Catalyst and process for (co)polymerizing alpha-olefins
Katalysator und Verfahren zur (Co)Polymerisation von Alpha-Olefinen
Catalyseur et procédé de (co)polymérisation d’alpha-oléfines

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Remarks:
The file contains technical information submitted after the application was filed and not included in this specification.

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Description

The present invention relates to a catalyst formed by a bis(cyclopentadienyl) bis(amide) derivative of zirconium and/or hafnium and an aluminoxide co-catalyst, and to its use in the (co)polymerization of ethylene and other alpha-olefins.

In the art, it is generally known that ethylene, or, in general, alpha-olefins, can be polymerized by means of the low-pressure process, with Ziegler-Natta catalysts.

The useful catalysts for the intended purpose are generally formed by a compound of a transition metal (elements of Groups from IV to VII of the Periodic Table of the Elements), in mixture with an organometallic compound or hydride of the elements of Groups from I to III of said Periodic Table, by operating in suspension, in solution, or in the absence of solvents or diluents. For this known art, reference is made to the description by J. Boor, in "Ziegler-Natta Catalysts and Polymerization", Academic Press, New York (1979).

A particular class of catalysts active in olefin polymerization is constituted by the combination of an aluminoxide with a cyclopentadienyl derivative of such a metal as titanium, zirconium and hafnium (Group IVB), also referred to as "metallosenes", which can be defined by the following formula:

\[
\begin{array}{c}
\text{Cp} & \text{R} \\
\downarrow & \downarrow \\
\text{M} & \text{M} \\
\downarrow & \downarrow \\
\text{Cp} & \text{R}
\end{array}
\]

wherein M represents a metal of Group IVB of the Periodic Table of the Elements; each R represents a halogen atom, an alkyl group or an aryl group; and each Cp independently represents a cyclopentadienyl, indenyl or fluorenyl group.

As to the prior art, reference is made to the description made by H. Sinn, W. Kaminsky, in Adv. Organomet. Chem. 18, 99 (1980) and in U.S. patent No. 4,542,199.

These catalysts display a high catalytic activity and the capability of producing polymers with desired characteristics as a function of the particular catalytic composition used and of the olefin, or olefin mixture, submitted to polymerization. Reference is made, for instance, the disclosures of U.S. patent Nos. 4,530,914; 4,935,474; 4,937,299; and 5,001,205; and of European patent application publication Nos. 35,242; 318,049; 384,171 and 387,609.

WO-A-87/03867 discloses a class of catalysts for the polymerisation of ethylene and other alpha-olefins, formed by a metallocen comprising a di(hydrocarbon)amino group such as bis(cyclopentadienyl) bis(dimethylamide) zirconium, bis(cyclopentadienyl)bis(dimethylamide) titanium or bis(cyclopentadienyl)bis(diethylamide) hafnium and an aluminoxide as co-catalyst.

The present Applicant has found now, according to the present invention, that when they are used together with an aluminoxide, particular metallosenes containing substituted amicid groups in their molecular structure constitute extremely active catalysts in the polymerization of olefins.

Therefore, a purpose of the present invention is a polymerization catalyst formed by a metallocene containing substituted amicid groups and an alumin oxide.

Another purpose of the present invention is the processes for the (co)polymerization of ethylene and other alpha-olefins, which use said catalyst.

Further purposes of the present invention will be evident from the following disclosure.

Therefore, in a first aspect thereof, the present invention relates to a catalyst for the (co)polymerization of ethylene and other alpha-olefins, formed by:

(a) a bis(cyclopentadienyl) bis(amide) derivative of an element of Group IVB of the Periodic Table of the Elements, to be defined by means of the formula:
$$\text{Cp} \quad \text{NR}^1 \text{R}^2$$
$$\backslash \quad /$$
$$\quad \text{M} \quad (I)$$
$$/ \quad \backslash$$
$$\text{Cp} \quad \text{NR}^3 \text{R}^4$$

wherein:

M represents a metal selected from zirconium and hafnium;
each R\(^1\), R\(^2\), R\(^3\) and R\(^4\) represent an ethyl group; and each Cp independently represents a cyclopentadienyl, indenyl or fluorenyl group, possibly bearing one or more C1-C4 alkyl substituents; said groups Cp may also be linked with each other by means of a bridge structure of carbon atoms or an alkyl silicane structure; and

(b) an aluminoxane co-catalyst, with the proviso that the derivative (a) is not bis(cyclopentadienyl) bis(diethylamide) hafnium.

In particular, in said formula (I) the metal M is zirconium.

In the preferred embodiment, the derivative (a) is bis(cyclopentadienyl) bis(diethylamide) zirconium.

In said formula (I), Cp is preferably selected from cyclopentadienyl, indenyl and fluorenyl groups, which may be not substituted, or may bear one or more C1-C4 alkyl substituents. When both Cp groups in the compound (I) are connected with each other by a bridge structure, said bridge structure preferably is formed by a linear or branched alkylene group of from 1 to 4 carbon atoms, or is a dialkylsilyl, and, preferably, a dimethylsilyl group. Examples of bridge-connected Cp groups are bis(cyclopentadienyl) ethylene, bis(indenyl) ethylene, (cyclopentadienyl-1-fluorenyl) isopropyl and bis(cyclopentadienyl) dimethylsilyl.

Specific examples of compounds (I) are consequently the following: bis(cyclopentadienyl) bis(diethylamide) zirconium; ethylene-bis(indenyl) bis(diethylamide) zirconium; ethylene-bis(indenyl) bis(diethylamide) hafnium; and isopropyl (cyclopentadienyl-fluorenyl) bis(diethylamide) hafnium.

In those catalysts which are destined to the production of polyolefins with a broadened molecular weight distribution, compounds (I) containing two metals "M" different from each other can be used.

The compound (I) in which both Cp radicals represent the cyclopentadienyl group and all of R\(^1\), R\(^2\), R\(^3\) and R\(^4\) represent the ethyl group, can be prepared as described by G. Chandra and M.F. Lapper in J. Chem. Soc. (A), 1968, page 1940.

According to the present invention, in association with the compound (I) disclosed hereinabove, an aluminoxane is used as co-catalyst.

As known, aluminoxanes are compounds containing Al-O-Al bonds, with a variable O:Al ratio, which can be obtained in the art by causing an alkyl aluminium, or alkyl aluminium halide to react, under controlled conditions, with water, and, in the case of trimethyl aluminium, also with a hydrous salt, such as aluminium sulfate hexahydrate, copper sulfate pentahydrate and iron sulfate pentahydrate. In particular, in the catalyst according to the present invention, said aluminoxane and compound (I) are contained in such proportions that the atomic ratio of aluminium contained in said aluminoxane to the metal of Group IVB contained in the compound (I) is comprised within the range of from 10:1 to 10\(^2\):1, and preferably from 10\(^2\):1 to 10\(^4\):1.

The catalytic systems according to the present invention are useful in ethylene polymerization to yield linear polyethylene, and in the polymerization of propylene or higher alpha-olefins, to yield atactic, syndiotactic or isotactic polymers, as a function of the particular catalytic composition selected and of the specific polymerization conditions. The catalytic systems are furthermore active in the copolymerization of ethylene with propylene and/or other olefins (formation of LLDPE) and in the terpolymerization of ethylene, propylene and diene.

The polymerization can be carried out by means of the suspension technique, in an inert diluent, or in gas phase, with temperatures which generally are comprised within the range of from 20 to 120°C, under a pressure which generally is comprised within the range of from 1 to 300 bars, using a molecular weight regulator agent, such as, e.g., hydrogen.

The following experimental examples are reported in order to better illustrate the invention.

**Example 1**

To an autoclave of 5 litres, of stainless steel, Brignole type, equipped with magnetic-driven anchor stirrer and
temperature-controlled by means of electrical resistors, the following are charged:

- n-Hexane (polymerization grade) 1,900 ml
- Catalyst Cp₂Zr[N(C₆H₅)₂] 0.00752 g
- Co-catalyst (MAO* solution at 10% by weight in toluene) 40 ml
- Molecular weight regulator agent (H₂) 0.5 bar
- Ethylene 14.43 bars

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, under a total pressure of 15 bars, at a temperature of 70°C and over a polymerization time of 1.0 hour. Under these conditions, 0.258 kg of polyethylene is obtained in a yield of 34.4 kg of polymer per each catalyst gram, corresponding to 138 kg of polymer per each gram of zirconium in the catalyst.

Example 2

Ethylene is polymerized in the same way as in above Example 1, with the following variants:

- Catalyst Cp₂Zr[N(C₆H₅)₂] 0.00191 g
- Co-catalyst (MAO solution at 10% by weight in toluene) 8.7 ml

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, during a polymerization time of 1.5 hours. Under these conditions, 0.1625 kg of polyethylene is obtained in a yield of 85 kg of polymer per each catalyst gram, corresponding to 341 kg of polymer per each gram of zirconium in the catalyst.

Example 3

Ethylene is polymerized in the same way as in above Example 1, with the following variants:

- Catalyst Cp₂Zr[N(C₆H₅)₂] 0.002 g
- Co-catalyst (MAO solution at 10% by weight in toluene) 11 ml

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, during a polymerization time of 1.16 hours. Under these conditions, 0.198 kg of polyethylene is obtained in a yield of 99 kg of polymer per each catalyst gram, corresponding to 398 kg of polymer per each gram of zirconium in the catalyst.

The resulting polyethylene displays a melt-flow index (ASTM D 1238 E) of 1.78 g/10 minutes.

Example 4

Ethylene is polymerized in the same reactor as of Example 1, under the following conditions:

- n-Hexane (polymerization grade) 1,900 ml
- Catalyst Cp₂Zr[N(C₆H₅)₂] 0.001 g
- Co-catalyst (MAO solution at 10% by weight in toluene) 5.1 ml
- Molecular weight regulator agent (H₂) 0.5 bar
- Ethylene 14.5 bars

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, under a total pressure of 15 bars, at a temperature of 700°C and during a polymerization time of 1.5 hours. Under these conditions, 0.166 kg of polyethylene is obtained in a yield of 166 kg of polymer per each catalyst gram, corresponding to 664 kg of polymer per each gram of zirconium in the catalyst.

The so obtained polyethylene displays the following characteristics:

- Melt-flow index (ASTM D 1238 E) 8.8 g/10 minutes
- Melt-flow index (ASTM D 1238 F) 167.5 g/10 minutes
- Shear sensitivity 19
- Density (23°C) 0.9630 g/ml

(*) MAO is oligomeric methyl aluminoxane.
Example 5

Ethylene is polymerized in the same reactor as of Example 1, under the following conditions:

- n-Hexane (polymerization grade) 1,900 ml
- Catalyst Cp₂Zr(N(C₅H₅)₂)₂ 0.0007 g
- Co-catalyst (MAO solution at 10% by weight in toluene) 3.8 ml
- Molecular weight regulator agent (H₂) 0.5 bar
- Ethylene 14.5 bars

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, under a total pressure of 15 bars, at a temperature of 40°C and during a polymerization time of 1.5 hours. Under these conditions, 0.166 kg of polyethylene is obtained in a yield of 33 kg of polymer per each catalyst gram, corresponding to 132 kg of polymer per each gram of zirconium in the catalyst.

The so obtained polyethylene displays the following characteristics:

- Melt-flow index (ASTM D 1238 E) 6.01 g/10 min
- Melt-flow index (ASTM D 1238 F) 162.9 g/10 min
- Shear sensitivity 27.1

Example 6

Ethylene is polymerized in the same reactor as of Example 1, under the following conditions:

- n-Hexane (polymerization grade) 1,900 ml
- Catalyst Cp₂Zr(N(C₅H₅)₂)₂ 0.0007 g
- Co-catalyst (MAO solution at 10% by weight in toluene) 3.8 ml
- Molecular weight regulator agent (H₂) 0.05 bar
- Ethylene 12.5 bars

The polymerization is carried out with an atomic ratio of Al:Zr of 2,500:1, under a total pressure of 15 bars, at a temperature of 120°C and during a polymerization time of 1.5 hours. Under these conditions, 0.0333 kg of polyethylene is obtained in a yield of 48 kg of polymer per each catalyst gram, corresponding to 191 kg of polymer per each gram of zirconium in the catalyst.

The so obtained polyethylene displays the following characteristics:

- Melt-flow index (ASTM D 1238 E) 4.12 g/10 minutes
- Melt-flow index (ASTM D 1238 F) 72.3 g/10 minutes
- Shear sensitivity 17.6
- Density (23°C) 0.9517 g/ml

Claims

1. Catalyst for the (co)polymerization of ethylene and other alpha-olefins, formed by:

   (a) a bis(cyclopentadienyl) bis(amide) derivative of an element of Group IVB of the Periodic Table of the Elements, to be defined by means of the formula:
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\[
\begin{array}{c}
\text{C} \quad \text{N} \quad \text{R}^1 \quad \text{R}^2 \\
\text{\_ \_}
\end{array}
\]

wherein:

M represents a metal selected from zirconium and hafnium;

each \( R^1, R^2, R^3 \) and \( R^4 \) represent an ethyl group; and each Cp independently represents a cyclopenta
dienyl, indenyl or fluorenyl group, possibly bearing one or more C1-C4 alkyl substituents; said groups Cp may also be linked with each other by means of a bridge structure of carbon atoms or an alkyl silanic
structure; and

(b) an aluminoxane co-catalyst, with the proviso that the derivative (a) is not bis(cyclopentadienyl) bis(diethylan
amide) hafnium.

2. Catalyst according to claim 1, characterized in that in said formula (I) the metal M is zirconium.

3. Catalyst according to claim 1, characterized in that the derivative (a) is bis(cyclopentadienyl) bis(diethy
lamide) zirconium.

4. Catalyst according to claim 1, characterized in that the Cp moieties, in said formula (I), individually represent a
cyclopentadienyl, indenyl and fluorenyl group, which may be not substituted or may bear one or more C1-C4 alkyl
substituents, or both Cp groups jointly represent a bis(cyclopentadienyl) ethylene, bis(indenyl) ethylene, (cyclopentad
dienyl-1-fluorenyl) isopropyl and a bis(cyclopentadienyl) dimethylsilyl group.

5. Catalyst according to claim 1, characterized in that said compounds (I) are selected from bis(cyclopentadienyl)
bis(diethy lamide) zirconium; ethylene-bis(indenyl) bis(diethy lamide) zirconium; ethylene-bis(indenyl) bis(diethyla
mide) hafnium; and isopropyl (cyclopentadienyl-fluorenyl) bis(diethy lamide) hafnium.

6. Catalyst according to claim 1, characterized in that the atomic ratio of aluminum contained in the co-catalyst (b)
to the Group IVB metal contained in the compound (I) is comprised within the range of from 10:1 to 10^4:1, and
preferably of from 10^2:1 to 10^4:1.

7. Process for the (co)polymerization of ethylene and other alpha-olefins, characterized in that in said process the
catalyst according to claims from 1 to 6 is used.

Patentansprüche

1. Katalysator zur (Co)polymerisation von Ethylen und anderen \( \alpha \)-Olefinen, gebildet aus:

(a) einem Bis(cyclopentadienyl)-bis(amid)-Derivat eines Elements der Gruppe IVB des Periodensystems der
Elemente, das durch die Formel
Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß in Formel (I) das Metall M Zirkonium ist.

2. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß das Derivat (a) Bis(cyclopentadienyl)-bis(diethylamid)-Zirkonium ist.

3. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß die Cp-Einheiten in Formel (I) unabhängig voneinander eine Cyclopentadienyl- Indenyl- bzw. Fluorenylgruppe bedeuten, die unsubstituiert sein kann oder die einen oder mehr C1-C4- Alkyl substituenten tragen kann, oder daß beide Gruppen Cp gemeinsam eine Bis(cyclopentadienyl)-ethylen-, Bis(indenyl)-ethylen-, (Cyclopentadienyl-1-fluorenyl)-isopropyl- oder eine Bis(cyclopentadienyl)-dimethylsilyle Gruppe darstellen.

4. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindungen (I) unter Bis(cyclopentadienyl)-bis(diethylamid)-Zirkonium, Ethylen-bis(indenyl)-bis(diethylamid)-Zirkonium, Ethylen-bis-(indenyl)-bis(diethylamid)-Hafnium und Isopropyl(cyclopentadienyl-fluorenyl)-bis(diethylamid)-Hafnium ausgewählt sind.

5. Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß das Atomverhältnis von in dem Cokatalysator (b) enthaltenem Aluminium zu dem in Verbindung (I) enthaltenen Metall der Gruppe IVB im Bereich von 10⁻¹ bis 10⁵⁻¹ und vorzugsweise im Bereich von 10⁻² bis 10⁻¹ liegt.

6. Verfahren zum (Co)polymerisations von Ethylen und anderen α-Olefinen, dadurch gekennzeichnet, daß bei dem Verfahren der Katalysator nach Ansprüchen 1 bis 6 verwendet wird.

Revendications

1. Catalyseur de (co)polymerisation d'éthylène et d'autres alpha-oléfines, constitué de

   a) un dérivé bis(cyclopentadiényl)bis(amido) d'un élément du groupe IVB de la Classification Périodique des Eléments, représenté par la formule

   
   \[
   \text{Cp} \quad \text{M} \quad \text{NR}_1^1 \text{R}_2^2 \\
   \quad \text{Cp} \quad \text{NR}_3^3 \text{R}_4^4
   \]

   dans laquelle:
M représente un métal choisi parmi le zirconium et le hafnium. 
\( R^1, R^2, R^3 \) et \( R^4 \) représentent chacun un groupe éthyle, et chaque \( C_p \) représente indépendamment un groupe cyclopentadiényle, indényle ou fluorényle, portant éventuellement un ou plusieurs substituants alkyle en \( C_{14} \); ces groupes représentés par \( C_p \) pouvant aussi être reliés l'un à l'autre par une structure pontante constituée d'atomes de carbone ou par une structure de type alkyl-silane ; et

b) un co-catalyseur de type aluminoxane ;

sous réserve que le dérivé (a) ne soit pas le bis(cyclopentadiényl)-bis(diéthylamido)hafnium.

2. Catalyseur conforme à la revendication 1, caractérisé en ce que, dans la formule (I), le métal représenté par \( M \) est le zirconium.

3. Catalyseur conforme à la revendication 1, caractérisé en ce que le dérivé (a) est le bis(cyclopentadiényl)bis(diéthylamido)zirconium.

4. Catalyseur conforme à la revendication 1, caractérisé en ce que les symboles \( C_p \) de la formule (I) représentent chacun, individuellement, un groupe cyclopentadiényle, indényle ou fluorényle qui peut ne porter aucun substituant ou porter un ou plusieurs substituants alkyle en \( C_{14} \), ou bien les deux symboles \( C_p \) représentent conjointement un groupe bis(cyclopentadiényl)éthylène, bis(indényl)éthylène, (cyclopentadiényl)(1-fluorényl)isopropyle ou bis(cyclopentadiényl)diméthylsilyle.

5. Catalyseur conforme à la revendication 1, caractérisé en ce que le composé de formule (I) est choisi parmi les suivants : bis(cyclopentadiényl)bis(diéthylamido)zirconium, [éthylène-bis(indényl)]bis(diéthylamido)zirconium, [éthylène-bis(indényl)]bis(diéthylamido)hafnium, et [isopropyl(cyclopentadiényl)(fluorényl)]bis(diéthylamido)hafnium.

6. Catalyseur conforme à la revendication 1, caractérisé en ce que le rapport atomique de l'aluminium contenu dans le co-catalyseur (b) au métal du groupe IVB contenu dans le composé de formule (I) se situe dans l'intervalle allant de \( 10/1 \) à \( 10^3/1 \), et de préférence, dans celui qui va de \( 10^2/1 \) à \( 10^4/1 \).

7. Procédé de (co)polyématisation d'éthylène et d'autres alpha-oléfines, caractérisé en ce que l'on emploie, dans ce procédé, un catalyseur conforme à l'une des revendications 1 à 6.