CATALYSTS OF THE ZIEGLER-NATTA TYPE FOR THE (CO) POLYMERIZATION OF -OLEFINS WITH A HIGH PRODUCTIVITY

SUMMARY

In a first aspect, there is provided a solid catalyst for the (co)polymerization of α-olefins, comprising titanium, magnesium, aluminium, chlorine and at least one metal selected from hafnium and zirconium, in the following molar ratios:

M/Ti = 0.2 - 5.0 ; Mg/Ti = 3.0 - 15.0 ; Al/Ti = 0.1-4.0 ; Cl/Ti = 15.0 -60.0

wherein M is a metal selected from hafnium and zirconium or a mixture thereof, preferably hafnium, characterized in that at least 60% of the titanium is in oxidation state +3 and, when examined via XPS spectroscopy, the solid has an absorption band characteristic of a binding energy ranging from 454 to 458 eV, and wherein titanium, magnesium, said metal M, aluminium and chlorine represent at least 80% by weight, preferably from 85 to 100% by weight, of the catalyst.

In a second aspect, there is provided a process for the preparation of a solid catalyst for the (co)polymerization of α-olefins as defined herein, comprising the following steps:

(i) preparing a mixture of at least one magnesium chloride, a titanium compound, a compound of a metal M as defined above, and a carboxylic acid R-COOH, wherein R is an organic group having from 2 to 30, preferably from 5 to 15 carbon atoms, in such quantities as to respect the following molar or atomic ratios:

M/Ti = 0.2 – 5.0; Mg/Ti = 3.0 – 20.0; R – COOH/(Mg +M) = 1.5 - 8

in a hydrocarbon liquid medium, wherein at least one of said metal compounds, preferably at least magnesium chloride, is substantially insoluble as such;

(ii) maintaining the mixture prepared in step (i) at a temperature ranging from 50 to 200°C, preferably from 60 to 130°C for at least one minute, preferably for a time of 0.5 to 4 hours, in a closed container, and filtering the possible undissolved residue to obtain a solution;

(iii) adding to the solution obtained in step (ii), cooled to a temperature ranging from 20 to 40°C, an aluminium alkyl chloride having the following general formula (I)

$$AlR'_nCl_{(3-n)} \qquad (I)$$

wherein R' is a linear or branched alkyl radical, containing from 1 to 20 carbon atoms and "n" is a decimal number having values ranging from 0.5 to 2.5, preferably from 0.9 to 2.1;
at least in a quantity which is sufficient to precipitate, in the form of solid compound, 70%, preferably 80%, of the metals Mg, M and Ti present in the solution of said step (ii) to obtain a suspension;

(iv) heating the suspension obtained in step (iii) to a temperature ranging from 50 to 130°C, preferably from 70 to 110°C, for a time of 5 to 180 minutes, preferably from 40 to 150 minutes, in order to complete the solid precipitation, and separating the solid

compound precipitated from the reaction liquid, to obtain a solid precursor of said catalyst;

(v) treating said solid precursor with a further quantity of aluminium alkyl chloride having formula (I), the same or different from that added in said step (iii), with an Al/Ti ratio from 5 to 150, at a temperature ranging from -10 to 50°C, preferably from 10 to 50 °C, and separating the catalyst thus obtained from the reaction liquid.

In a third aspect, there is provided a precursor of solid catalyst as defined herein, consisting, for at least 80% by weight, preferably from 90 to 100% by weight of titanium, magnesium, aluminium, chlorine and at least one metal M selected from hafnium and zirconium, preferably hafnium, in the following molar ratios:

M/Ti = 0.2 – 5.0; Mg/Ti = 3.0 – 15.0; Al/Ti = 0.1-3.0; Cl/Ti = 18.0 - 60.0,

characterized in that at least 60%, preferably at least 80%, of the titanium is in oxidation state +3 and has a particle size with a narrow Gaussian distribution having a maximum point of between 2 and 15 μm, and dimensions of the granules which is such that 80% by weight of the same ranges from 1 to 30 μm.

In a fourth aspect, there is provided a catalytic system for the (co)polymerization of α-olefins comprising, in contact with each other, a co-catalyst consisting of a hydride or an organometallic compound of a metal of groups 1, 2 or 13 of the periodic table of elements, and a solid catalyst as defined herein.

In a fifth aspect, there is provided a process for the (co)polymerization of α-olefins comprising the polymerization of at least one α-olefin, both in continuous and in batch, in one or more steps, at low (0.1-1.0 MPa), medium (1.0-10 MPa) or high (10-150 MPa) pressure and temperatures ranging from 20 to 300°C, possibly in the presence of an inert diluent, in the presence of a suitable catalytic system, characterized in that the latter is a catalytic system as defined herein.

DETAILED DESCRIPTION

The present invention relates to a catalyst of the Ziegler-Natta type for the (co)polymerization of α-olefins, having a high productivity and thermal stability.

More specifically, the present invention relates to an enhanced catalyst of the Ziegler-Natta type with a high activity and thermal stability, which forms a catalytic system that is particularly effective in high-temperature polymerization and copolymerization processes of α-olefins, especially ethylene, for obtaining high industrial productivities.

It is well-known that α-olefins, and in particular ethylene, can be polymerized in low, medium or high pressure processes with catalysts of the Ziegler-Natta type (ZN) to give substantially linear polymers with high molecular weights. These catalysts generally consist of a compound based on one or more elements of the fourth to sixth groups of the Periodic Table, combined with an organometallic compound or a hydride of the elements of groups 1, 2 or 13 of the Periodic Table, especially an aluminium alkyl. ZN catalysts comprising a solid containing a transition metal (generally titanium), a bivalent metal (generally magnesium), a halogen (generally chlorine), and optionally an electron-donor compound, are particularly known. These solid catalysts, combined with an