalyst, produced in line with the process according to any of the aforesaid aspects.

10. An olefin homopolymerization/copolymerization process, wherein the supported nonmetallocene catalyst according to the aspect 9 is used as the main catalyst, in combination of one or more selected from the group consisting of an

aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt as the co-catalyst, for homopolymerization or copolymerization of the olefin.

11. The olefin homopolymerization/copolymerization process according to any of the aforesaid aspects, wherein a slurry polymerization procedure is involved, and under the conditions of a total polymerization pressure of 0.2 to 2.0 MPa (preferably 0.5 to 1.5 MPa), a partial pressure ratio of hydrogen gas to ethylene of 0.01-0.2:1 (preferable 0.02-0.1:1, most preferably 0.03-0.08:1), a polymerization temperature of 60 to 100 °C (preferably 70 to 95 °C, more preferably 80 to 90 °C), and an amount of an optional comonomer of 0.5 to 10 g per 1mg of the main catalyst (preferably 1 to 5 g per 1mg of the main catalyst), the homopolymerization of ethylene or the copolymerization of ethylene with at least one alpha-olefin(s) selected from a C₃ to C₁₂ alpha-olefin (preferably a C₃ to C₈ alpha-olefin) is conducted to obtain an ethylene polymer.

12. An ethylene polymer, characterized by having a recurring unit derived from ethylene and optionally a recurring unit derived from at least one alpha-olefin(s) selected from a C₃ to C₁₂ alpha-olefin (preferably a C₃ to C₈ alpha-olefin), a bulk density of 0.33 to 0.50 g/cm³, preferably 0.38 to 0.46 g/cm³, more preferably 0.40 to 0.44 g/cm³, an oligomer content of less than 2 g/L, a fine (less than 75 μm) powder content of less than 5 wt%, a melt index (at 190 °C and 2.16 kg load) of 0.02 to 5 g/10min, a molecular weight distribution Mw/Mn of 2.5 to 20 (preferably 4 to 10), a density of 0.94 to 0.96 g/cm³, an average particle size of 200 to 400 μm, a specific surface area of 0.2 to 3.0 m²/g, preferably 1.0 to 3.0 m²/g, more preferably 1.5 to 3.0 m²/g, a pore volume of 0.001 to 0.15 cm³/g, preferably 0.01 to 0.15 cm³/g, more preferably 0.05 to 0.12 cm³/g, a pore size of 10 to 80 nm, preferably 20 to 70 nm, more preferably 20 to 60 nm, and with respect to the total weight 100 wt% of the ethylene polymer, a content of the recurring unit derived from ethylene of 95 to 100 wt%, and a content of the recurring unit derived from the at least one alpha-olefin(s) of 0 to 5 wt%.

13. A chlorinated polyethylene, obtained by chlorination of the ethylene polymer according to the aspect 12 or by chlorination of an ethylene polymer produced in line with the process according to the aspect 11.

Effect of the Invention

The process for producing the supported nonmetallocene catalyst according to this invention is simple in terms of procedure, industrially feasible and stable in terms of dynamics.

By using a catalyst system composed of the supported nonmetallocene catalyst produced in line with the present process and a co-catalyst, only a relatively low amount of the co-catalyst (for example methyl aluminoxane or triethyl aluminum) is needed to achieve a relatively high olefin polymerization activity, and when used in a copolymerization, this catalyst system shows a significant comonomer effect, i.e.

under relatively the same conditions, the activity for copolymerization is higher than that for homopolymerization.

According to this invention, the polyolefin (especially the ethylene polymer) produced in line with the present olefin homopolymerization / copolymerization process is characterized by superior particle morphology, high bulk density and specific surface area, variant pore structure, desirable particle size distribution and molecular weight distribution, and being especially suitable for use in direct production of a chlorinated polyolefin as the starting material.

Detailed Description of the Invention

This invention will be described in details hereinafter with reference to the following specific embodiments. However, it is known that the protection scope of this invention should not be construed as limited to these specific embodiments, but rather determined by the attached claims.

In the context of this specification, unless otherwise specified or identified as being unreasonable by a person skilled in the art, a hydrocarbon or hydrocarbon derivative group having 3 or more carbon atoms (for example propyl, propoxy, butyl, butane, butene, butenyl, hexane, etc.), when appears without the prefix "normal" or "n-", generally refers to its corresponding n-isomeride. For example, propyl generally refers to n-propyl, while butane generally refers to n-butane.

In the context of this specification, to simplify the description, a group or substituent on a compound is generally defined, however not specified as to its valence, i.e. whether it is mono-valent, bi-valent, tri-valent, tetra-valent or else. Nevertheless, it is easy for a person skilled in the art to identify this after taking into consideration the position or substitution condition of said group or substituent on said compound.

According to this invention, firstly, disclosed is a process for producing a supported nonmetallocene catalyst, comprising the step of contacting a nonmetallocene ligand with a chemical treating agent selected from a Group IVB metal compound in the presence of an alkoxy magnesium spherical carrier (hereinafter referred to as "contacting step").

According to one significant aspect of this invention, when the nonmetallocene ligand contacts the chemical treating agent in the presence of the alkoxy magnesium spherical carrier (as the carrier), a coordination reaction therebetween occurs to generate a nonmetallocene complex, which takes the IVB metal atom originated from the chemical treating agent as the central metal atom, and at the same time, the as-generated nonmetallocene complex is directly or immediately loaded onto or into the carrier (hereinafter referred to as "in-situ supporting reaction").

The alkoxy magnesium spherical carrier is further described as follows.

According to this invention, the alkoxy magnesium constituting the alkoxy magnesium spherical carrier is generally represented by the formula $Mg(OR_a)(OR_b)$.

In this formula, R_a and R_b are the same as or different from each other, and each independently selected from a C_1 - C_{18} straight-chain or branched alkyl, preferably each independently selected from a C_1 - C_{10} straight-chain or branched alkyl, more preferably each independently selected from a C_1 - C_6 straight-chain or branched alkyl, further preferably each independently selected from a C_1 - C_4 straight-chain or branched alkyl, more preferably each independently selected from a C_2 - C_4 straight-chain or branched alkyl.

According to this invention, as the alkoxy magnesium, exemplified could be dimethoxy magnesium ($Mg(OCH_3)_2$), diethoxy magnesium ($Mg(OC_2H_5)_2$), dipropoxy magnesium ($Mg(OC_3H_7)_2$), dibutoxy magnesium ($Mg(OC_4H_9)_2$), di-isobutoxy magnesium ($Mg(i-OC_4H_9)_2$), di(2-ethylhexyloxy) magnesium, ethoxy propoxy magnesium ($Mg(OC_2H_5)(OC_3H_7)$), ethoxy butoxy magnesium ($Mg(OC_2H_5)(OC_4H_9)$), and etc., preferably diethoxy magnesium ($Mg(OC_2H_5)_2$).

The alkoxy magnesium or the alkoxy magnesium spherical carrier could be used with one kind or as a mixture of two or more kinds at any ratio therebetween, without any limitation.

According to this invention, the alkoxy magnesium spherical carrier can be produced by any conventional process, or can be any commercially available one, without any limitation.

According to this invention, in general, the alkoxy magnesium spherical carrier has a sphericity (measured on a laser particle size analyzer, wherein the sphericity is calculated as the value obtained by dividing the measured longest dimension of the spherical carrier by the measured shortest dimension of the spherical carrier) of 1 to 3, preferably 1 to 1.5.

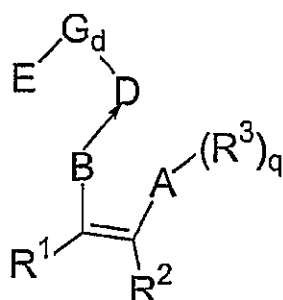
According to this invention, in general, the alkoxy magnesium spherical carrier has a bulk density (measured in accordance with the Chinese national standard GB1636-79) of 0.2 to 1.0 g/cm^3 , preferably 0.25 to 0.7 g/cm^3 , more preferably 0.3 to 0.5 g/cm^3 .

According to this invention, in general, the alkoxy magnesium spherical carrier has an average particle size (measured on a laser particle size analyzer) of 5 to $2000\text{ }\mu\text{m}$, preferably 50 to $1500\text{ }\mu\text{m}$, more preferably 100 to $1000\text{ }\mu\text{m}$.

According to this invention, the term "nonmetallocene complex" refers to a single-site catalyst for olefin polymerization, and completely different from a metallocene complex, to an organic metallic compound containing in its structure no cyclopentadienyl or any derivative thereof (e.g. a metallocene ring, a fluorene ring or an indene ring), and capable of exhibiting a catalysis activity for olefin polymerization when used in combination with a co-catalyst like that identified as below in this specification, which is hereinafter also referred to as a nonmetallocene complex for olefin polymerization. The compound contains a central metal atom and at least one multi-dentate ligand (preferably a tri or more -dentate ligand) bonding to the central metal atom by a coordination bond. The term "nonmetallocene ligand" corresponds to the aforesaid multi-dentate ligand.

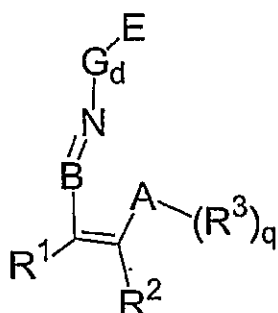
According to this invention, the nonmetallocene ligand is selected from the

compounds having the following structure,



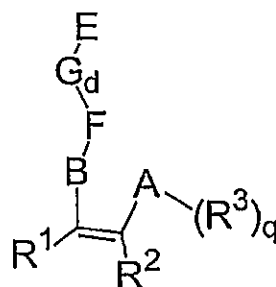
According to this invention, the groups A, D and E (the coordination groups) in the compound form a coordination bond by a coordination reaction with the Group IVB metal atom contained in the Group IVB metal compound used as the chemical treating agent herein through the coordination atoms (for example, hetero atoms like N, O, S, Se and P) contained in these groups, whereby forming a complex (i.e. the nonmetallocene complex according to this invention) having said Group IVB metal atom as the central metal atom M.

According to a further embodiment of this invention, the nonmetallocene ligand is selected from the following compound (A) and the following compound (B),



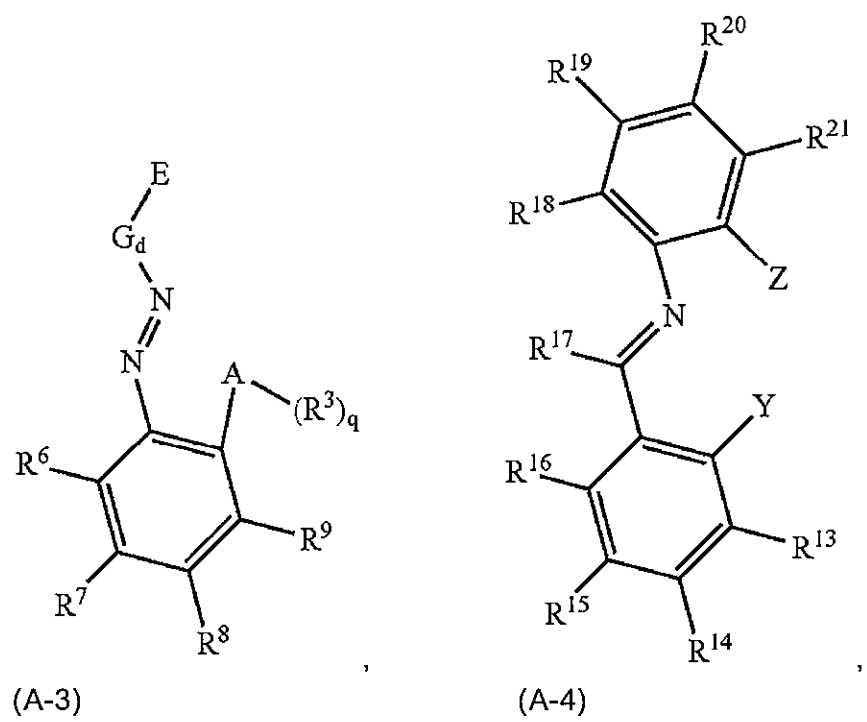
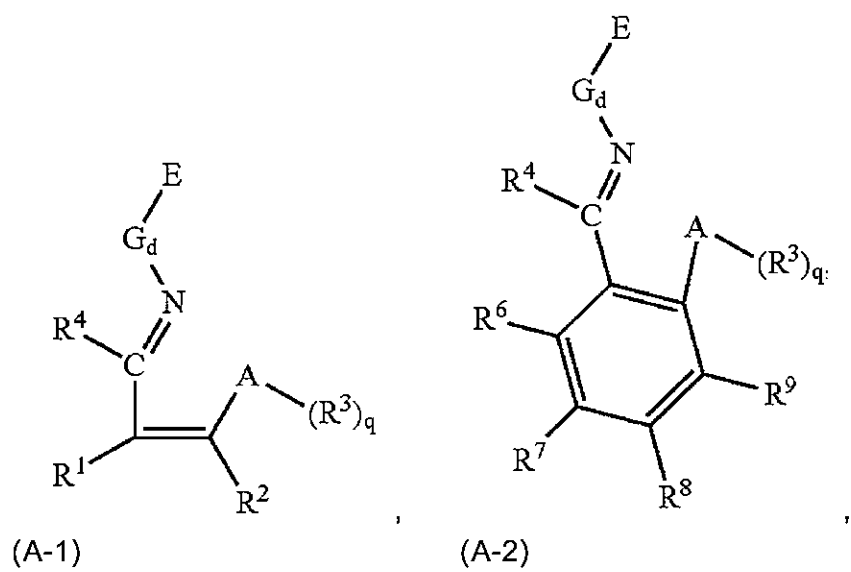
(A)

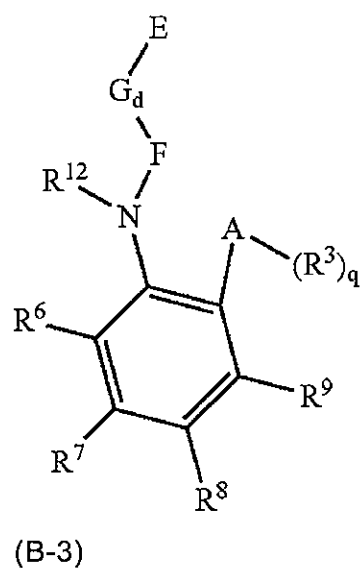
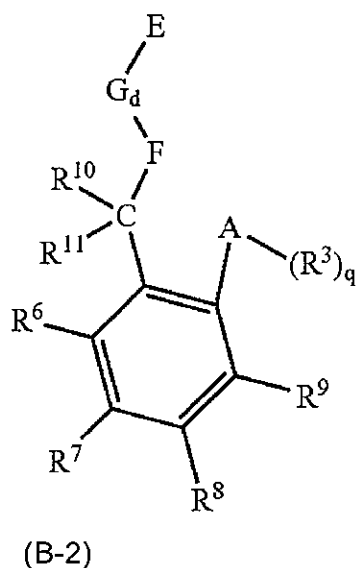
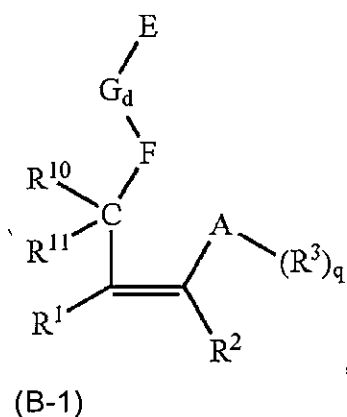
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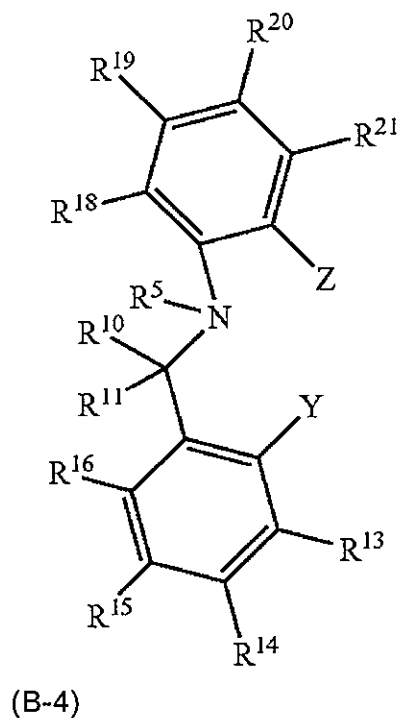
(B)

According to a further embodiment of this invention, the nonmetallocene ligand is selected from the following compound (A-1), the following compound (A-2), the following compound (A-3), the following compound (A-4), the following compound (B-1), the following compound (B-2), the following compound (B-3), and the following compound (B-4),





and



In all of the aforesaid formulae,

q is 0 or 1.

d is 0 or 1.

A is selected from the group consisting of an oxygen atom, a sulfur atom, a

selenium atom, NR^{22} , $\text{-NR}^{23}\text{R}^{24}$, $\text{-N(O)R}^{25}\text{R}^{26}$, PR^{27} , $\text{-PR}^{28}\text{R}^{29}$, $\text{-P(O)R}^{30}\text{OR}^{31}$, a sulfone group, a sulfoxide group and -Se(O)R^{39} , wherein N, O, S, Se and P each represents a coordination atom.

B is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, a phosphor-containing group and a $\text{C}_1\text{-C}_{30}$ hydrocarbyl.

D is selected from the group consisting of a nitrogen atom, an oxygen atom, a

sulfur atom, a selenium atom, a phosphor atom, a nitrogen-containing group, a phosphor-containing group, a C₁-C₃₀ hydrocarbyl, a sulfone group, and a sulfoxide group, wherein N, O, S, Se and P each represents a coordination atom.

E is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group (-CN), wherein N, O, S, Se and P each represents a coordination atom.

F is selected from the group consisting of a nitrogen atom, a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom.

G is selected from the group consisting of a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group.

Y is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom.

Z is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group (-CN), for example, -NR²³R²⁴, -N(O)R²⁵R²⁶, -PR²⁸R²⁹, -P(O)R³⁰R³¹, -OR³⁴, -SR³⁵, -S(O)R³⁶, -SeR³⁸ or -Se(O)R³⁹, wherein N, O, S, Se and P each represents a coordination atom.

→ represents a single bond or a double bond.

— represents a covalent bond or an ionic bond.

R¹ to R⁴, R⁶ to R²¹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl (preferably a halogenated hydrocarbyl, for example -CH₂Cl and -CH₂CH₂Cl) and an inert functional group. R²² to R³⁶, R³⁸ and R³⁹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl (preferably a halogenated hydrocarbyl, for example -CH₂Cl and -CH₂CH₂Cl). These groups may be identical to or different from one another, and any adjacent groups (for example R¹ and R², R⁶ and R⁷, R⁷ and R⁸, R⁸ and R⁹, R¹³ and R¹⁴, R¹⁴ and R¹⁵, R¹⁵ and R¹⁶, R¹⁸ and R¹⁹, R¹⁹ and R²⁰, R²⁰ and R²¹, R²³ and R²⁴, or R²⁵ and R²⁶) may form a bond or a ring (preferably an aromatic ring, for example a unsubstituted benzene ring or a benzene ring substituted by one to four of a C₁-C₃₀ hydrocarbyl or a substituted C₁-C₃₀ hydrocarbyl (preferably a halogenated hydrocarbyl, for example -CH₂Cl and -CH₂CH₂Cl)) with one another.

R⁵ is selected from the group consisting of the lone pair electron on the nitrogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a selenium-containing group, and a phosphor-containing group, with the proviso that when R⁵ is the oxygen-containing group, the sulfur-containing group, the nitrogen-containing group, the selenium-containing

group or the phosphor-containing group, N, O, S, P and Se in the group R⁵ each can act as a coordination atom (to coordinate with the central metal atom M).

In the context of this invention, as the inert functional group, one or more selected from the group consisting of a halogen atom, an oxygen-containing group, a nitrogen-containing group, a silicon-containing group, a germanium-containing group, a sulfur-containing group, a tin-containing group, a C₁-C₁₀ ester group and a nitro group (-NO₂) can be exemplified, while a C₁-C₃₀ hydrocarbyl or a substituted C₁-C₃₀ hydrocarbyl is generally excluded.

In the context of this invention, restricted by the specific structure of the present nonmetallocene ligand, the inert functional group is characterized that:

(1) it will not interfere with the coordination process between the aforesaid group A, D, E, F, Y or Z and the central metal atom M, and

(2) its capability to form a coordination bond with the central metal atom M is inferior to the capability of the aforesaid group A, D, E, F, Y or Z to form a coordination bond with the central metal atom M, and will not displace the formed coordination between the central metal atom M and any of these groups A, D, E, F, Y and Z.

According to this invention, in all of the aforesaid formulae, if necessary, any two or more adjacent groups (for example R²¹ and the group Z, or R¹³ and the group Y) may form a ring with one another, preferably a C₆-C₃₀ aromatic hetero-ring containing the hetero atom originated from the group Z or Y, for example a pyridine ring, wherein the aromatic hetero-ring is optionally substituted by one or more substituent(s) selected from the group consisting of a C₁-C₃₀ hydrocarbyl and a substituted C₁-C₃₀ hydrocarbyl.

In the context of this invention, the halogen atom is selected from the group consisting of F, Cl, Br and I.

In the context of this invention, the nitrogen-containing group is selected from

the group consisting of $\begin{array}{c} \diagup \\ \text{NR}^{22} \\ | \end{array}$, -NR²³R²⁴, -T-NR²³R²⁴ and -N(O)R²⁵R²⁶.

In the context of this invention, the phosphor-containing group is selected from

the group consisting of $\begin{array}{c} \diagup \\ \text{PR}^{27} \\ | \end{array}$, -PR²⁸R²⁹, -P(O)R³⁰R³¹ and -P(O)R³²(OR³³).

In the context of this invention, the oxygen-containing group is selected from the group consisting of hydroxy, -OR³⁴ and -T-OR³⁴.

In the context of this invention, the sulfur-containing group is selected from the group consisting of -SR³⁵, -T-SR³⁵, -S(O)R³⁶ and -T-SO₂R³⁷.

In the context of this invention the selenium-containing group is selected from the group consisting of -SeR³⁸, -T-SeR³⁸, -Se(O)R³⁹ and -T-Se(O)R³⁹.

In the context of this invention, the group T is selected from the group consisting of a C₁-C₃₀ hydrocarbyl or a substituted C₁-C₃₀ hydrocarbyl.

In the context of this invention, R³⁷ is selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, and a substituted C₁-C₃₀ hydrocarbyl.

In the context of this invention, the C₁-C₃₀ hydrocarbyl is selected from the

group consisting of a C₁-C₃₀ alkyl group (for example a C₁-C₆ alkyl group, for example isobutyl group), a C₇-C₃₀ alkylaryl group (for example tolyl, xylyl, diisobutyl phenyl), a C₇-C₃₀ aralkyl group (for example benzyl), a C₃-C₃₀ cyclic alkyl group, a C₂-C₃₀ alkenyl group, a C₂-C₃₀ alkynyl group, a C₆-C₃₀ aryl group (for example phenyl, naphthyl, anthracyl), a C₈-C₃₀ fused-ring group and a C₄-C₃₀ heterocyclic group, wherein the heterocyclic group contains 1 to 3 hetero atom(s) selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom, including for example a pyridyl group, a pyrrolyl group, a furanyl group and a thienyl group.

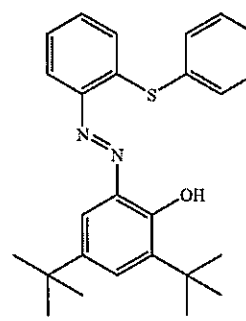
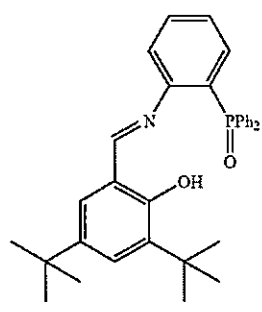
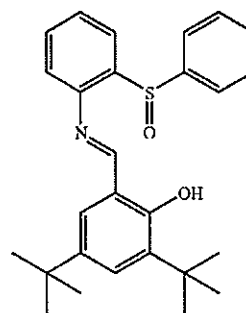
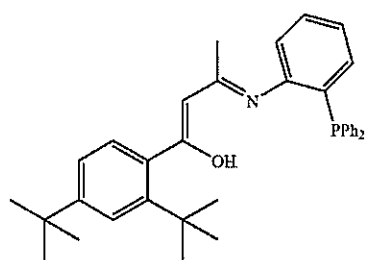
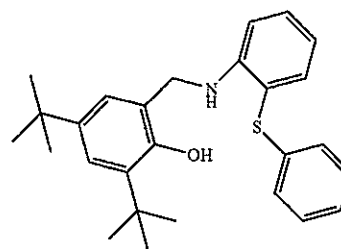
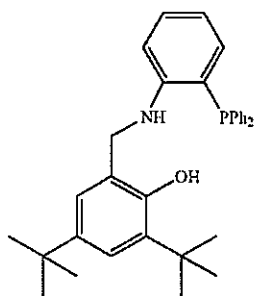
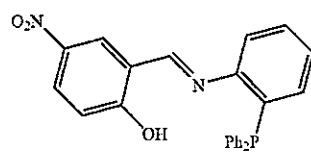
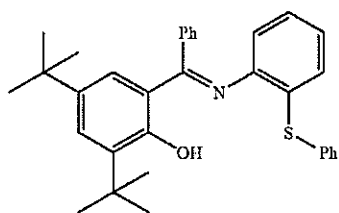
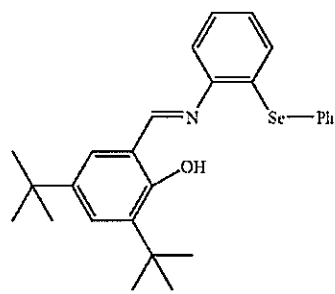
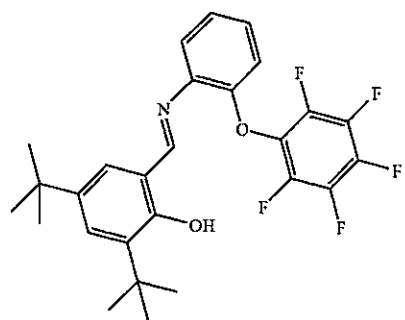
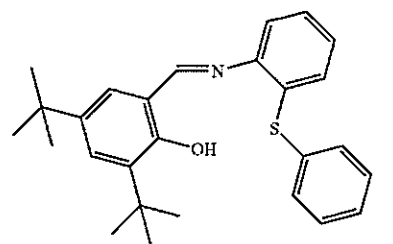
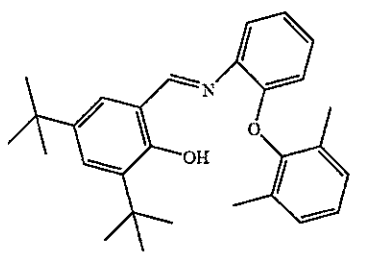
In the context of this invention, depending on the nature of the relevant groups to which the C₁-C₃₀ hydrocarbonyl bond, it is obvious to a person skilled in the art that the C₁-C₃₀ hydrocarbonyl may intend a C₁-C₃₀ hydrocarbon-diyl (a bivalent group, or referred to as a C₁-C₃₀ hydrocarbylene group) or a C₁-C₃₀ hydrocarbon-triyl (a trivalent group).

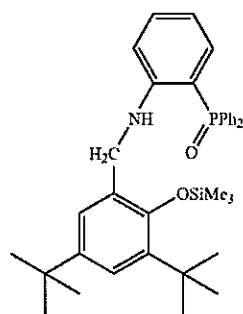
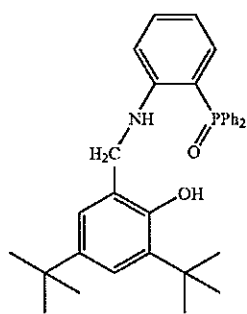
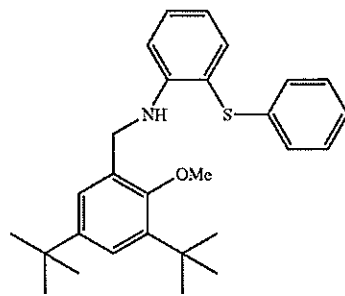
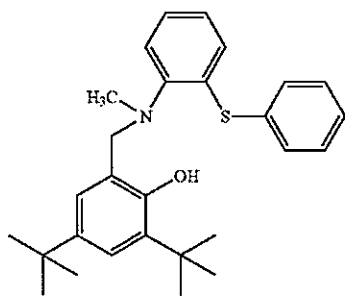
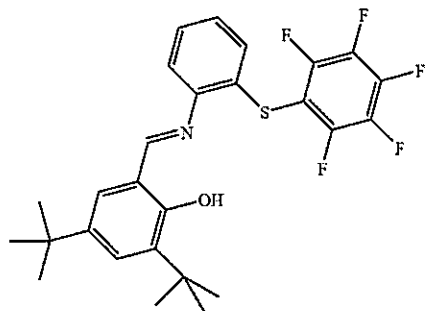
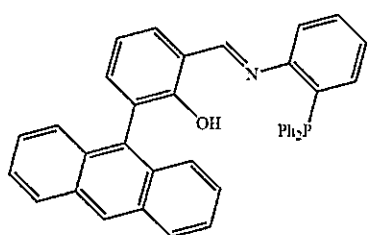
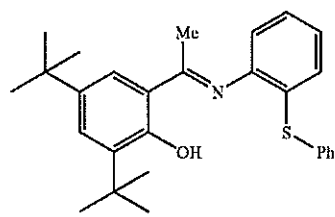
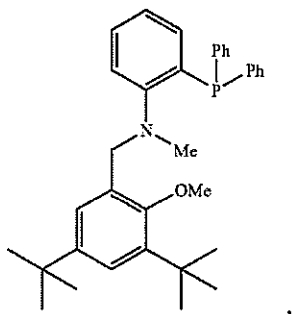
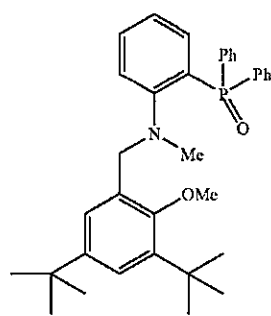
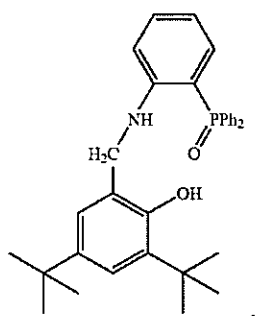
In the context of this invention, the substituted C₁-C₃₀ hydrocarbonyl intends the aforesaid C₁-C₃₀ hydrocarbonyl having one or more inert substituent(s). By inert, it means that these inert substituents will not substantially interfere with the coordination process between the aforesaid coordination groups (i.e. the aforesaid groups A, D, E, F, Y and Z, or further, if applicable, the group R⁵) and the central metal atom M (i.e. the aforesaid Group IVB metal atom). In other words, restricted by the specific chemical structure of the present nonmetallocene ligand, these substituents are incapable of or have no chance (due to for example steric hindrance) to coordinate with the Group IVB metal atom to form a coordination bond therewith. Generally, the inert substituent refers to the aforesaid halogen atom or C₁-C₃₀ alkyl group (for example a C₁-C₆ alkyl group, for example isobutyl group).

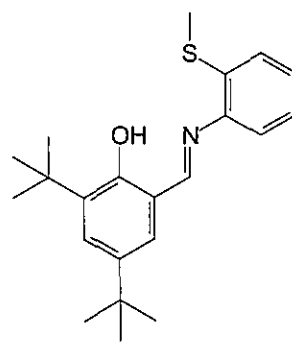
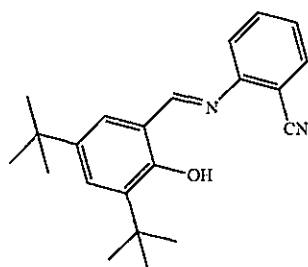
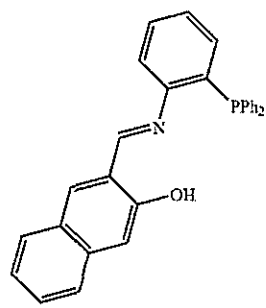
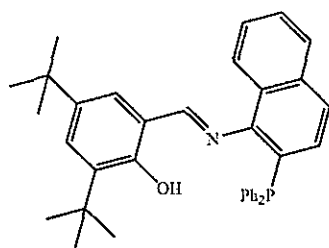
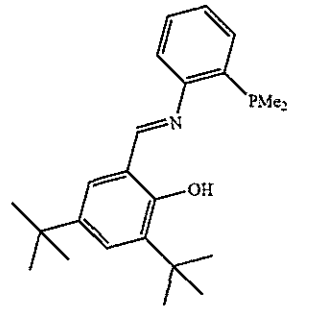
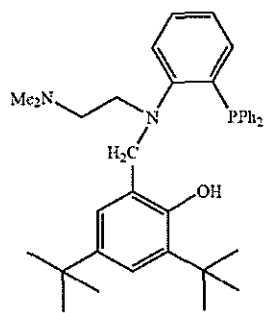
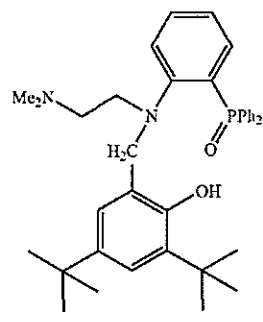
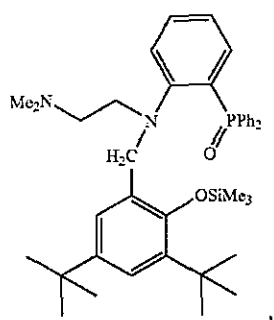
In the context of this invention, the silicon-containing group is selected from the group consisting of -SiR⁴²R⁴³R⁴⁴, and -T-SiR⁴⁵, the germanium-containing group is selected from the group consisting of -GeR⁴⁶R⁴⁷R⁴⁸, and -T-GeR⁴⁹, the tin-containing group is selected from the group consisting of -SnR⁵⁰R⁵¹R⁵², -T-SnR⁵³ and -T-Sn(O)R⁵⁴. R⁴² to R⁵⁴ are each independently selected from the group consisting of a hydrogen atom, the C₁-C₃₀ hydrocarbonyl or the substituted C₁-C₃₀ hydrocarbonyl, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring with one another. The group T is defined as aforesaid.

As the nonmetallocene ligand, the following compounds can be further exemplified.



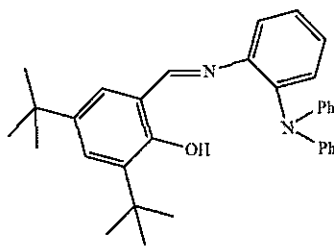
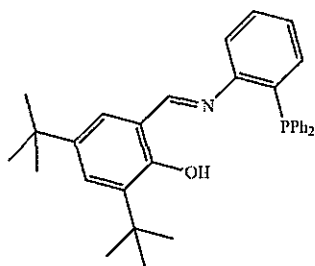


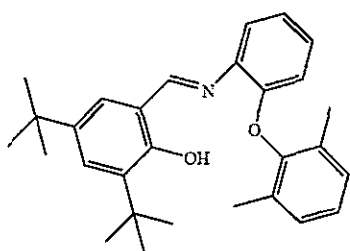




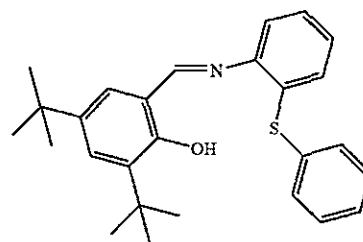
and

As the nonmetallocene ligand, the following compounds can be further exemplified.

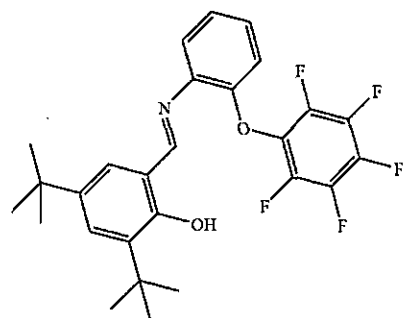




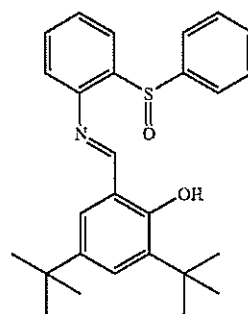
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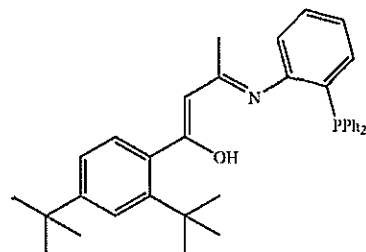
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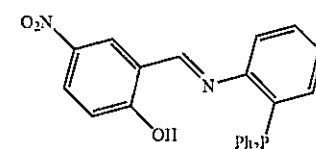
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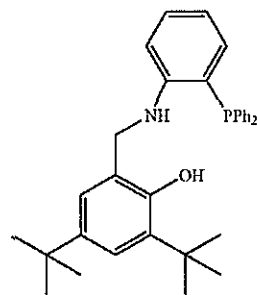
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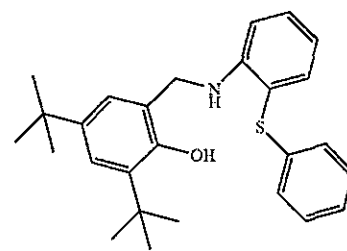
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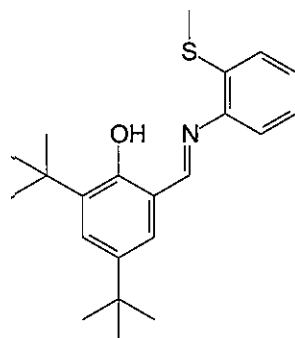
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and



As the nonmetallocene ligand, the following compounds can be further exemplified.

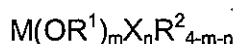
1:0.005-0.06, more preferably 1:0.01-0.04.

The chemical treating agent is further described as follows.

According to this invention, a Group IVB metal compound is used as the chemical treating agent.

As the Group IVB metal compound, exemplified is a Group IVB metal halide, a Group IVB metal alkyl halide, and a Group IVB metal alkoxy halide.

As the Group IVB metal halide, the Group IVB metal alkyl halide and the Group IVB metal alkoxy halide, exemplified is a compound having the following general formula.



wherein,

m is 0, 1, 2 or 3,

n is 0, 1, 2, 3, or 4,

M is a Group IVB metal in the Periodic Table of Elements, for example, titanium, zirconium, hafnium and the like,

X is a halogen atom, for example, F, Cl, Br, and I, and

R¹ and R² each independently is selected from the group consisting of a C₁-C₁₀ alkyl, for example, methyl, ethyl, propyl, n-butyl, isobutyl and the like, R¹ and R² could be identical to or different from each other.

Specifically, the Group IVB metal halide could be exemplified as for example, titanium tetrafluoride (TiF₄), titanium tetrachloride (TiCl₄), titanium tetrabromide (TiBr₄), titanium tetraiodide (TiI₄), zirconium tetrafluoride (ZrF₄), zirconium tetrachloride (ZrCl₄), zirconium tetrabromide (ZrBr₄), zirconium tetraiodide (ZrI₄), hafnium tetrafluoride (HfF₄), hafnium tetrachloride (HfCl₄), hafnium tetrabromide (HfBr₄), hafnium tetraiodide (HfI₄).

As the Group IVB metal alkyl halide, exemplified is trimethyl chloro titanium (TiCl(CH₃)₃), triethyl chloro titanium (TiCl(CH₃CH₂)₃), triisobutyl chloro titanium (TiCl(i-C₄H₉)₃), trin-butyl chloro titanium (TiCl(C₄H₉)₃), dimethyl dichloro titanium (TiCl₂(CH₃)₂), diethyl dichloro titanium (TiCl₂(CH₃CH₂)₂), diisobutyl dichloro titanium (TiCl₂(i-C₄H₉)₂), trin-butyl chloro titanium (TiCl(C₄H₉)₃), methyl trichloro titanium (Ti(CH₃)Cl₃), ethyl trichloro titanium (Ti(CH₃CH₂)Cl₃), isobutyl trichloro titanium (Ti(i-C₄H₉)Cl₃), n-butyl trichloro titanium (Ti(C₄H₉)Cl₃),

trimethyl bromo titanium (TiBr(CH₃)₃), triethyl bromo titanium (TiBr(CH₃CH₂)₃), triisobutyl bromo titanium (TiBr(i-C₄H₉)₃), trin-butyl bromo titanium (TiBr(C₄H₉)₃), dimethyl dibromo titanium (TiBr₂(CH₃)₂), diethyl dibromo titanium (TiBr₂(CH₃CH₂)₂), diisobutyl dibromo titanium (TiBr₂(i-C₄H₉)₂), trin-butyl bromo titanium (TiBr(C₄H₉)₃), methyl tribromo titanium (Ti(CH₃)Br₃), ethyl tribromo titanium (Ti(CH₃CH₂)Br₃), isobutyl tribromo titanium (Ti(i-C₄H₉)Br₃), n-butyl tribromo titanium (Ti(C₄H₉)Br₃),

trimethyl chloro zirconium (ZrCl(CH₃)₃), triethyl chloro zirconium (ZrCl(CH₃CH₂)₃), triisobutyl chloro zirconium (ZrCl(i-C₄H₉)₃), trin-butyl chloro zirconium (ZrCl(C₄H₉)₃), dimethyl dichloro zirconium (ZrCl₂(CH₃)₂), diethyl dichloro zirconium (ZrCl₂(CH₃CH₂)₂), diisobutyl dichloro zirconium

($\text{ZrCl}_2(\text{i-C}_4\text{H}_9)_2$), trin-butyl chloro zirconium ($\text{ZrCl}(\text{C}_4\text{H}_9)_3$), methyl trichloro zirconium ($\text{Zr}(\text{CH}_3)\text{Cl}_3$), ethyl trichloro zirconium ($\text{Zr}(\text{CH}_3\text{CH}_2)\text{Cl}_3$), isobutyl trichloro zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butyl trichloro zirconium ($\text{Zr}(\text{C}_4\text{H}_9)\text{Cl}_3$),

trimethyl bromo zirconium ($\text{ZrBr}(\text{CH}_3)_3$), triethyl bromo zirconium ($\text{ZrBr}(\text{CH}_3\text{CH}_2)_3$), triisobutyl bromo zirconium ($\text{ZrBr}(\text{i-C}_4\text{H}_9)_3$), trin-butyl bromo zirconium ($\text{ZrBr}(\text{C}_4\text{H}_9)_3$), dimethyl dibromo zirconium ($\text{ZrBr}_2(\text{CH}_3)_2$), diethyl dibromo zirconium ($\text{ZrBr}_2(\text{CH}_3\text{CH}_2)_2$), diisobutyl dibromo zirconium ($\text{ZrBr}_2(\text{i-C}_4\text{H}_9)_2$), trin-butyl bromo zirconium ($\text{ZrBr}(\text{C}_4\text{H}_9)_3$), methyl tribromo zirconium ($\text{Zr}(\text{CH}_3)\text{Br}_3$), ethyl tribromo zirconium ($\text{Zr}(\text{CH}_3\text{CH}_2)\text{Br}_3$), isobutyl tribromo zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butyl tribromo zirconium ($\text{Zr}(\text{C}_4\text{H}_9)\text{Br}_3$),

trimethyl chloro hafnium ($\text{HfCl}(\text{CH}_3)_3$), triethyl chloro hafnium ($\text{HfCl}(\text{CH}_3\text{CH}_2)_3$), triisobutyl chloro hafnium ($\text{HfCl}(\text{i-C}_4\text{H}_9)_3$), trin-butyl chloro hafnium ($\text{HfCl}(\text{C}_4\text{H}_9)_3$), dimethyl dichloro hafnium ($\text{HfCl}_2(\text{CH}_3)_2$), diethyl dichloro hafnium ($\text{HfCl}_2(\text{CH}_3\text{CH}_2)_2$), diisobutyl dichloro hafnium ($\text{HfCl}_2(\text{i-C}_4\text{H}_9)_2$), trin-butyl chloro hafnium ($\text{HfCl}(\text{C}_4\text{H}_9)_3$), methyl trichloro hafnium ($\text{Hf}(\text{CH}_3)\text{Cl}_3$), ethyl trichloro hafnium ($\text{Hf}(\text{CH}_3\text{CH}_2)\text{Cl}_3$), isobutyl trichloro hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butyl trichloro hafnium ($\text{Hf}(\text{C}_4\text{H}_9)\text{Cl}_3$),

trimethyl bromo hafnium ($\text{HfBr}(\text{CH}_3)_3$), triethyl bromo hafnium ($\text{HfBr}(\text{CH}_3\text{CH}_2)_3$), triisobutyl bromo hafnium ($\text{HfBr}(\text{i-C}_4\text{H}_9)_3$), trin-butyl bromo hafnium ($\text{HfBr}(\text{C}_4\text{H}_9)_3$), dimethyl dibromo hafnium ($\text{HfBr}_2(\text{CH}_3)_2$), diethyl dibromo hafnium ($\text{HfBr}_2(\text{CH}_3\text{CH}_2)_2$), diisobutyl dibromo hafnium ($\text{HfBr}_2(\text{i-C}_4\text{H}_9)_2$), trin-butyl bromo hafnium ($\text{HfBr}(\text{C}_4\text{H}_9)_3$), methyl tribromo hafnium ($\text{Hf}(\text{CH}_3)\text{Br}_3$), ethyl tribromo hafnium ($\text{Hf}(\text{CH}_3\text{CH}_2)\text{Br}_3$), isobutyl tribromo hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butyl tribromo hafnium ($\text{Hf}(\text{C}_4\text{H}_9)\text{Br}_3$).

As the Group IVB metal alkoxy halide, exemplified is trimethoxy chloro titanium ($\text{TiCl}(\text{OCH}_3)_3$), triethoxy chloro titanium ($\text{TiCl}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy chloro titanium ($\text{TiCl}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy chloro titanium ($\text{TiCl}(\text{OC}_4\text{H}_9)_3$), dimethoxy dichloro titanium ($\text{TiCl}_2(\text{OCH}_3)_2$), diethoxy dichloro titanium ($\text{TiCl}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dichloro titanium ($\text{TiCl}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy chloro titanium ($\text{TiCl}(\text{OC}_4\text{H}_9)_3$), methoxy trichloro titanium ($\text{Ti}(\text{OCH}_3)\text{Cl}_3$), ethoxy trichloro titanium ($\text{Ti}(\text{OCH}_3\text{CH}_2)\text{Cl}_3$), isobutoxy trichloro titanium ($\text{Ti}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butoxy trichloro titanium ($\text{Ti}(\text{OC}_4\text{H}_9)\text{Cl}_3$),

trimethoxy bromo titanium ($\text{TiBr}(\text{OCH}_3)_3$), triethoxy bromo titanium ($\text{TiBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo titanium ($\text{TiBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo titanium ($\text{TiBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo titanium ($\text{TiBr}_2(\text{OCH}_3)_2$), diethoxy dibromo titanium ($\text{TiBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo titanium ($\text{TiBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo titanium ($\text{TiBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo titanium ($\text{Ti}(\text{OCH}_3)\text{Br}_3$), ethoxy tribromo titanium ($\text{Ti}(\text{OCH}_3\text{CH}_2)\text{Br}_3$), isobutoxy tribromo titanium ($\text{Ti}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butoxy tribromo titanium ($\text{Ti}(\text{OC}_4\text{H}_9)\text{Br}_3$),

trimethoxy chloro zirconium ($\text{ZrCl}(\text{OCH}_3)_3$), triethoxy chloro zirconium ($\text{ZrCl}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy chloro zirconium ($\text{ZrCl}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy chloro zirconium ($\text{ZrCl}(\text{OC}_4\text{H}_9)_3$), dimethoxy dichloro zirconium ($\text{ZrCl}_2(\text{OCH}_3)_2$), diethoxy dichloro zirconium ($\text{ZrCl}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dichloro zirconium

($\text{ZrCl}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy chloro zirconium ($\text{ZrCl}(\text{OC}_4\text{H}_9)_3$), methoxy trichloro zirconium ($\text{Zr}(\text{OCH}_3)\text{Cl}_3$), ethoxy trichloro zirconium ($\text{Zr}(\text{OCH}_3\text{CH}_2)\text{Cl}_3$), isobutoxy trichloro zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butoxy trichloro zirconium ($\text{Zr}(\text{OC}_4\text{H}_9)\text{Cl}_3$),

trimethoxy bromo zirconium ($\text{ZrBr}(\text{OCH}_3)_3$), triethoxy bromo zirconium ($\text{ZrBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo zirconium ($\text{ZrBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo zirconium ($\text{ZrBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo zirconium ($\text{ZrBr}_2(\text{OCH}_3)_2$), diethoxy dibromo zirconium ($\text{ZrBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo zirconium ($\text{ZrBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo zirconium ($\text{ZrBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo zirconium ($\text{Zr}(\text{OCH}_3)\text{Br}_3$), ethoxy tribromo zirconium ($\text{Zr}(\text{OCH}_3\text{CH}_2)\text{Br}_3$), isobutoxy tribromo zirconium ($\text{Zr}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butoxy tribromo zirconium ($\text{Zr}(\text{OC}_4\text{H}_9)\text{Br}_3$),

trimethoxy chloro hafnium ($\text{HfCl}(\text{OCH}_3)_3$), triethoxy chloro hafnium ($\text{HfCl}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy chloro hafnium ($\text{HfCl}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy chloro hafnium ($\text{HfCl}(\text{OC}_4\text{H}_9)_3$), dimethoxy dichloro hafnium ($\text{HfCl}_2(\text{OCH}_3)_2$), diethoxy dichloro hafnium ($\text{HfCl}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dichloro hafnium ($\text{HfCl}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy chloro hafnium ($\text{HfCl}(\text{OC}_4\text{H}_9)_3$), methoxy trichloro hafnium ($\text{Hf}(\text{OCH}_3)\text{Cl}_3$), ethoxy trichloro hafnium ($\text{Hf}(\text{OCH}_3\text{CH}_2)\text{Cl}_3$), isobutoxy trichloro hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Cl}_3$), n-butoxy trichloro hafnium ($\text{Hf}(\text{OC}_4\text{H}_9)\text{Cl}_3$),

trimethoxy bromo hafnium ($\text{HfBr}(\text{OCH}_3)_3$), triethoxy bromo hafnium ($\text{HfBr}(\text{OCH}_3\text{CH}_2)_3$), triisobutoxy bromo hafnium ($\text{HfBr}(\text{i-OC}_4\text{H}_9)_3$), tri-n-butoxy bromo hafnium ($\text{HfBr}(\text{OC}_4\text{H}_9)_3$), dimethoxy dibromo hafnium ($\text{HfBr}_2(\text{OCH}_3)_2$), diethoxy dibromo hafnium ($\text{HfBr}_2(\text{OCH}_3\text{CH}_2)_2$), diisobutoxy dibromo hafnium ($\text{HfBr}_2(\text{i-OC}_4\text{H}_9)_2$), tri-n-butoxy bromo hafnium ($\text{HfBr}(\text{OC}_4\text{H}_9)_3$), methoxy tribromo hafnium ($\text{Hf}(\text{OCH}_3)\text{Br}_3$), ethoxy tribromo hafnium ($\text{Hf}(\text{OCH}_3\text{CH}_2)\text{Br}_3$), isobutoxy tribromo hafnium ($\text{Hf}(\text{i-C}_4\text{H}_9)\text{Br}_3$), n-butoxy tribromo hafnium ($\text{Hf}(\text{OC}_4\text{H}_9)\text{Br}_3$).

As the Group IVB metal compound, preference is given to the Group IVB metal halide, such as TiCl_4 , TiBr_4 , ZrCl_4 , ZrBr_4 , HfCl_4 and HfBr_4 , such as TiCl_4 and ZrCl_4 .

The Group IVB metal compound could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

When the chemical treating agent presents as a liquid at the normal temperature, the chemical treating agent can be used as such. When the chemical treating agent presents a solid at the normal temperature, for ease of metering and handling, it is preferably to use said chemical treating agent in the form of a solution. Of course, when the chemical treating agent presents a liquid at the normal temperature, said chemical treating agent can be also used in the form of a solution if needed, without any specific limitation.

In preparation of the solution of the chemical treating agent, there is no limitation as to the solvent (hereinafter referred to as "solvent for dissolving the chemical treating agent") to be used herein, as long as the solvent is capable of dissolving the chemical treating agent and does not change (for example dissolve) the formed carrier structure of the alkoxy magnesium spherical carrier.

Specifically, as the solvent for dissolving the chemical treating agent, exemplified is a C₅₋₁₂ alkane, a C₅₋₁₂ cyclic alkane, a halogenated C₅₋₁₂ alkane and a halogenated C₅₋₁₂ cyclic alkane, for example pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, cyclo pentane, cyclo heptane, cyclo octane, chloro pentane, chloro hexane, chloro heptane, chloro octane, chloro nonane, chloro decane, chloro undecane, chloro dodecane, chlorinated cyclo hexane and so on, preferably pentane, hexane, decane and cyclohexane, most preferably decane.

The solvent could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

Further, there is no limitation as to the concentration of the chemical treating agent in the solution, which could be determined as needed, as long as it is sufficient for the solution to deliver the predetermined amount of the chemical treating agent for the reaction. As aforesaid, if the chemical treating agent presents as a liquid, it is convenient to use said chemical treating agent as such for the treatment, while it is also acceptable to convert it into a solution before use. Generally, the molar concentration of the chemical treating agent in its solution is, but not limiting to, 0.01 to 1.0 mol/L.

According to this invention, as the amount of the chemical treating agent to be used, it is preferably that the ratio by molar of the alkoxy magnesium spherical carrier (based on Mg) to the chemical treating agent (based on the Group IVB metal) is 1:1-30, preferably 1:2-20, more preferably 1:4-10.

According to this invention, as the way to conduct the contacting step, exemplified is a way of contacting the nonmetallocene ligand, the chemical treating agent and the alkoxy magnesium spherical carrier in the presence of a solvent (hereinafter referred to as "solvent for contacting").

According to this invention, there is no limitation as to the solvent for contacting to be used herein, as long as the solvent is capable of dissolving the nonmetallocene ligand and the chemical treating agent and does not change (for example dissolve) the formed carrier structure of the alkoxy magnesium spherical carrier.

Specifically, as the solvent for contacting, exemplified is a C₅₋₁₂ alkane, a C₅₋₁₂ cyclic alkane, a halogenated C₅₋₁₂ alkane and a halogenated C₅₋₁₂ cyclic alkane, for example pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, cyclo pentane, cyclo heptane, cyclo octane, chloro pentane, chloro hexane, chloro heptane, chloro octane, chloro nonane, chloro decane, chloro undecane, chloro dodecane, chlorinated cyclo hexane and so on, preferably pentane, hexane, decane and cyclohexane, most preferably decane.

The solvent for contacting could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

According to this invention, as the amount of the solvent for contacting to be used, it is preferably that the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting is 1mol:75-8000ml, preferably 1mol:150-6000ml, more

preferably 1mol:200-4000ml.

According to this invention, there is no limitation as to the sequence for contacting the nonmetallocene ligand, the chemical treating agent and the alkoxy magnesium spherical carrier, exemplified can be a simultaneous contacting of the three or a successive contacting at any sequence.

According to a preferred embodiment of this invention, in the presence of the solvent for contacting, the nonmetallocene ligand contacts the alkoxy magnesium spherical carrier (hereinafter referred to as "first contacting step"), and then the chemical treating agent is added for a further contact (hereinafter referred to as "second contacting step").

As the way to conduct the first contacting step, the following two embodiments can be exemplified.

According to the first embodiment, the nonmetallocene ligand is firstly dissolved in the solvent for contacting so as to prepare a solution. The dissolving can be conducted generally at the normal temperature for a duration necessary for the nonmetallocene ligand to sufficiently dissolve. During dissolving of the nonmetallocene ligand, a stirring (e.g. at a stirring speed of 100 to 1000 rpm) may be used if needed. Then, under stirring (e.g. at a stirring speed of 100 to 1000 rpm), the alkoxy magnesium spherical carrier is introduced into the thus obtained solution, and the stirring (e.g. at a stirring speed of 100 to 1000 rpm) is continued at a temperature of 50 to 150 °C (preferably 60 to 130 °C) until a slurry is formed. There is no limitation as to the duration of the stirring, as long as a homogeneous slurry can be obtained, it can be for example, 5 to 120 min, preferably 15 to 60 min.

Alternatively, according the second embodiment, under stirring (e.g. at a stirring speed of 100 to 1000 rpm), at a temperature of 50 to 150 °C (preferably 60 to 130 °C), the alkoxy magnesium spherical carrier is introduced into the solvent for contacting, or the solvent for contacting is introduced into the alkoxy magnesium spherical carrier, at the same time or after that, the nonmetallocene ligand is introduced, and the stirring (e.g. at a stirring speed of 100 to 1000 rpm) is continued at the same temperature until a slurry is formed. There is no limitation as to the duration of the stirring, as long as a homogeneous slurry can be obtained, it can be for example, 5 to 120 min, preferably 15 to 60 min.

After the slurry is prepared as aforesaid, the slurry further contacts the chemical treating agent (i.e. the second contacting step), and then the supported nonmetallocene catalyst of this invention is obtained.

As the way to conduct the second contacting step, exemplified is that under stirring (e.g. at a stirring speed of 100 to 1000 rpm), at a temperature of 50 to 150 °C (preferably 80 to 130 °C), the chemical treating agent or a solution of the chemical treating agent is (preferably continuously) introduced into the slurry. The introducing generally continues for 0.5 to 8 hours, preferably 1 to 6 hours, most preferably 2 to 5 hours. After completion of this introduction, the stirring is continued at a temperature of 50 to 150 °C (preferably 80 to 150 °C) for 0.1 to 24 hours, preferably 1 to 6 hours, so as to obtain a reaction mixture.

After completion of the second contacting step, the reaction mixture is filtered, washed and dried, so as to obtain the supported nonmetallocene catalyst of this invention.

According to this invention, the filtering, washing and drying can be conducted with a conventional manner. If needed, the washing can be generally conducted for 1 to 8 times, preferable 2 to 6 times, most preferably 2 to 4 times. Herein, the solvent for washing can be the same as the solvent for contacting.

The drying can be conducted in line with a conventional process, for example, drying under an inert gas atmosphere, vacuum drying or vacuum drying under heat, preferably drying under an inert gas atmosphere or vacuum drying under heat, most preferably vacuum drying under heat. The drying is generally conducted at a temperature ranging from the normal temperature to 140°C for a duration of, generally, 2 to 20 hours, but not limiting to this.

It is known that any of the aforementioned processes and steps is preferably carried out under a substantial water-free and oxygen-free condition. By substantial water-free and oxygen-free condition, it means that water and oxygen in the system concerned is continuously controlled to be less than 100 ppm. Further, the support nonmetallocene catalyst according to this invention, after prepared, is usually stored under an inert gas atmosphere (e.g. nitrogen gas, Ar gas or He gas) at a sealed condition under a slightly positive pressure before use.

In one embodiment, this invention relates to the supported nonmetallocene catalyst produced in line with the aforesaid process, also referred to as a supported nonmetallocene catalyst for olefin polymerization.

In a further embodiment according to this invention, this invention relates to an olefin homopolymerization/copolymerization process, wherein the supported nonmetallocene catalyst of this invention is used as the catalyst for olefin polymerization, to homopolymerize or copolymerize olefin(s) and obtain a polyolefin as the product.

In the context of the olefin homopolymerization/copolymerization process of this invention, one can directly refer to the prior art for any content or information that has not been expressively and specifically described hereinafter, for example, the reactor for polymerization, the amount of olefin(s), the way by which the catalyst or olefin is introduced, unneccessitating the need of detailing same further herein.

According to the present olefin homopolymerization/copolymerization process, the supported nonmetallocene catalyst of this invention is used as the main catalyst, one or more selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt is used as the co-catalyst, to homopolymerize or copolymerize olefin.

As the way of adding the main catalyst and the co-catalyst to the polymerization system, exemplified is a way wherein the main catalyst is added prior to the co-catalyst, or vise versa, or the main catalyst and the co-catalyst contact with each other by mixing and then added altogether, or separately but

simultaneously added. As the way of adding the main catalyst and the co-catalyst separately, exemplified is the case wherein the main catalyst and the co-catalyst are successively added to one feed line or multiple feed lines. When the main catalyst and the co-catalyst are to be added separately but simultaneously, multiple feed lines are required. For a continuous polymerization, the way of simultaneously and continuously adding to multiple feed lines is preferred, while for a batch polymerization, the way of mixing the main catalyst and the co-catalyst with each other and then adding to one feed line altogether, or adding to a feed line the co-catalyst and then adding the main catalyst to the same feed line, is preferred.

There is no limitation as to how to conduct the olefin homopolymerization/copolymerization, any conventional process known to a person skilled in the art can be used, for example, a slurry process, a bulk process or a gas phase process, preferably the slurry process.

According to this invention, as the olefin to be used, exemplified is a C₂ to C₁₀ mono-olefin, a diolefin, a cyclic olefin and other ethylenic unsaturated compounds.

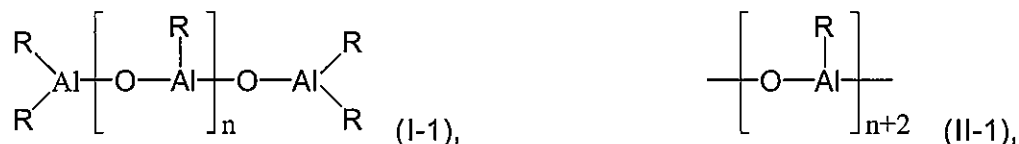
Specifically, as the C₂ to C₁₀ mono-olefin, exemplified is ethylene, propylene, 1-butene, 1-hexene, 1-heptene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-undecene, 1-dodecene and styrene. As the cyclic olefin, exemplified is 1-cyclopentene and norbornene. As the diolefin, exemplified is 1,4-butadiene, 2,5-pentadiene, 1,6-hexadiene, norbornadiene and 1,7-octadiene. As the other ethylenic unsaturated compound, exemplified is vinyl acetate, and (meth)acrylate.

According to this invention, the homopolymerization or copolymerization can be conducted for a duration of, generally, 1 to 15 hours, preferably 2 to 6 hours, more preferably 2 to 4 hours, but not limiting to this.

According to this invention, by homopolymerization, it refers to the polymerization of a single kind of olefin, by copolymerization, it refers to the polymerization between two or more of the aforesaid olefins.

According to this invention, the co-catalyst is selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron ammonium salt, such as the aluminoxane and the alkylaluminum.

As the aluminoxane, exemplified is a linear aluminoxane ((R)(R)Al-(Al(R)-O)_n-O-Al(R)(R)) having the following formula (I-1), and a cyclic aluminoxane $(-\text{Al}(\text{R})-\text{O}-)_{n+2}$ having the following formula (II-1).



wherein the Rs are identical to or different from one another, preferably identical to one another, and each independently selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl, and iso-butyl, most preferably methyl, n is an integer of 1 to 50, preferably of 10 to 30.

Specifically, the aluminoxane could be preferably selected from the group

consisting of methyl aluminosilane, ethyl aluminosilane, isobutyl aluminosilane and n-butyl aluminosilane, preferably methyl aluminosilane (MAO) and isobutyl aluminosilane (IBAO), most preferably methyl aluminosilane (MAO).

The aluminosilane could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the alkylaluminum, exemplified is a compound having a general formula (III-1) as follows:

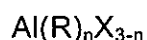


wherein the Rs are identical to or different from one another, preferably identical to one another, and each independently selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl and iso-butyl, most preferably methyl.

Specifically, the alkylaluminum could be selected from the group consisting of trimethyl aluminum (Al(CH₃)₃), triethyl aluminum (Al(CH₃CH₂)₃), tripropyl aluminum (Al(C₃H₇)₃), triisobutyl aluminum (Al(i-C₄H₉)₃), tri-n-butyl aluminum (Al(C₄H₉)₃), triisooamyl aluminum (Al(i-C₅H₁₁)₃), tri-n-amyl aluminum (Al(C₅H₁₁)₃), tri-hexyl aluminum (Al(C₆H₁₃)₃), tri-iso-hexyl aluminum (Al(i-C₆H₁₃)₃), diethyl methyl aluminum (Al(CH₃)(CH₃CH₂)₂) and ethyl dimethyl aluminum (Al(CH₃CH₂)(CH₃)₂), and the like, wherein preference is given to trimethyl aluminum, triethyl aluminum, triisobutyl aluminum and tripropyl aluminum, more preferably triethyl aluminum and triisobutyl aluminum, most preferably triethyl aluminum.

The alkylaluminum could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the halogenated alkyl aluminum, exemplified is a compound having a general formula as follows:



wherein the Rs are identical to or different from one another, preferably identical to one another, and each independently selected from the group consisting of a C₁-C₈ alkyl, preferably methyl, ethyl, and iso-butyl, most preferably methyl, X is halogen, preferably Cl, n is 1 or 2.

Specifically, the halogenated alkyl aluminum could be selected from the group consisting of monochloro dimethyl aluminum (Al(CH₃)₂Cl), dichloro methyl aluminum (Al(CH₃)Cl₂), monochloro diethyl aluminum (Al(CH₃CH₂)₂Cl), dichloro ethyl aluminum (Al(CH₃CH₂)Cl₂), monochloro dipropyl aluminum (Al(C₃H₇)₂Cl), dichloro propyl aluminum (Al(C₃H₇)Cl₂), monochloro di-n-butyl aluminum (Al(C₄H₉)₂Cl), dichloro n-butyl aluminum (Al(C₄H₉)Cl₂), monochloro diisobutyl aluminum (Al(i-C₄H₉)₂Cl), dichloro isobutyl aluminum (Al(i-C₄H₉)Cl₂), monochloro di-n-pentylaluminum (Al(C₅H₁₁)₂Cl), dichloro n-pentylaluminum (Al(C₅H₁₁)Cl₂), monochloro diiso-pentylaluminum (Al(i-C₅H₁₁)₂Cl), dichloro iso-pentylaluminum (Al(i-C₅H₁₁)Cl₂), monochloro di-n-hexyl aluminum (Al(C₆H₁₃)₂Cl), dichloro n-hexyl aluminum (Al(C₆H₁₃)Cl₂), monochloro diiso-hexyl aluminum (Al(i-C₆H₁₃)₂Cl), dichloro iso-hexyl aluminum (Al(i-C₆H₁₃)Cl₂), monochloro methylethyl aluminum (Al(CH₃

(CH₂CH₃)Cl), monochloro methylpropyl aluminum (Al(CH₃) (C₃H₇)Cl), monochloro methyl*n*-butyl aluminum (Al(CH₃) (C₄H₉)Cl), monochloro methylisobutyl aluminum (Al(CH₃) (*i*-C₄H₉)Cl), monochloro ethylpropyl aluminum (Al(CH₂CH₃) (C₃H₇)Cl), monochloro ethyl*n*-butyl aluminum (AlCH₂CH₃)(C₄H₉)Cl), monochloro methylisobutyl aluminum (AlCH₂CH₃)(*i*-C₄H₉)Cl), preferably monochloro diethyl aluminum, dichloro ethyl aluminum, monochloro di*n*-butyl aluminum, dichloro *n*-butyl aluminum, monochloro diisobutyl aluminum, dichloro isobutyl aluminum, monochloro di*n*-hexyl aluminum, dichloro *n*-hexyl aluminum, more preferably chloro diethyl aluminum, dichloro ethyl aluminum and monochloro di*n*-hexyl aluminum, most preferably monochloro diethyl aluminum.

The halogenated alkyl aluminum could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

As the fluoroborane, the alkylboron and the alkylboron ammonium salt, exemplified is one conventionally used in this field, but without any limitation thereto.

Further, according to this invention, the co-catalyst could be used with one kind or as a mixture of two or more kinds of the aforesaid co-catalysts at any ratio therebetween as needed, but without any limitation thereto.

According to this invention, depending on how the olefin homopolymerization/copolymerization is conducted (e.g. via a slurry polymerization), a solvent for polymerization may be involved.

As the solvent for polymerization, one conventionally used in this field for olefin homopolymerization/copolymerization can be used, but without any limitation thereto.

As the solvent for polymerization, exemplified is a C₄₋₁₀ alkane (for example, butane, pentane, hexane, heptane, octane, nonane, or decane), a halogenated C₁₋₁₀ alkane (for example, dichloro methane), a C₆₋₁₂ cyclic alkane (for example, cyclohexane, cycloheptane, cyclooctane, cyclononane, or cyclodecane), and a C₆₋₂₀ aromatic hydrocarbon (for example toluene or xylene), and so on. Hexane, pentane, heptane or cyclohexane is preferred for this purpose, most preferably hexane.

The solvent for polymerization could be used with one kind or as a mixture of two or more kinds at any ratio therebetween.

According to this invention, the total polymerization pressure under which the olefin homopolymerization/copolymerization is conducted is generally between 0.1 to 10MPa, preferably 0.1 to 4MPa, most preferably 0.5 to 1.5MPa, but without any limitation thereto. According to this invention, the polymerization temperature at which the olefin homopolymerization/copolymerization is conducted is generally from 10°C to 200°C, preferably 40°C to 100°C, more preferably 80°C to 95°C, but without any limitation thereto.

Further, according to this invention, the olefin homopolymerization/copolymerization can be conducted in the presence of or in the absence of hydrogen gas. If presents, the partial pressure of hydrogen gas

may be generally between 0.01 to 1MPa, preferably 0.05 to 0.2MPa, but without any limitation thereto.

According to the olefin homopolymerization/copolymerization process of this invention, the ratio by molar of the co-catalyst (based on Al or B) to the supported nonmetallocene catalyst (based on the central metal atom M) of this invention is generally 1 to 1000:1, preferably 10 to 500:1, more preferably 15 to 300:1, but without any limitation thereto.

According to this invention, the polyolefin produced in line with the present olefin homopolymerization / copolymerization process is characterized by superior particle morphology, high bulk density and specific surface area, variant pore structure, desirable particle size distribution and molecular weight distribution, easy to be chlorinated, and therefore can be used for directly producing a chlorinated polyolefin.

According to this invention, the homopolymerization of ethylene or the copolymerization of ethylene with at least one α -olefin(s) (herein referred to as "comonomer") selected from a C_3 to C_{12} α -olefin is further preferred. As the C_3 to C_{12} α -olefin, a C_3 to C_8 α -olefin is further preferred. As the α -olefin to be used herein, exemplified is propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methyl-1-pentene, 1-dodecene or 4-methyl-1-hexene, preferably propylene, 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene, more preferably propylene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The α -olefin could be used with one kind or as a mixture of two or more kinds.

According to this invention, it presents, the comonomer could be used at an amount of 0.5 to 10 g per 1mg of the main catalyst, preferably 1 to 5 g per 1mg of the main catalyst.

According to this invention, when conducting the aforesaid homopolymerization of ethylene or copolymerization of ethylene with the comonomer, a slurry polymerization procedure is preferred, under the conditions of a total polymerization pressure of 0.2 to 2.0 MPa, preferably 0.5 to 1.5 MPa, a partial pressure ratio of hydrogen gas to ethylene of 0.01-0.2:1, preferable 0.02-0.1:1, most preferably 0.03-0.08:1, and a polymerization temperature of 60 to 100 °C, preferably 70 to 95 °C, more preferably 80 to 90 °C.

According to this invention, the ethylene polymer produced in line with the aforesaid homopolymerization of ethylene or copolymerization of ethylene with the comonomer, has a recurring unit derived from ethylene, and optionally has a recurring unit derived from the at least one α -olefin(s), wherein with respect to the total weight 100 wt% of the ethylene polymer, a content of the recurring unit derived from ethylene of 95 to 100 wt%, and a content of the recurring unit derived from the at least one α -olefin(s) of 0 to 5 wt%.

According to this invention, the ethylene polymer has a bulk density of 0.33 to 0.50 g/cm³, preferably 0.38 to 0.46 g/cm³, more preferably 0.40 to 0.44 g/cm³.

According to this invention, the ethylene polymer has an oligomer content of less than 2 g/L.

According to this invention, the ethylene polymer has a fine (less than 75 μm) powder content of less than 5 wt%.

According to this invention, the ethylene polymer has a melt index (at 190 °C and 2.16 kg load) of 0.02 to 5 g/10min.

According to this invention, the ethylene polymer has a molecular weight distribution Mw/Mn of 2.5 to 20, preferably 4 to 10.

According to this invention, the ethylene polymer has a density of 0.94 to 0.96 g/cm³.

According to this invention, the ethylene polymer has an average particle size of 200 to 400 μm .

According to this invention, the ethylene polymer has a specific surface area of 0.2 to 3.0 m²/g, preferably 1.0 to 3.0 m²/g, more preferably 1.5 to 3.0 m²/g.

According to this invention, the ethylene polymer has a pore volume of 0.001 to 0.15 cm³/g, preferably 0.01 to 0.15 cm³/g, more preferably 0.05 to 0.12 cm³/g.

According to this invention, the ethylene polymer has a pore size of 10 to 80 nm, preferably 20 to 70 nm, more preferably 20 to 60 nm.

According to this invention, the aforesaid polyolefin or ethylene polymer can be directly chlorinated by any chlorination process known in this field as the starting material, to produce the corresponding chlorinated polyolefin, especially chlorinated polyethylene. As the chlorination process, exemplified is a solvent chlorination process, a suspension chlorination process, a solid phase chlorination process, with the suspension chlorination process preferred. As the suspension chlorination process, exemplified is an acid phase suspension chlorination process, an aqueous phase suspension chlorination process or a solution suspension chlorination process. These processes can be conducted in any manner known in this field, detailed description thereon omitted.

According to this invention, by the chlorination process, a chlorinated polyolefin (especially chlorinated polyethylene) having a chlorine content of 30-70wt% can be produced. The chlorinated polyolefin (especially chlorinated polyethylene) is characterized by a relatively low Mooney viscosity (e.g. 60 or less) and a relatively high tensile strength (e.g. 10 MPa or more).

Example

The present invention is further illustrated by using the following examples, not limiting to same.

The bulk density of the polymer was measured according to the Chinese National Standard GB 1636-79 (unit: g/cm³).

The particle size distribution of the polymer was measured on a laser particle size analyzer (Model LS230, Beckman Coulter company, USA) with a size measuring range of 0.04 to 2000.00 μm . The fine (less than 75 μm) powder content of the polymer was automatically obtained from the analyzer.

The specific surface area, the pore volume and the pore size of the polymer were measured with a five-point method on a physical adsorption analyzer (Model

ASAP2010, Micromeritics company, USA), with nitrogen gas as the adsorption media and at the liquid nitrogen temperature (77K).

The oligomer content in the polymer was obtained as follows.

About 10 g of the polymer powder was weighted as the sample and placed into a paper container with a known weight. Then, the sample and the paper container were placed together into an extractor containing n-heptane, and then the extractor was placed into a thermostatic oil bath. The extraction was conducted at $80\pm 2^{\circ}\text{C}$ for 6 hours. After completion of the extraction, the paper container with any polymer residue thereon was placed into a vacuum oven and dried at 90°C till no weight loss, and then placed into a silica gel drying chamber, cooled for 30 min therein, and then weighted (to the accuracy of 0.1 mg). The oligomer content was calculated in line with the following formula.

$$X = \frac{m_1 - m_2}{m_1} \times 100$$

In this formula, X represents the oligomer content, %; m_1 represents the weight of the sample before extraction, g; m_2 represents the weight of the sample after extraction and drying, g.

The measurement was repeated for two times and the oligomer content in the polymer was finally reported as the average of these two measurements, with a deviation of not greater than 5%.

The melt index of the polymer (at 190°C and 2.16 kg load) was measured in accordance with ASTM D 1238.

The density of the polymer was measured with a density gradient method in accordance with the Chinese National Standard GB/T1033.2-2010.

The content of the Group IVB metal (for example Ti) and the content of the Mg element in the supported nonmetallocene catalyst were determined by the ICP-AES method, while the content of the nonmetallocene ligand was determined by the element analysis method.

The polymerization activity of the catalyst was calculated as follows.

Upon completion of the polymerization, the polymer product in the reactor was filtered and dried, and then weighed for its weight (by mass). Then, the polymerization activity of the catalyst was expressed by a value obtained by dividing the weight of the polymer product by the weight (by mass) of the supported nonmetallocene catalyst used (unit: kg polymer per 1g Cat).

The molecular weights M_w , M_n and the molecular weight distribution (M_w/M_n) of the polymer were determined at a test temperature of 150°C by using the GPC V2000 type gel permeation chromatographer (from WATERS Co., USA), with 1,2,4-trichlorobenzene as the solvent.

The chlorinated polyethylene sample was prepared in accordance with the Chinese Standard HG/T2704-2002.

The chlorine content of the chlorinated polyethylene was measured in accordance with the Chinese National Standard GB/T7139-2002 (the B method).

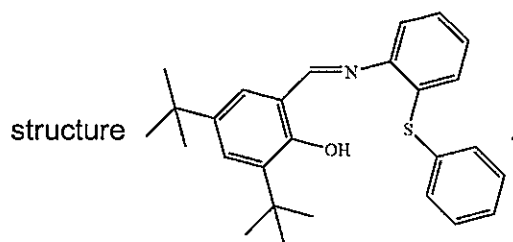
The Mooney viscosity of the chlorinated polyethylene was measured in accordance with the Chinese National Standard GB/T1232.1-2000, with a preheat time of 1 min, a rotation time of 4 min and a test temperature of 125°C.

The tensile strength of the chlorinated polyethylene was measured in accordance with the Chinese National Standard GB/T 528-2009 with an I type dumbbell-shaped cutter.

Example I

Example I-1

The alkoxy magnesium spherical carrier was diethoxy magnesium spherical carrier (having a sphericity of 1.42, a bulk density of 0.32g/cm³, and an average particle size of 420μm), the solvent for contacting was n-octane, the chemical treating agent was titanium tetrachloride, the nonmetallocene ligand has the



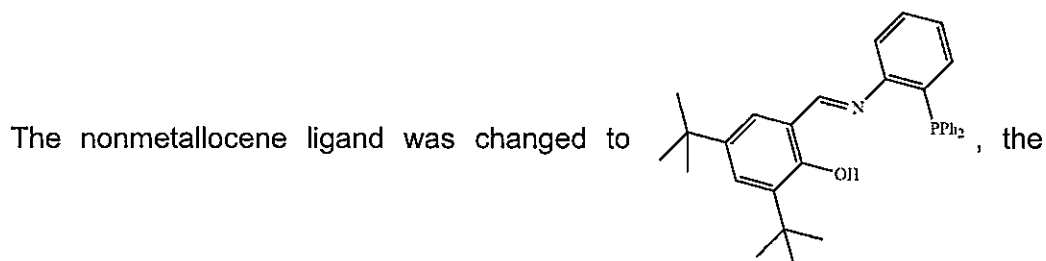
The diethoxy magnesium spherical carrier (5g) and the nonmetallocene ligand were weighted, added thereto n-heptane, and stirred at 300rpm for 30min, heated to 90°C to obtain a homogeneous dispersion. Then, to the dispersion, titanium tetrachloride was continuously dropwise added for a duration of 2 hours, after completion of the addition, the reaction continued under stirring at 90°C for 6 hours, filtered, washed with hexane for 3 times (60ml each time), and finally vacuum dried at the normal temperature to obtain a supported nonmetallocene catalyst.

In this example, the ratio of the diethoxy magnesium spherical carrier to n-heptane was 1mol:1000ml, the ratio by molar of the diethoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.01, the ratio by molar of the diethoxy magnesium spherical carrier to titanium tetrachloride was 1:2.1.

The thus obtained supported nonmetallocene catalyst was named as CAT-1.

Example I-2

Substantially the same as the Example I-1, except for the following changes:



solvent for contacting was changed to heptane, the chemical treating agent was changed to zirconium tetrachloride (ZrCl₄), the reaction temperature was changed to

85°C, after completion of the addition, the reaction continued under stirring at 85°C for 10 hours.

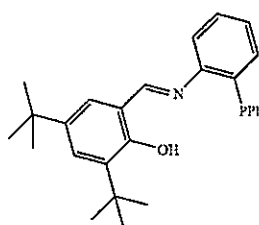
In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:1500ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.015, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:3.

The thus obtained supported nonmetallocene catalyst was named as CAT-2.

Example I-3

Substantially the same as the Example I-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dipropoxy magnesium spherical carrier ($\text{Mg}(\text{OPr})_2$) (having a sphericity of 1.83, a bulk density of $0.40\text{g}/\text{cm}^3$, and an average particle size of $530\mu\text{m}$), the nonmetallocene ligand was



, the solvent for contacting was changed to ethyl benzene, the

reaction temperature was changed to 95°C, after completion of the addition, the reaction continued under stirring at 95°C for 4 hours.

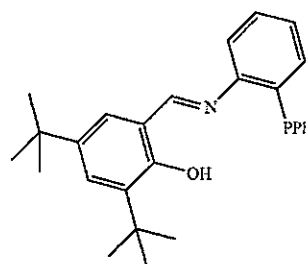
In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:2000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.02, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:5.

The thus obtained supported nonmetallocene catalyst was named as CAT-3.

Example I-4

Substantially the same as the Example I-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dibutoxy magnesium spherical carrier ($\text{Mg}(\text{OC}_4\text{H}_9)_2$) (having a sphericity of 2.07, a bulk density of $0.62\text{g}/\text{cm}^3$, and an average particle size of $630\mu\text{m}$), the nonmetallocene ligand was



, the solvent for contacting was changed to decane, the

chemical treating agent was ethoxy trichloro titanium ($\text{Ti}(\text{OCH}_2\text{CH}_3)\text{Cl}_3$), the reaction temperature was changed to 100°C, after completion of the addition, the reaction continued under stirring at 100°C for 3 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:3500ml, the ratio by molar of the alkoxy magnesium

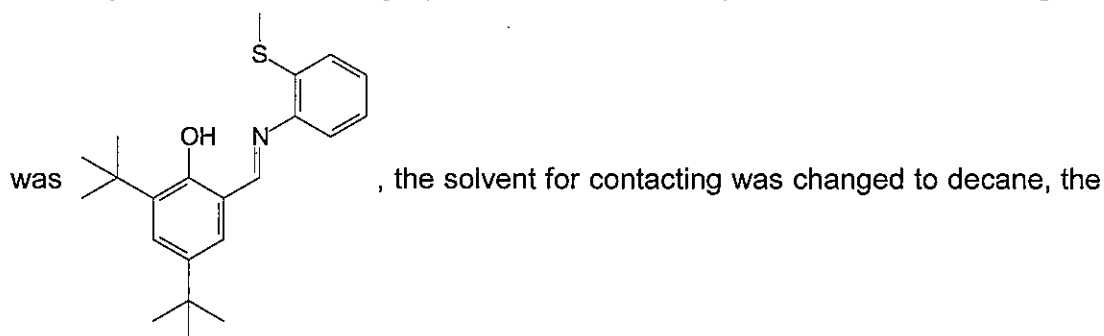
spherical carrier to the nonmetallocene ligand was 1:0.02, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:10.

The thus obtained supported nonmetallocene catalyst was named as CAT-4.

Example I-5

Substantially the same as the Example I-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dimethoxy magnesium spherical carrier ($\text{Mg}(\text{OCH}_3)_2$) (having a sphericity of 2.2, a bulk density of 0.25g/cm^3 , and an average particle size of $275\mu\text{m}$), the nonmetallocene ligand



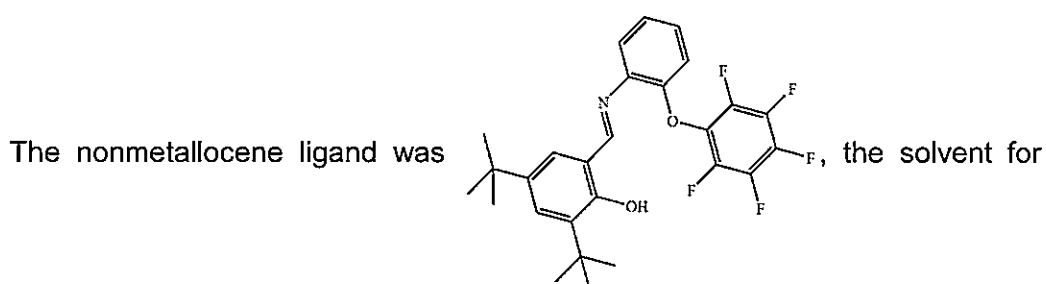
chemical treating agent was ethoxy trichloro titanium ($\text{Ti}(\text{OCH}_2\text{CH}_3)\text{Cl}_3$), the reaction temperature was changed to 110°C , after completion of the addition, the reaction continued under stirring at 110°C for 8 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:4000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.03, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:14.

The thus obtained supported nonmetallocene catalyst was named as CAT-5.

Example I-6

Substantially the same as the Example I-1, except for the following changes:



contacting was changed to 2-ethyl octane, the chemical treating agent was ethyl trichloro titanium ($\text{Ti}(\text{CH}_2\text{CH}_3)\text{Cl}_3$), the reaction temperature was changed to 120°C , after completion of the addition, the reaction continued under stirring at 120°C for 16 hours.

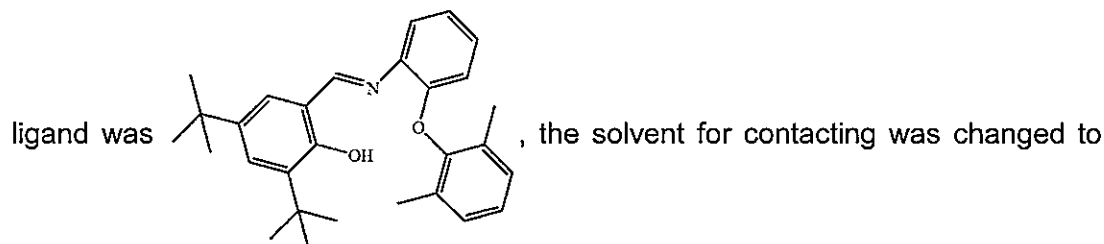
In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:6000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.05, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:8.

The thus obtained supported nonmetallocene catalyst was named as CAT-6.

Example I-7

Substantially the same as the Example I-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to ethoxy propoxy magnesium spherical carrier ($\text{Mg}(\text{OEt})(\text{OPr})$) (having a sphericity of 1.3, a bulk density of $0.52\text{g}/\text{cm}^3$, and an average particle size of $350\mu\text{m}$), the nonmetallocene



methyl ethyl benzene, the chemical treating agent was changed to methoxy tribromo titanium ($\text{Ti}(\text{OCH}_3)\text{Br}_3$), the reaction temperature was changed to 120°C , after completion of the addition, the reaction continued under stirring at 120°C for 25 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:8000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.06, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:3.5.

The thus obtained supported nonmetallocene catalyst was named as CAT-7.

Comparative Example I-A

Substantially the same as the Example I-1, except for the following changes:

No nonmetallocene ligand was added.

The thus obtained catalyst was named as CAT-A.

Comparative Example I-B

Substantially the same as the Example I-1, except for the following changes:

The ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was changed to 1:0.02.

The thus obtained catalyst was named as CAT-B.

Comparative Example I-C

Substantially the same as the Example I-1, except for the following changes:

The ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was changed to 1:0.04.

The thus obtained catalyst was named as CAT-C.

Comparative Example I-D

Substantially the same as the Example I-1, except for the following changes:

The ratio by molar of the alkoxy magnesium spherical carrier to the chemical

treating agent was changed to 1:4.

The thus obtained catalyst was named as CAT-D.

Comparative Example I-E

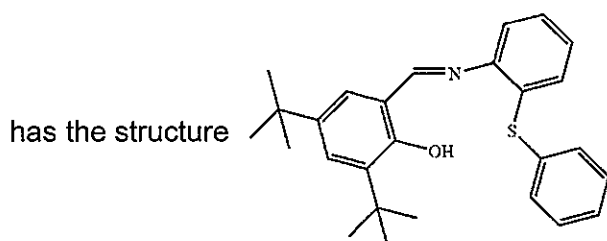
Substantially the same as the Example I-1, except for the following changes:

The reaction temperature was changed to 100°C.

The thus obtained catalyst was named as CAT-E.

Comparative Example I-F

The magnesium compound was anhydrous MgCl_2 , the solvent for dissolving the magnesium compound and the nonmetallocene ligand was tetrahydrofuran, the chemical treating agent was titanium tetrachloride. The nonmetallocene ligand



Anhydrous MgCl_2 (5g) and the nonmetallocene ligand was weighed, added thereto tetrahydrofuran at the normal temperature to completely dissolve same, after stirred for 2 hours, hexane as the precipitating agent was added thereto to precipitate same, filtered, washed with hexane for 2 times (60ml each time), dried by evenly heating at 60°C under vacuum to obtain a modified carrier.

To the modified carrier, 60ml hexane was added, then under stirring, titanium tetrachloride was dropwise added thereto for a duration of 30 min, after that, the reaction continued under stirring at 60°C for 4 hours, filtered, wash with hexane for 2 times (60ml each time), and finally vacuum dried at the normal temperature to obtain a supported nonmetallocene catalyst.

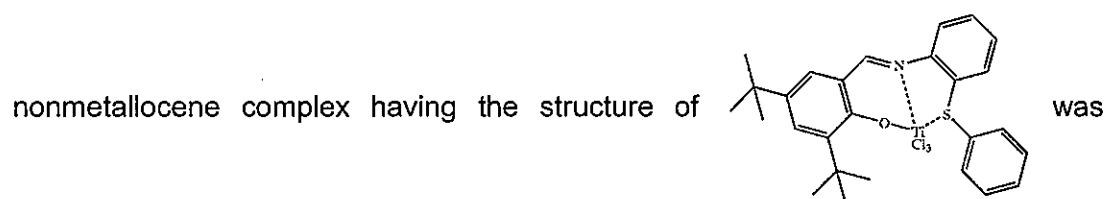
In this example, the ratio of MgCl_2 to tetrahydrofuran was 1mol:210ml, the ratio by molar of MgCl_2 to the nonmetallocene ligand was 1:0.01, the ratio by volume of the precipitating agent to tetrahydrofuran was 1:1, the ratio by molar of MgCl_2 to titanium tetrachloride was 1:0.15.

The thus obtained supported nonmetallocene catalyst was named as CAT-F.

Comparative Example I-G

Substantially the same as the Example I-1, except for the following changes:

No nonmetallocene ligand was added during the preparation. Rather, a



dissolved in dichloromethane, and then added thereto the solid obtained by the

Example I-1, the reaction continued under stirring at the normal temperature for 2 hours, and then vacuum dried to obtain a catalyst.

In this example, the ratio by molar of the diethoxy magnesium spherical carrier to the nonmetallocene complex was 1:0.01, the amount of dichloromethane used was 5ml.

The thus obtained supported nonmetallocene catalyst was named as CAT-G.

Example I-8 (Application Example)

The catalysts CAT-1 to CAT-7 and CAT-A to CAT-G obtained from the aforesaid Example I-1 to Example I-7 and Comparative Example I-A to Comparative Example I-F were used for ethylene homopolymerization or copolymerization under the following conditions according to the following processes respectively.

Homopolymerization: an autoclave for polymerization (5L), a slurry polymerization process, hexane (2.5L) as the solvent, a total polymerization pressure of 0.8MPa, a polymerization temperature of 85°C, a partial pressure of hydrogen gas of 0.2MPa, a polymerization time of 2 hours.

Specifically, 2.5L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, a mixture of the test catalyst (50mg) and a co-catalyst (triethylaluminum) was added thereto, wherein the ratio by molar of the co-catalyst (based on Al) to the test catalyst (based on the central metal atom) was 100:1. Then, hydrogen gas was supplied thereto till 0.2MPa, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table I-1.

Copolymerization: an autoclave for polymerization (5L), a slurry polymerization process, hexane (2.5L) as the solvent, a total polymerization pressure of 0.8MPa, a polymerization temperature of 85°C, a partial pressure of hydrogen gas of 0.2MPa, a polymerization time of 2 hours.

Specifically, 2.5L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, a mixture of the test catalyst (50mg) and a co-catalyst (triethylaluminum) was added thereto, wherein the ratio by molar of the co-catalyst (based on Al) to the test catalyst (based on the central metal atom) was 100:1. Then, butene-1 (10g) was added thereto all at once as the comonomer, and then hydrogen gas was supplied thereto till 0.2MPa, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying. The particulars of the polymerization reaction and the evaluation to the polymerization were listed in the following Table I-1.

Table I-1. The results of the olefin polymerization obtained with the supported nonmetallocene catalysts

experiment No.	catalyst No.	type	catalyst activity (kgPE/gCat)	bulk density (g/cm ³)	molecular weight distribution	specific surface area (m ² g ⁻¹)	pore size (nm)
1	CAT-1	homopolymerization	6.2	0.38	3.62	1.57	47.43
2	CAT-1	copolymerization	7.1	0.38	3.85	1.76	50.87
3	CAT-2	homopolymerization	7.4	0.37	3.58	1.49	48.32
4	CAT-2	copolymerization	9.4	0.37	3.74	1.84	48.26
5	CAT-3	homopolymerization	8.7	0.37	3.63	1.77	49.35
6	CAT-3	copolymerization	11.3	0.39	3.83	1.92	52.06
7	CAT-4	copolymerization	25.2	0.39	5.21	-	-
8	CAT-5	copolymerization	17.8	0.36	4.62	-	-
9	CAT-6	copolymerization	12.5	0.37	12.55	-	-
10	CAT-7	copolymerization	5.4	0.36	21.42	-	-
11	CAT-A	copolymerization	6.8	0.38	4.65	1.32	47.26
12	CAT-B	copolymerization	7.7	0.40	3.73	1.66	51.74
13	CAT-C	copolymerization	8.2	0.39	3.57	1.65	51.37
14	CAT-D	copolymerization	12.5	0.41	4.20	1.62	46.29
15	CAT-E	copolymerization	8.0	0.37	4.37	1.73	47.92
16	CAT-F	copolymerization	21.1	0.32	3.02	0.48	28.25
17	CAT-G	copolymerization	4.3	0.36	2.85	0.25	21.74

Upon comparison of the experiment No.1 with the experiment No.2, the experiment No.3 with the experiment No.4, the experiment No.5 with the experiment No.6 in Table I-1, it is clear that upon copolymerization, the catalyst activity increases significantly, which implies that the supported nonmetallocene catalyst of this invention shows a significant comonomer effect.

Upon comparison of the experiment No.1 with the experiment Nos. 11 to 13 in Table I-1, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene ligand to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer narrows or broadens accordingly. This fact indicates that the nonmetallocene ligand shows a function of narrowing the molecular weight distribution of the polymer. Upon comparison of the experiment No.1 with the experiment No.14 in Table I-1, it is clear that the activity of the catalyst increases as the amount of the chemical treating agent to be introduced into the catalyst increases. Upon comparison of the experiment No.1 with the experiment No.15 in Table I-1, it is clear that the catalyst activity changes as the reaction temperature changes, and the molecular weight distribution of the polymer broadens as the reaction temperature increases. In view of this, it is easy for a person skilled in the art to in accordance with this invention, produce different catalysts in terms of activity and the performances of the resultant polymer by changing the nonmetallocene ligand to be used or the reaction temperature involved.

Upon comparison of the experiment Nos.1 to 15 with the experiment No.16 in Table I-1, it is clear that the polymer produced in line with this invention has a relatively high bulk density, a relatively high specific surface area and a relatively high pore size.

Upon comparison of the experiment No.2 with the experiment No.17 in Table I-1, it is clear that the supported nonmetallocene catalyst produced in line with this invention shows a relatively higher catalyst activity for olefin polymerization, and results in a polymer having a relatively higher bulk density, a relatively higher specific surface area, a relatively higher pore size, and a more desirable molecular weight distribution, as compared with a supported nonmetallocene catalyst produced by directly supporting a nonmetallocene complex onto a carrier, which makes the polymer produced in line with this invention more suitable for use in preparation of a chlorination polyethylene by a chlorination process.

Chlorination Example

The chlorination was conducted in line with an aqueous phase suspension chlorination process. Specifically, to 3500kg of water, under stirring, 10kg of a dispersing agent (sodium polymethacrylate), 1.2kg of a suspension stabilizer (a copolymer of ethylene oxide and propylene oxide), 0.7kg of an emulsifier

(polyvinylpyrrolidone) were successively added, and then 550kg of the polymer produced in line with this invention was added, after heated to 35-45°C, 2.5 to 3kg of an initiator (benzoperoxide) was added thereto, after heated under a sealed condition to 60°C, chlorine gas was supplied thereto in three stages. In the first stage, with respect to 100 parts by weight of the polymer, 170 to 195 parts by weight of chlorine gas was supplied, with a chlorination temperature of 75 to 80°C, a chlorination pressure of <0.2MPa and a chlorination duration of 45 to 60 min. In the second stage, with respect to 100 parts by weight of the polymer, 260 to 290 parts by weight of chlorine gas was supplied, with a chlorination temperature of 100 to 110°C, a chlorination pressure of <0.3MPa and a chlorination duration of 1.5 to 2.5 hours. In the third stage, with respect to 100 parts by weight of the polymer, 150 to 165 parts by weight of chlorine gas was supplied, with a chlorination temperature of 125 to 132°C, a chlorination pressure of <0.4MPa and a chlorination duration of 95 to 105 min. At the end, a chlorinated polyethylene suspension was obtained, then filtered, pressed, neutralized, washed with water, centrifugal separated and dried, a chlorinated polyethylene having a chlorine content of 33-37wt% was obtained.

The polymer used in this Chlorination Example was the polymer produced in line with the experiment No.2 in Table I-1, and a chlorinated polyethylene having a chlorine content of 35.1wt% was obtained, which shows a Mooney viscosity of 59, a VOC content of 0.24wt%, a melting enthalpy of <2J/g, a Shore hardness of 49A, a tensile strength of 12.2MPa, and a elongation at break of 776%.

Example II

The ethylene homopolymerization or copolymerization involved in the following Examples and Comparative Examples was conducted in line with the following process.

Homopolymerization: an autoclave for polymerization (5L), a slurry polymerization process, hexane (2.5L) as the solvent, a total polymerization pressure of 0.8MPa, a polymerization temperature of 85°C, a polymerization time of 2 hours.

Specifically, 2.5L hexane was added to the autoclave for polymerization, and the stirring means was started. Then, a mixture of the test catalyst (50mg) and a co-catalyst (triethylaluminum) was added thereto, wherein the ratio by molar of the co-catalyst (based on Al) to the test catalyst (based on the central metal atom) was 100:1. Then, hydrogen gas was supplied thereto till a predetermined partial pressure, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying.

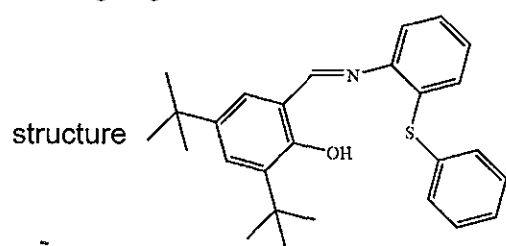
Copolymerization: an autoclave for polymerization (5L), a slurry polymerization process, hexane (2.5L) as the solvent, a total polymerization pressure of 0.8MPa, a polymerization temperature of 85°C, a polymerization time of 2 hours.

Specifically, 2.5L hexane was added to the autoclave for polymerization, and

the stirring means was started. Then, a mixture of the test catalyst (50mg) and a co-catalyst (triethylaluminum) was added thereto, wherein the ratio by molar of the co-catalyst (based on Al) to the test catalyst (based on the central metal atom) was 100:1. Then, butene-1 (10g) was added thereto all at once as the comonomer, and then hydrogen gas was supplied thereto till a predetermined partial pressure, and finally ethylene was continuously supplied thereto to keep the total polymerization pressure constant at 0.8MPa. Upon completion of the polymerization, the inside of the autoclave was vented to the atmosphere, and the resultant polymer product was discharged from the autoclave, and weighed for its weight (by mass) after drying.

Example II-1

The alkoxy magnesium spherical carrier was a diethoxy magnesium spherical carrier (having a sphericity of 1.42, a bulk density of 0.32g/cm³, and an average particle size of 420μm), the solvent for contacting was n-octane, the chemical treating agent was titanium tetrachloride, the nonmetallocene ligand has the



The diethoxy magnesium spherical carrier (5g) and the nonmetallocene ligand were weighted, added thereto n-heptane, and stirred at 300rpm for 30min, heated to 90°C to obtain a homogeneous dispersion. Then, to the dispersion, titanium tetrachloride was continuously dropwise added for a duration of 2 hours, after completion of the addition, the reaction continued under stirring at 90°C for 6 hours, filtered, washed with hexane for 3 times (60ml each time), and finally vacuum dried at the normal temperature to obtain a supported nonmetallocene catalyst.

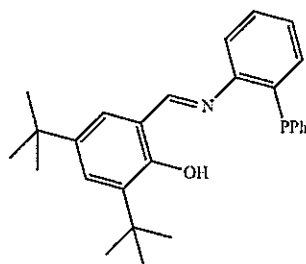
In this example, the ratio of the diethoxy magnesium spherical carrier to n-heptane was 1mol:1000ml, the ratio by molar of the diethoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.01, the ratio by molar of the diethoxy magnesium spherical carrier to titanium tetrachloride was 1:2.1.

The supported nonmetallocene catalyst was used for ethylene homopolymerization, with a hydrogen gas partial pressure of 0.2MPa, showing a catalyst activity of 6.2kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.7 g/L, a fine (less than 75 μm) powder content of 4.6wt%, a melt index (at 190 °C and 2.16 kg load) of 0.84g/10min, a molecular weight distribution (Mw/Mn) of 3.62, a density of 0.961g/cm³, an average particle size of 350μm, a specific surface area of 1.57m²/g, a pore volume of 0.00355cm³/g, a pore size of 47.43 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Example II-2

Substantially the same as the Example II-1, except for the following changes:

The nonmetallocene ligand was



contacting was changed to heptane, the chemical treating agent was changed to zirconium tetrachloride (ZrCl_4), the reaction temperature was changed to 85°C , after completion of the addition, the reaction continued under stirring at 85°C for 10 hours.

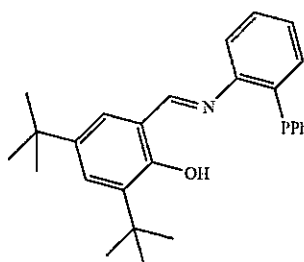
In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:1500ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.015, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:3.

The supported nonmetallocene catalyst was used for ethylene copolymerization, with a hydrogen gas partial pressure of 0.15MPa, showing a catalyst activity of 9.8 kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm^3 , an oligomer content of 1.3g/L, a fine (less than $75\mu\text{m}$) powder content of 3.4wt%, a melt index (at 190°C and 2.16 kg load) of 0.26g/10min, a molecular weight distribution (M_w/M_n) of 3.86, a density of 0.958g/cm^3 , an average particle size of $362\mu\text{m}$, a specific surface area of $1.73\text{m}^2/\text{g}$, a pore volume of $0.0038\text{cm}^3/\text{g}$, a pore size of 49.46 nm, a content of the recurring unit derived from ethylene of 98.5 wt%, a content of the recurring unit derived from butene-1 of 1.5 wt%.

Example II-3

Substantially the same as the Example II-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dipropoxy magnesium spherical carrier ($\text{Mg}(\text{OPr})_2$) (having a sphericity of 1.83, a bulk density of 0.40g/cm^3 , and an average particle size of $530\mu\text{m}$), the nonmetallocene ligand was



the reaction temperature was changed to 95°C , after completion of the addition, the reaction continued under stirring at 95°C for 4 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:2000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.02, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:5.

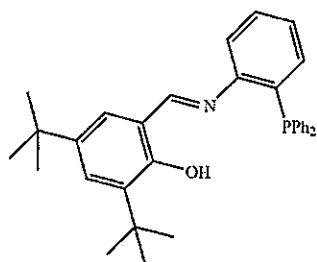
The supported nonmetallocene catalyst was used for ethylene

copolymerization, with a hydrogen gas partial pressure of 0.10MPa, showing a catalyst activity of 13.5kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.39g/cm³, an oligomer content of 0.7g/L, a fine (less than 75 μm) powder content of 3.2wt%, a melt index (at 190 °C and 2.16 kg load) of 0.15g/10min, a molecular weight distribution (Mw/Mn) of 3.83, a density of 0.955g/cm³, an average particle size of 348μm, a specific surface area of 1.94m²/g, a pore volume of 0.0046cm³/g, a pore size of 52.18 nm, a content of the recurring unit derived from ethylene of 99.2 wt%, a content of the recurring unit derived from butene-1 of 0.8 wt%.

Example II-4

Substantially the same as the Example II-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dibutoxy magnesium spherical carrier (Mg(OC₄H₉)₂) (having a sphericity of 2.07, a bulk density of 0.62g/cm³, and an average particle size of 630μm), the nonmetallocene ligand was



, the solvent for contacting was changed to decane, the chemical treating agent was ethoxy trichloro titanium (Ti(OCH₂CH₃)Cl₃), the reaction temperature was changed to 100°C, after completion of the addition, the reaction continued under stirring at 100°C for 3 hours.

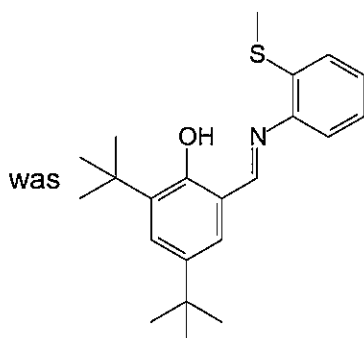
In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:3500ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.02, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:10.

The supported nonmetallocene catalyst was used for ethylene copolymerization, with a hydrogen gas partial pressure of 0.05MPa, showing a catalyst activity of 32.8kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.39g/cm³, an oligomer content of 0.3g/L, a fine (less than 75 μm) powder content of 2.1wt%, a melt index (at 190 °C and 2.16 kg load) of 0.02g/10min, a molecular weight distribution (Mw/Mn) of 4.02, a density of 0.953g/cm³, an average particle size of 376μm, a specific surface area of 1.76m²/g, a pore volume of 0.00236cm³/g, a pore size of 49.17 nm, a content of the recurring unit derived from ethylene of 99.7 wt%, a content of the recurring unit derived from butene-1 of 0.3 wt%.

Example II-5

Substantially the same as the Example II-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to dimethoxy magnesium spherical carrier (Mg (OCH₃)₂) (having a sphericity of 2.2, a bulk density of 0.25g/cm³, and an average particle size of 275μm), the nonmetallocene ligand



was , the solvent for contacting was changed to decane, the

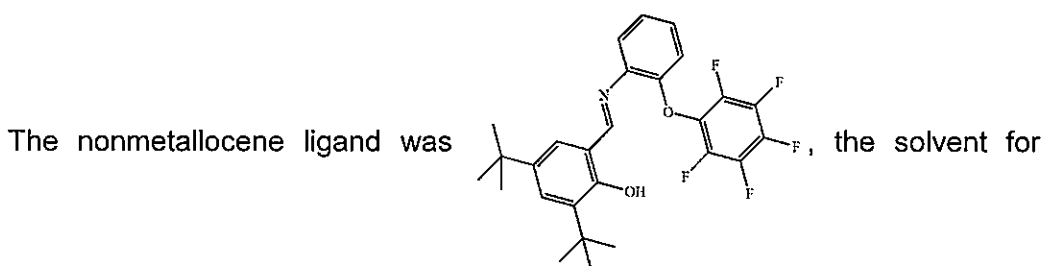
chemical treating agent was ethoxy trichloro titanium ($\text{Ti}(\text{OCH}_2\text{CH}_3)\text{Cl}_3$), the reaction temperature was changed to 110°C , after completion of the addition, the reaction continued under stirring at 110°C for 8 hours.

5 In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:4000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.03, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:14.

10 The supported nonmetallocene catalyst was used for ethylene copolymerization, with a hydrogen gas partial pressure of 0.20MPa, showing a catalyst activity of 27.6kgPE/gCat, the performances of the polymer was measured as: a bulk density of $0.38\text{g}/\text{cm}^3$, an oligomer content of 0.8g/L, a fine (less than $75\mu\text{m}$) powder content of 3.7wt%, a melt index (at 190°C and 2.16 kg load) of 0.75g/10min, a molecular weight distribution (M_w/M_n) of 3.52, a density of 0.958g/ cm^3 , an average particle size of $402\mu\text{m}$, a specific surface area of $1.45\text{m}^2/\text{g}$,
15 a pore volume of $0.0037\text{cm}^3/\text{g}$, a pore size of 55.62 nm, a content of the recurring unit derived from ethylene of 99.5 wt%, a content of the recurring unit derived from butene-1 of 0.5 wt%.

20 Example II-6

Substantially the same as the Example II-1, except for the following changes:



contacting was changed to 2-ethyl octane, the chemical treating agent was ethyl trichloro titanium ($\text{Ti}(\text{CH}_2\text{CH}_3)\text{Cl}_3$), the reaction temperature was changed to 120°C ,
25 after completion of the addition, the reaction continued under stirring at 120°C for 16 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:6000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.05, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:8.
30

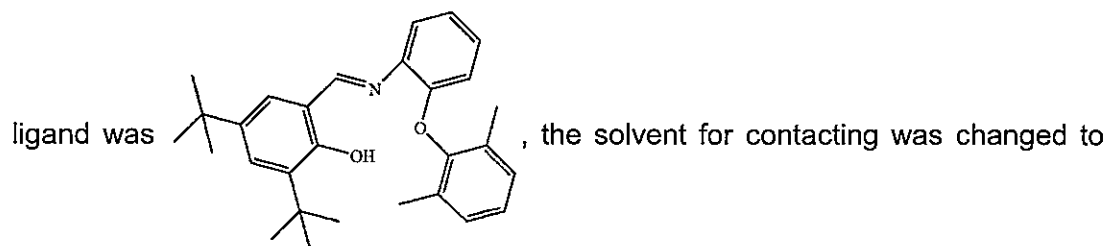
The supported nonmetallocene catalyst was used for ethylene

homopolymerization, with a hydrogen gas partial pressure of 0.2MPa, showing a catalyst activity of 17.4kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.5g/L, a fine (less than 75 μm) powder content of 4.1wt%, a melt index (at 190 °C and 2.16 kg load) of 0.67g/10min, a molecular weight distribution (Mw/Mn) of 3.40, a density of 0.961g/cm³, an average particle size of 372μm, a specific surface area of 1.52m²/g, a pore volume of 0.00326cm³/g, a pore size of 49.28 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Example II-7

Substantially the same as the Example II-1, except for the following changes:

The alkoxy magnesium spherical carrier was changed to ethoxy propoxy magnesium spherical carrier (Mg(OEt)(OPr)) (having a sphericity of 1.3, a bulk density of 0.52g/cm³, and an average particle size of 350μm), the nonmetallocene



methyl ethyl benzene, the chemical treating agent was changed to methoxy tribromo titanium (Ti(OCH₃)Br₃), the reaction temperature was changed to 120°C, after completion of the addition, the reaction continued under stirring at 120°C for 25 hours.

In this example, the ratio of the alkoxy magnesium spherical carrier to the solvent for contacting was 1mol:8000ml, the ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was 1:0.06, the ratio by molar of the alkoxy magnesium spherical carrier to the chemical treating agent was 1:3.5.

The supported nonmetallocene catalyst was used for ethylene homopolymerization, with a hydrogen gas partial pressure of 0.2MPa, showing a catalyst activity of 9.4kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.37g/cm³, an oligomer content of 1.2g/L, a fine (less than 75 μm) powder content of 3.7wt%, a melt index (at 190 °C and 2.16 kg load) of 0.45g/10min, a molecular weight distribution (Mw/Mn) of 3.31, a density of 0.961g/cm³, an average particle size of 380μm, a specific surface area of 1.55m²/g, a pore volume of 0.00295cm³/g, a pore size of 50.26 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Comparative Example II-A

Substantially the same as the Example II-1, except for the following changes:

No the nonmetallocene ligand was added.

The catalyst was used for ethylene homopolymerization, showing a catalyst activity of 5.5kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.9g/L, a fine (less than 75 μm) powder

content of 5.2wt%, a melt index (at 190 °C and 2.16 kg load) of 1.04g/10min, a molecular weight distribution (Mw/Mn) of 4.21, a density of 0.961g/cm³, an average particle size of 316μm, a specific surface area of 1.35m²/g, a pore volume of 0.00326cm³/g, a pore size of 47.23 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Comparative Example II-B

Substantially the same as the Example II-1, except for the following changes:

The ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was changed to 1:0.02.

The supported nonmetallocene catalyst was used for ethylene homopolymerization, showing a catalyst activity of 7.4kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.4g/L, a fine (less than 75 μm) powder content of 4.1wt%, a melt index (at 190 °C and 2.16 kg load) of 0.77g/10min, a molecular weight distribution (Mw/Mn) of 3.47, a density of 0.961g/cm³, an average particle size of 356μm, a specific surface area of 1.54m²/g, a pore volume of 0.00348cm³/g, a pore size of 48.65 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Comparative Example II-C

Substantially the same as the Example II-1, except for the following changes:

The ratio by molar of the alkoxy magnesium spherical carrier to the nonmetallocene ligand was changed to 1:0.04.

The supported nonmetallocene catalyst was used for ethylene homopolymerization, showing a catalyst activity of 7.8kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.0g/L, a fine (less than 75 μm) powder content of 3.8wt%, a melt index (at 190 °C and 2.16 kg load) of 0.68g/10min, a molecular weight distribution (Mw/Mn) of 3.24, a density of 0.961g/cm³, an average particle size of 352μm, a specific surface area of 1.54m²/g, a pore volume of 0.00327cm³/g, a pore size of 49.32 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Comparative Example II-D

Substantially the same as the Example II-1, except for the following changes:

The alkoxy magnesium spherical carrier to the chemical treating agent 的 the ratio by molar of was changed to 1:4.

The supported nonmetallocene catalyst was used for ethylene homopolymerization, showing a catalyst activity of 9.7kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.39g/cm³, an oligomer content of 2.2g/L, a fine (less than 75 μm) powder content of 4.5wt%, a melt index (at 190 °C and 2.16 kg load) of 1.05/10min, a molecular weight distribution (Mw/Mn) of 3.85, a density of 0.961g/cm³, an average particle size of 363μm, a specific surface area of 1.47m²/g, a pore volume of 0.00284cm³/g, a pore size of 45.63 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Comparative Example II-E

Substantially the same as the Example II-1, except for the following changes:

The reaction temperature was changed to 100°C.

- 5 The supported nonmetallocene catalyst was used for ethylene homopolymerization, showing a catalyst activity of 6.1kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 1.7g/L, a fine (less than 75 μm) powder content of 4.7wt%, a melt index (at 190 °C and 2.16 kg load) of 0.91g/10min, a molecular weight distribution (Mw/Mn) of 4.12, a density of 0.961g/cm³, an average particle size of 350μm, a specific surface area of 1.84m²/g, a pore volume of 0.00394cm³/g, a pore size of 51.32 nm, a content of the recurring unit derived from ethylene of 100 wt%.

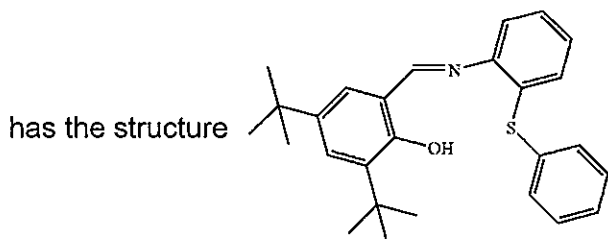
Comparative Example II-F

- 15 Substantially the same as the Example II-1, except for the following changes:

- The supported nonmetallocene catalyst was used for ethylene copolymerization, with a hydrogen gas partial pressure of 0.2MPa, showing a catalyst activity of 7.1kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.38g/cm³, an oligomer content of 17g/L, a fine (less than 75 μm) powder content of 4.8wt%, a melt index (at 190 °C and 2.16 kg load) of 0.95g/10min, a molecular weight distribution (Mw/Mn) of 3.85, a density of 0.958g/cm³, an average particle size of 354μm, a specific surface area of 1.94m²/g, a pore volume of 0.0040cm³/g, a pore size of 50.22 nm, a content of the recurring unit derived from ethylene of 98.7 wt%, a content of the recurring unit derived from butene-1 of 1.3 wt%.

Comparative Example II-G

- 30 The magnesium compound was anhydrous MgCl₂, the solvent for dissolving the magnesium compound and the nonmetallocene ligand was tetrahydrofuran, the chemical treating agent was titanium tetrachloride. The nonmetallocene ligand



- 35 Anhydrous MgCl₂ (5g) and the nonmetallocene ligand was weighted, added thereto tetrahydrofuran at the normal temperature to completely dissolve same, after stirred for 2 hours, hexane as the precipitating agent was added thereto to precipitate same, filtered, washed with hexane for 2 times (60ml each time), dried by evenly heating at 60°C under vacuum to obtain a modified carrier.

To the modified carrier, 60ml hexane was added, then under stirring, titanium tetrachloride was dropwise added thereto for a duration of 30 min, after that, the reaction continued under stirring at 60°C for 4 hours, filtered, wash with hexane for

2 times (60ml each time), and finally vacuum dried at the normal temperature to obtain a supported nonmetallocene catalyst.

In this example, the ratio of MgCl_2 to tetrahydrofuran was 1mol:210ml, the ratio by molar of MgCl_2 to the nonmetallocene ligand was 1:0.01, the ratio by volume of the precipitating agent to tetrahydrofuran was 1:1, the ratio by molar of MgCl_2 to titanium tetrachloride was 1:0.15.

The catalyst was used for ethylene homopolymerization, with a hydrogen gas partial pressure of 0.2MPa, showing a catalyst activity of 16.5kgPE/gCat, the performances of the polymer was measured as: a bulk density of 0.32g/cm^3 , an oligomer content of 3.4g/L, a fine (less than $75\text{ }\mu\text{m}$) powder content of 5.7wt%, a melt index (at $190\text{ }^\circ\text{C}$ and 2.16 kg load) of 1.05g/10min, a molecular weight distribution (M_w/M_n) of 3.1, a density of 0.961g/cm^3 , an average particle size of $285\text{ }\mu\text{m}$, a specific surface area of $0.52\text{m}^2/\text{g}$, a pore volume of $0.0021\text{cm}^3/\text{g}$, a pore size of 32.31 nm, a content of the recurring unit derived from ethylene of 100 wt%.

Upon comparison of Example II-1 with Comparative Example II-A to Comparative Example II-C, it is clear that the activity of the catalyst increases or decreases as the amount of the nonmetallocene ligand to be introduced into the catalyst increases or decreases, while the molecular weight distribution of the polymer narrows or broadens accordingly. This fact indicates that the nonmetallocene ligand shows a function of narrowing the molecular weight distribution of the polymer. Upon comparison of Example II-1 with Comparative Example II-D, it is clear that the activity of the catalyst increases as the amount of the chemical treating agent to be introduced into the catalyst increases. Upon comparison of Example II-1 with Comparative Example II-E, it is clear that the catalyst activity changes as the reaction temperature changes, and the molecular weight distribution of the polymer broadens as the reaction temperature increases. In view of this, it is easy for a person skilled in the art to in accordance with this invention, produce different catalysts in terms of activity and the performances of the resultant polymer by changing the nonmetallocene ligand to be used or the reaction temperature involved.

Upon comparison of Example II-1 with Comparative Example II-F, it is clear that upon copolymerization, the catalyst activity increases significantly, which implies that the supported nonmetallocene catalyst of this invention shows a significant comonomer effect.

Upon comparison of Example II-1 with Comparative Example II-G, it is clear that the polymer produced in line with this invention has a relatively high bulk density, a relatively high specific surface area and a relatively high pore size.

Example II-4 (Application Example)

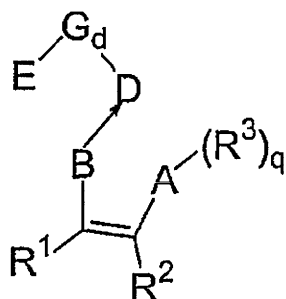
The chlorination was conducted in line with an aqueous phase suspension chlorination process. Specifically, to 3500kg of water, under stirring, 10kg of a dispersing agent (sodium polymethacrylate), 1.2kg of a suspension stabilizer (a copolymer of ethylene oxide and propylene oxide), 0.7kg of an emulsifier (polyvinylpyrrolidone) were successively added, and then 550kg of the polymer produced in line with this invention was added, after heated to 35-45°C, 2.5 to 3kg of an initiator (benzoperoxide) was added thereto, after heated under a sealed condition to 60°C, chlorine gas was supplied thereto in three stages. In the first stage, with respect to 100 parts by weight of the polymer, 170 to 195 parts by weight of chlorine gas was supplied, with a chlorination temperature of 75 to 80°C, a chlorination pressure of <0.2MPa and a chlorination duration of 45 to 60 min. In the second stage, with respect to 100 parts by weight of the polymer, 260 to 290 parts by weight of chlorine gas was supplied, with a chlorination temperature of 100 to 110°C, a chlorination pressure of <0.3MPa and a chlorination duration of 1.5 to 2.5 hours. In the third stage, with respect to 100 parts by weight of the polymer, 150 to 165 parts by weight of chlorine gas was supplied, with a chlorination temperature of 125 to 132°C, a chlorination pressure of <0.4MPa and a chlorination duration of 95 to 105 min. At the end, a chlorinated polyethylene suspension was obtained, then filtered, pressed, neutralized, washed with water, centrifugal separated and dried, a chlorinated polyethylene was obtained.

The polymer used herein was the polyethylene produced in line with Example II-1, and a chlorinated polyethylene having a chlorine content of 34.7wt% was obtained, which shows a Mooney viscosity of 84, a VOC content of 0.24 wt%, a melting enthalpy of <2J/g, a Shore hardness of 54A, a tensile strength of 10.3MPa, and a elongation at break of 790%.

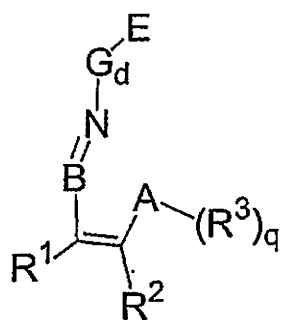
It will be apparent to those skilled in the art that various modifications and variation can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

Claims:

1. A process for producing a supported nonmetallocene catalyst, comprising the step of contacting a nonmetallocene ligand, a chemical treating agent and an alkoxy magnesium spherical carrier in the presence of a solvent selected from a C₅₋₁₂ alkane, a C₅₋₁₂ cyclic alkane, a halogenated C₅₋₁₂ alkane and a halogenated C₅₋₁₂ cyclic alkane.
2. The process according to claim 1, wherein in the presence of the solvent, the nonmetallocene ligand contacts the alkoxy magnesium spherical carrier, and then the chemical treating agent is added for a further contact.
3. The process according to claim 1, wherein the alkoxy magnesium is represented by the formula Mg(OR_a)(OR_b), wherein R_a and R_b are the same as or different from each other, and each independently selected from a C₁-C₁₈ straight-chain or branched alkyl, preferably each independently selected from a C₁-C₁₀ straight-chain or branched alkyl, more preferably each independently selected from a C₁-C₆ straight-chain or branched alkyl, further preferably each independently selected from a C₁-C₄ straight-chain or branched alkyl, more preferably each independently selected from a C₂-C₄ straight-chain or branched alkyl, most preferably both ethyl.
4. The process according to claim 1, wherein the alkoxy magnesium spherical carrier has a sphericity of 1 to 3, preferably 1 to 1.5, a bulk density of 0.2 to 1.0 g/cm³, preferably 0.25 to 0.7 g/cm³, more preferably 0.3 to 0.5 g/cm³, and an average particle size of 5 to 2000 μm, preferably 50 to 1500 μm, more preferably 100 to 1000 μm.
5. The process according to claim 1, wherein the nonmetallocene ligand is one or more selected from the group consisting of the compounds having the following structure,

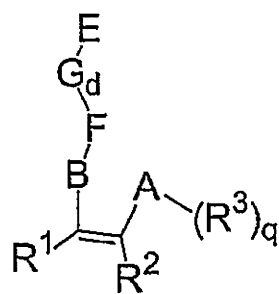


preferably one or more selected from the group consisting of the following compound (A) and the following compound (B),



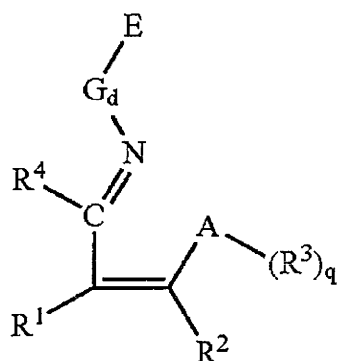
(A)

and

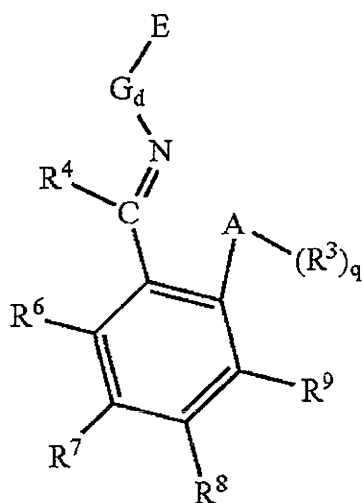


(B)

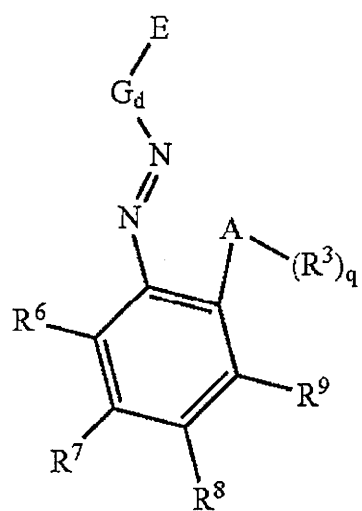
more preferably one or more selected from the group consisting of the following compound (A-1), the following compound (A-2), the following compound (A-3), the following compound (A-4), the following compound (B-1), the following compound (B-2), the following compound (B-3), and the following compound (B-4),



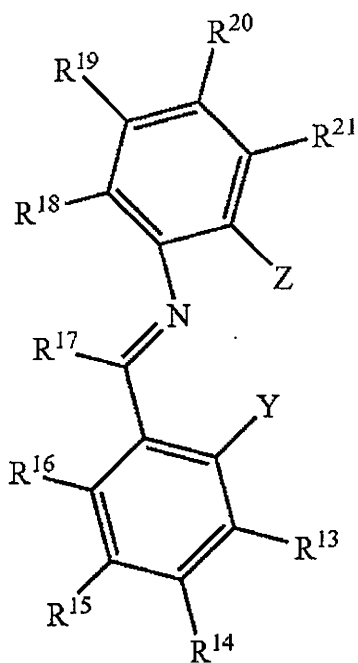
(A-1)



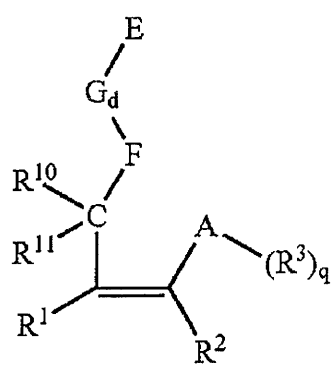
(A-2)



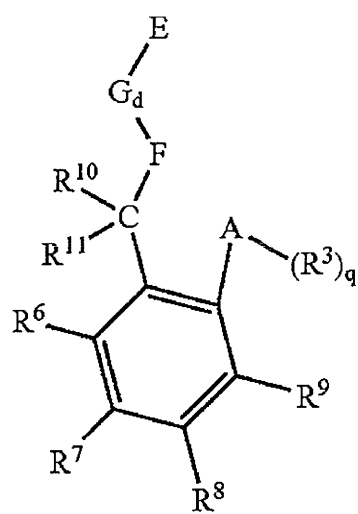
(A-3)



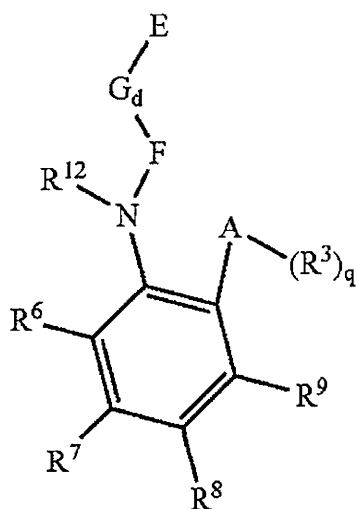
(A-4)



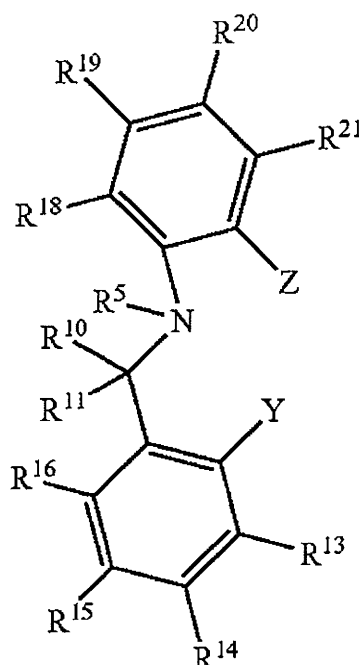
(B-1)



(B-2)



(B-3)



(B-4)

in all of the aforesaid formulae,

q is 0 or 1;

5 d is 0 or 1;

A is selected from the group consisting of an oxygen atom, a sulfur atom, a

selenium atom, $\begin{smallmatrix} \diagup \\ \text{NR}^{22} \\ \diagdown \end{smallmatrix}$, $\text{-NR}^{23}\text{R}^{24}$, $\text{-N(O)R}^{25}\text{R}^{26}$, $\begin{smallmatrix} \diagup \\ \text{PR}^{27} \\ \diagdown \end{smallmatrix}$, $\text{-PR}^{28}\text{R}^{29}$, $\text{-P(O)R}^{30}\text{OR}^{31}$, a
sulfone group, a sulfoxide group and -Se(O)R^{39} , wherein N, O, S, Se and P each
represents a coordination atom;

10 B is selected from the group consisting of a nitrogen atom, a
nitrogen-containing group, a phosphor-containing group and a $\text{C}_1\text{-C}_{30}$ hydrocarbyl;

D is selected from the group consisting of a nitrogen atom, an oxygen atom, a
sulfur atom, a selenium atom, a phosphor atom, a nitrogen-containing group, a
phosphor-containing group, a $\text{C}_1\text{-C}_{30}$ hydrocarbyl, a sulfone group or a sulfoxide
15 group, wherein N, O, S, Se and P each represents a coordination atom;

E is selected from the group consisting of a nitrogen-containing group, an
oxygen-containing group, a sulfur-containing group, a selenium-containing group, a
phosphor-containing group and a cyano group, wherein N, O, S, Se and P each
represents a coordination atom;

20 F is selected from the group consisting of a nitrogen atom, a
nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a
selenium-containing group and a phosphor-containing group, wherein N, O, S, Se
and P each represents a coordination atom;

G is selected from the group consisting of a $\text{C}_1\text{-C}_{30}$ hydrocarbyl, a substituted
25 $\text{C}_1\text{-C}_{30}$ hydrocarbyl and an inert functional group;

Y is selected from the group consisting of a nitrogen-containing group, an
oxygen-containing group, a sulfur-containing group, a selenium-containing group

and a phosphor-containing group, wherein N, O, S, Se and P each represents a coordination atom;

5 Z is selected from the group consisting of a nitrogen-containing group, an oxygen-containing group, a sulfur-containing group, a selenium-containing group, a phosphor-containing group and a cyano group, wherein N, O, S, Se and P each represents a coordination atom;

→ represents a single bond or a double bond;

— represents a covalent bond or an ionic bond;

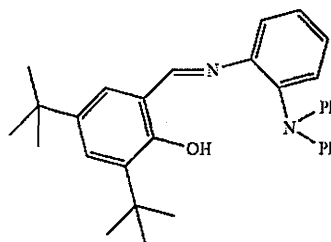
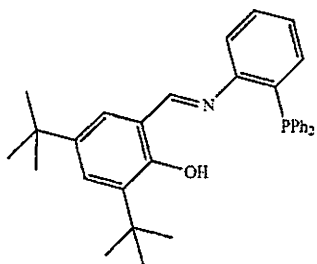
10 R¹ to R⁴, R⁶ to R²¹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl and an inert functional group, R²² to R³⁶, R³⁸ and R³⁹ are each independently selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl and a substituted C₁-C₃₀ hydrocarbyl, wherein these groups may be identical to or different from one another, and any adjacent groups may form a bond or a ring (preferably an aromatic ring) with one another;

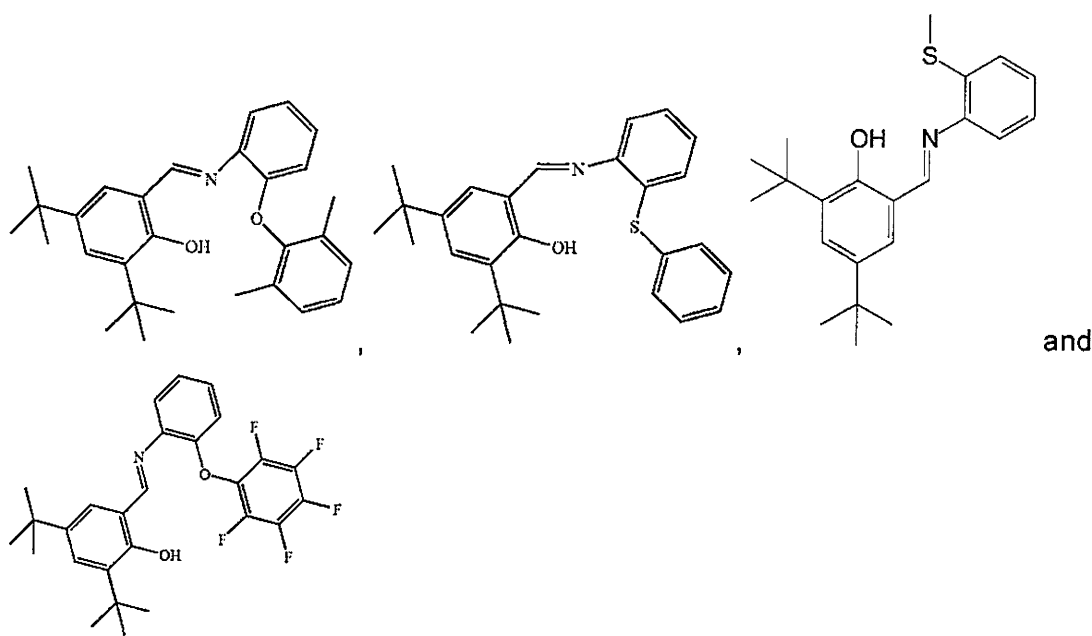
the inert functional group is selected from the group consisting of a halogen atom, an oxygen-containing group, a nitrogen-containing group, a silicon-containing group, a germanium-containing group, a sulfur-containing group, a tin-containing group, a C₁-C₁₀ ester group and a nitro group,

20 R⁵ is selected from the group consisting of the lone pair electron on the nitrogen atom, a hydrogen atom, a C₁-C₃₀ hydrocarbyl, a substituted C₁-C₃₀ hydrocarbyl, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a selenium-containing group, and a phosphor-containing group, with the proviso that when R⁵ is the oxygen-containing group, the sulfur-containing group, the nitrogen-containing group, the selenium-containing group or the phosphor-containing group, N, O, S, P and Se in the group R⁵ each can act as a coordination atom; and

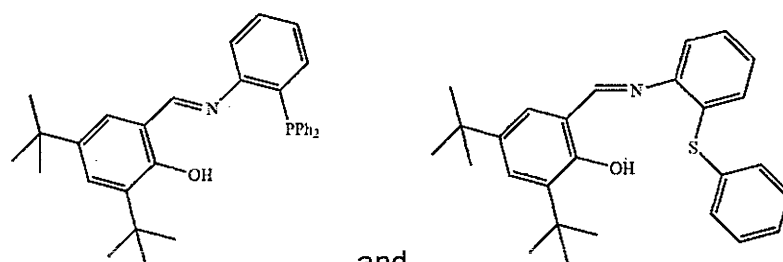
the substituted C₁-C₃₀ hydrocarbyl is selected from a C₁-C₃₀ hydrocarbyl having one or more substituent(s) selected from a halogen atom and a C₁-C₃₀ alkyl group,

30 the nonmetallocene ligand is more preferably one or more selected from the group consisting of the following compounds,





more preferably one or more selected from the group consisting of the following compounds,



5

and

6. The process according to claim 5, wherein,

the halogen atom is selected from the group consisting of F, Cl, Br and I,

the nitrogen-containing group is selected from the group consisting of



-NR²³R²⁴, -T-NR²³R²⁴ and -N(O)R²⁵R²⁶,

10 the phosphor-containing group is selected from the group consisting of



-PR²⁸R²⁹, -P(O)R³⁰R³¹ and -P(O)R³²(OR³³),

the oxygen-containing group is selected from the group consisting of hydroxy, -OR³⁴ and -T-OR³⁴,

15 the sulfur-containing group is selected from the group consisting of -SR³⁵, -T-SR³⁵, -S(O)R³⁶ and -T-SO₂R³⁷,

the selenium-containing group is selected from the group consisting of -SeR³⁸, -T-SeR³⁸, -Se(O)R³⁹ and -T-Se(O)R³⁹,

the group T is selected from the group consisting of a C₁-C₃₀ hydrocarbyl and a substituted C₁-C₃₀ hydrocarbyl,

20 R³⁷ is selected from the group consisting of a hydrogen atom, a C₁-C₃₀ hydrocarbyl, and a substituted C₁-C₃₀ hydrocarbyl,

the C₁-C₃₀ hydrocarbyl is selected from the group consisting of a C₁-C₃₀ alkyl

- group, a C₇-C₃₀ alkylaryl group, a C₇-C₃₀ aralkyl group, a C₃-C₃₀ cyclic alkyl group, a C₂-C₃₀ alkenyl group, a C₂-C₃₀ alkynyl group, a C₆-C₃₀ aryl group, a C₈-C₃₀ fused-ring group and a C₄-C₃₀ heterocycle group, wherein the heterocycle group contains 1 to 3 hetero atom(s) selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom,
- 5 the silicon-containing group is selected from the group consisting of -SiR⁴²R⁴³R⁴⁴, and -T-SiR⁴⁵,
- the germanium-containing group is selected from the group consisting of -GeR⁴⁶R⁴⁷R⁴⁸, and -T-GeR⁴⁹,
- 10 the tin-containing group is selected from the group consisting of -SnR⁵⁰R⁵¹R⁵², -T-SnR⁵³ and -T-Sn(O)R⁵⁴,
- R⁴² to R⁵⁴ are each independently selected from the group consisting of a hydrogen atom, the C₁-C₃₀ hydrocarbyl and the substituted C₁-C₃₀ hydrocarbyl, wherein these groups may be identical to or different from one another, and any
- 15 adjacent groups may form a bond or a ring with one another, and
- the group T is defined as aforesaid.
7. The process according to claim 1, wherein ratio by molar of the alkoxy magnesium spherical carrier (based on Mg) to the nonmetallocene ligand is 1:0.001-0.08, preferably 1:0.005-0.06, more preferably 1:0.01-0.04, and ratio by
- 20 molar of the alkoxy magnesium spherical carrier (based on Mg) to the chemical treating agent (based on the Group IVB metal) is 1:1-30, preferably 1:2-20, more preferably 1:4-10.
8. The process according to claim 1, wherein the Group IVB metal compound is one or more selected from the group consisting of a Group IVB metal halide, a
- 25 Group IVB metal alkyl halide, and a Group IVB metal alkoxy halide, preferably one or more of the Group IVB metal halide, more preferably one or more selected from the group consisting of TiCl₄, TiBr₄, ZrCl₄, ZrBr₄, HfCl₄ and HfBr₄, more preferably one or more selected from the group consisting of TiCl₄ and ZrCl₄.
9. A supported nonmetallocene catalyst, produced in line with the process
- 30 according to any of claims 1 to 8.
10. Use of the supported nonmetallocene catalyst according to claim 9 in olefin homopolymerization/copolymerization as the main catalyst, in combination of one or more selected from the group consisting of an aluminoxane, an alkylaluminum, a halogenated alkyl aluminum, a fluoroborane, an alkylboron and an alkylboron
- 35 ammonium salt as the co-catalyst, for homopolymerization or copolymerization of the olefin.
11. The use according to claim 10, wherein a slurry polymerization procedure is involved, and under the conditions of a total polymerization pressure of 0.2 to 2.0 MPa (preferably 0.5 to 1.5 MPa), a partial pressure ratio of hydrogen gas to
- 40 ethylene of 0.01-0.2:1 (preferable 0.02-0.1:1, most preferably 0.03-0.08:1), a polymerization temperature of 60 to 100 °C (preferably 70 to 95 °C, more preferably 80 to 90 °C), and an amount of an optional comonomer of 0.5 to 10 g per 1mg of the main catalyst (preferably 1 to 5 g per 1mg of the main catalyst), the

homopolymerization of ethylene or the copolymerization of ethylene with at least one alpha-olefin(s) selected from a C₃ to C₁₂ alpha-olefin (preferably a C₃ to C₈ alpha-olefin) is conducted to obtain an ethylene polymer.