CLAIMS

1. 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.

2. The solid catalyst according to claim 1, wherein said elements are present in the following atomic ratios with respect to Ti:

M/Ti = 0.5 - 4.0; Mg/Ti = 6.0 - 13.0; Al/Ti = 0.2 - 2.0; Cl/Ti = 18.0 - 50.0.

~~3. The solid catalyst according to one of the previous claims 1 or 2, 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.~~

43. The solid catalyst according to any of the previous claims, wherein at least 80%, preferably al least 90% of the titanium is in oxidation state +3, and the solid

has an absorption band characteristic of a binding energy centred around the value of 456±1 eV.

54. The solid catalyst according to any of the previous claims, having a particle size with a Gaussian distribution having a maximum point between 2 and 15 μm and dimensions of the granules which are such that 80% by weight of the same ranges from 1 to 30 μm, preferably from 2 to 20 μm.

65. The solid catalyst according to any of the previous claims, wherein the titanium is included in a quantity of up to 10% by weight, preferably from 1 to 5% by weight, with respect to the total weight of the solid.

76. The solid catalyst according to any of the previous claims, wherein at least 10%, preferably from 15 to 40% of the surface Ti atoms has a higher electronic charge density.

87. The solid catalyst according to any of the previous claims, also comprising up to 20% by weight, preferably up to 10% by weight of a residue mainly consisting of carboxylate.

98. A process for the preparation of a solid catalyst for the (co)polymerization of α-olefins according to any of the previous claims from 1 to 87, 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 ~~higher than or equal to 5, preferably between 10 and 200~~from 5 to 150, at a temperature ranging from -10 to ~~120~~50°C, preferably from 10 to 50 °C, and separating the catalyst thus obtained from the reaction liquid.

~~10~~9. The process according to claim ~~9~~8, characterized in that, in said step (iii) the temperature of the reaction mixture is not higher than 45°C and the difference between the maximum temperature and the minimum temperature of the mixture during the reaction is equal to or lower than 15°C.

~~11~~10. The process according to one of the previous claims ~~9~~—8 or ~~10~~9, wherein, in step (iii) the aluminium alkyl chloride having formula (I) is added in molar quantities equal to or higher than two times, preferably from 3 to 5 times, the quantity in moles of carboxylic acid RCOOH introduced in step (i).

~~12~~11. The process according to one of the previous claims from ~~9~~—8 to ~~11~~10, wherein, in said step (v) the Al/Ti ratio ranges from 20 to 150 and the reaction is carried out at a temperature ranging from 15 to 35°C.

~~13~~12. The process according to one of the previous claims from ~~9~~—8 to ~~12~~11, wherein, in step (i) the reagents are introduced in the following atomic ratios between the

elements:

$M/Ti = 0.5 - 4.0$; $Mg/Ti = 5.0 - 16.0$; $R - COOH/(Mg + M) = 2.0 - 4.5$.

~~14~~13. The process according to one of the previous claims from ~~9~~8 to ~~13~~12, wherein, in step (i) the quantities in moles of carboxylic acid RCOOH ranges from 1.2 to 5 times the equivalents of the insoluble compounds.

~~15~~14. The process according to one of the previous claims from ~~9~~8 to ~~14~~13, wherein, at the end of step (ii) the overall quantity of compounds which remain undissolved in the mixture is at the most 30%, preferably lower than 10% by weight with respect to the total weight of the initial insoluble product introduced in step (i).

~~16~~15. The process according to one of the previous claims from ~~9~~8 to ~~15~~14, wherein, said step (ii) is carried out with no significant loss of material towards the outside.

~~17~~16. The process according to one of the previous claims from ~~9~~8 to ~~16~~15, wherein, in step (iv), the suspension is heated to a temperature ranging from 70 to 110°C for a time of 40 to 150 minutes.

~~18~~17. The process according to one of the previous claims from ~~9~~8 to ~~17~~16, wherein, at the end of step (iv), the solid precursor is subjected to washings with a hydrocarbon solvent until a level of aluminium lower than 1.5 mM/L is reached in the mother liquor.

~~19~~18. A precursor of solid catalyst according to any of the previous claims from 1 to ~~8~~7, 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:

$M/Ti = 0.2 - 5.0$; $Mg/Ti = 3.0 - 15.0$; $Al/Ti = 0.1\text{-}3.0$; $Cl/Ti = 18.0 - 60.0$,

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.

~~20~~19. The precursor according to claim ~~19~~18, characterized by a particle size wherein the average particle dimension ranges from 3 to 12 μm and 80% by weight of the particles has a higher dimension ranging from 2 to 20 μm.

~~21~~20. A catalytic system for the(co)polymerisation 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 according to any of the previous claims from 1 to ~~8~~7.

~~22~~21. The catalytic system according to claim ~~21~~20, wherein said co-catalyst is selected from aluminium trialkyls containing from 1 to 10, preferably from 2 to 6 carbon atoms in each alkyl radical.

~~23~~22. The catalytic system according to claim ~~21~~20, wherein said co-catalyst consists of an aluminum oxane,

particularly a polymeric methyl aluminum oxane.

~~24~~23. The catalytic system according to one of the previous claims ~~22~~21 and ~~23~~22, wherein the atomic ratio between the aluminium (in the co-catalyst) and titanium (in the solid catalysts) ranges from 5:1 to 1000:1, preferably from 20:1 to 500:1.

~~25~~24. 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 according to any of the previous claims from ~~21~~20 to ~~24~~23.

~~26~~25. The (co)polymerization process according to claim ~~25~~24, wherein at least one α-olefin is ethylene.

~~27~~26. The (co)polymerization process according to one of the claims ~~25~~24 or ~~26~~25, wherein ethylene is polymerized to give linear polyethylene or α-olefins having from 3 to 10 carbon atoms are co-polymerized.

~~28~~27. The (co)polymerization process according to any of the previous claims from ~~25~~24 to ~~27~~26, characterized in that it is effected in a solution of an inert solvent, at temperatures ranging from 130 to 300°C and pressures ranging from 1 to 25 MPa.

~~29~~28. The (co)polymerization process according to any of the previous claims from ~~25~~24 to ~~28~~27, wherein said

inert solvent is selected from aliphatic or cyclo-aliphatic

hydrocarbons having from 6 to 10 carbon atoms.

~~30~~29. The (co)polymerization process according to any of the previous claims from ~~25~~24 to ~~29~~28, wherein the polymerization temperature ranges from 150 to 250°C.