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(54) **Preparation of silica-or alu-
minina-supported polymerization
catalysts**

(57) An olefin polymerization and copolymerization catalyst which is active in the presence of an alkyl aluminium cocatalyst is prepared by reacting, in the presence of a solvent, particles of a silica or aluminium material having reactive surface groups which has been treated with a fluorine compound, with a compound or complex of the formula $(MgR_2)_m(AIR'_3)_n$ or MgR_2 , where R and R' are alkyl or aryl groups and m/n is from 0.5 to 10, to form a hydrocarbon insoluble reaction product which is then reacted in the presence of a solvent, with a titanium, vanadium or zirconium halide, oxyhalide or alkoxyhalide. Such catalysts are used to polymerize or copolymerize 1-olefin(s) in

the presence of an alkyl aluminium cocatalyst.

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SPECIFICATION

Olefin polymerization catalyst and the production and use thereof

- 5 This invention is concerned with a method of preparing an olefin polymerization and copolymerization catalyst which is active in the presence of an alkyl aluminium cocatalyst, with the catalyst so prepared, and with the use of the catalyst to effect the polymerisation or copolymerization of 1-olefins. The invention is more specifically concerned with olefin polymerization catalysts of this kind which are supported on silica and/or aluminium particles. 5
- 10 Our British Specification 2055859A describes a method of preparing an olefin polymerization catalyst which is active in the presence of an alkyl aluminium cocatalyst, which comprises 10
- (a) reacting dry particles comprising silica, alumina or silica-alumina having active surface hydroxyl or oxide groups in the presence of a hydrocarbon liquid with a complex of the formula $(MgR_2)_m(AIR'_3)_n$, in which R and R' are alkyl groups and m/n is from 0.5 to 10, so as to form a 15 reaction product which is insoluble in the hydrocarbon liquid, 15
- (b) reacting the reaction product in the presence of said hydrocarbon liquid with a halide, oxyhalide or alkoxyhalide of titanium, vanadium or zirconium, and
- (c) evaporating the hydrocarbon liquid from the final reaction product.
- Four prior art patents describe catalysts made with an organomagnesium compound and 20 silica: U.S. Patent 3,821,186, British Specification 1,484,154, U.S. Patent 3,787,384 and U.S. Patent 4,148,754. 20
- Fluorinated supports for olefin polymerization catalysts are described in U.S. Patents 3,936,431 and 3,987,031. In U.S. Patent 3,936,431, the support is a complex oxide having the formula $MgO.Al_2O_3$, and after reaction with the fluorinating agent, the F/Al ratio must be 25 from 0.1 to 0.15. In U.S. Patent 3,978,031, the support is alumina, which acquires a F/Al ratio of 0.01 to 0.30 by the fluorination reaction. The use of silica itself is not disclosed in either of these patents. 25
- In addition, neither discloses contacting the fluorinated support with an organomagnesium compound before contact with the titanium compound as in one aspect of the present invention.
- 30 These two patents disclose the use of organomagnesium compounds as cocatalyst, but for no other purpose. 30
- U.S. Patent 3,513,150 describes treating gamma-alumina with gaseous titanium tetrachloride and then a gas containing a chlorinating agent, for the purpose of making an olefin polymerization catalyst.
- 35 U.S. Patent 3,888,789 describes treating a high surface area oxide with a halogenating agent X_2 or RX_n , where X is preferably chlorine or bromine, and R is SO, SO_2 or a hydrocarbon radical. 35
- In U.S. Patent 4,144,390, a magnesium alkoxide or phenoxide is treated with a halogenating agent as a first step in catalyst preparation.
- We have now found that by fluorinating particles of silica and/or alumina with simultaneous 40 or subsequent heat treatment at a temperature of 50° to 700°C, supported catalysts prepared otherwise as described in our British Specification 2055859A are rendered more reactive at titanium levels of less than about 6% by weight. It is thus possible to prepare catalysts of this kind with equivalent reactivity, but with a reduced titanium content. 40
- We have further found that instead of using a complex of a dialkyl magnesium compound 45 with trialkyl aluminium as the organomagnesium compound, as described in said British Specification 2055859A, it is also possible to use an uncomplexed dialkyl magnesium compound. 45
- According to the present invention, therefore, there is provided a method of preparing an olefin polymerization and copolymerization catalyst which is active in the presence of an alkyl 50 aluminium cocatalyst, which method comprises: 50
- (a) treating particles of silica and/or alumina with a fluorine compound with simultaneous or subsequent heating to a temperature of from 50°C to 700°C so as to complete the reaction and expel by-products,
- (b) reacting the particles from step (a) in the presence of a hydrocarbon solvent with a 55 compound or complex of the formula $(MgR_2)_m(AIR'_3)_n$ or MgR_2 , wherein R and R' are alkyl groups and m/n is from 0.5 to 10, so as to obtain a reaction mixture containing a first reaction product which is insoluble in the hydrocarbon solvent, and 55
- (c) reacting the first reaction product in the reaction mixture from step (b) with a halogen-containing transition metal compound to form a second reaction product, the transition metal 60 compound having the formula $Tr(OR'')_aX_{4-a}$ or $TrOX_3$, wherein Tr is a transition metal selected from titanium, vanadium, and zirconium, R'' is an alkyl group having 1-20 carbon atoms, X is a halogen atom, and a is zero or an integer less than 4. 60
- The present invention also comprises an olefin polymerization and copolymerization catalyst prepared by the method according to the invention, and a method of polymerizing or 65 copolymerizing 1-olefins using this catalyst and an alkyl aluminium cocatalyst. 65

The catalyst of this invention is highly active and is suitable for polymerization of ethylene and other 1-olefins, particularly of 2–8 carbon atoms, such as propylene, butene and hexene, for example, to form copolymers of low- and medium-densities. It is equally well suited for particle form and gas phase polymerization processes and is particularly effective in the selective
5 production of high-density polyethylene having a narrow molecular weight distribution and high melt index for injection moulding applications. The catalyst is also well suited for the production of high-strength fibres or film having a low melt index. 5

The catalyst does not require an excess of titanium and therefore obviates the need for removal of catalyst residues from product polymer. The catalyst is suitable for use in particle
10 form polymerization plants designed for conventional silica-supported chromium oxide catalysts. Heretofore, titanium catalysts have not been extensively used in such plants due to the substantial excess of corrosive titanium compounds typically used in the preparation of such catalysts. The present catalyst is readily injected into particle form reactors using conventional automatic feeding valves and corrosion-resistant construction materials are not required. 10

The inorganic oxide material used is silica, alumina or silica-alumina. The inorganic oxide may
15 contain small amounts of other metal oxides, such as magnesia, titania, zirconia and thoria. The inorganic oxide material is utilized in finely divided form and may be preactivated by heating in an inert atmosphere at temperatures of up to about 900°C. 15

The fluorine-treated catalysts of this invention can be further modified with alcohols so that
20 there is a greater response to hydrogen, thereby facilitating the production of very high melt index polyethylene in the particle form process. The fluorine-treated catalysts do not suffer a reactivity loss upon alcohol treatment to the same degree as otherwise similar catalysts which have not been treated with fluorine. 20

The transition metal compound is reacted with the reaction product of the organomagnesium
25 compound and the fluorinated inorganic material, preferably in equimolar ratio, so that the resultant solid catalyst component incorporates substantially all of the titanium in a highly active form. It is therefore unnecessary to remove non-reactive titanium from the catalyst or from product polymer, as opposed to prior titanium catalysts which require excess titanium during preparation. 25

The catalyst is, because of its high activity, equally well suited for use in the particle form
30 polymerization process in which the solid catalyst component, the cocatalyst, and olefin monomer are contacted in a suitable solvent, such as the solvent used in the catalyst forming reaction, or in a gas phase process in which no solvent is necessary. 30

Product polymer melt index (MI) is readily controlled by polymerization temperature control or
35 by hydrogen addition. Due to the high activity of the catalyst, a relatively high partial pressure of hydrogen may be used in order to obtain a high product melt index. The high activity of the catalyst also enables olefins less reactive than ethylene to be copolymerized. 35

The steps of the method according to the invention, and preferred materials and conditions for
40 use therein, will now be described in greater detail. 40

1. The Fluorine Compound Treatment

In general, any fluorine compound which will react with silica or alumina to combine an
effective amount of fluorine is suitable for use with this invention. Examples of gaseous fluorinating agents are F₂, HF, BF₃, SiF₄, SF₄, SOF₂, XeF₂ and COF₂. The treatment of the
45 inorganic oxide particles with gaseous fluorinating agents is preferably conducted in a fluid bed at a temperature and duration adjusted to combine the desired amount of fluorine with the silica or alumina. 45

In most cases, the gaseous fluorinating agents are very reactive. The bed can be fluidized with
nitrogen to which a small amount of the fluorinating agent is added. Examples of liquid
50 fluorinating agents are boron trifluoride etherate, disulfur decafluoride, iodine pentafluoride, diethylamino sulfur trifluoride, and benzyl fluoride. The treatment of the silica or alumina can be done by mixing the liquid with the silica in an inert atmosphere. Any excess of the liquid fluorinating agent can be removed by distillation at normal pressure, or at reduced pressure if needed. Vacuum or heat treatment of the reaction mixture also serves to remove reaction
55 products not chemically combined with the solid oxide. 55

Solutions of fluorinating agents, such as fluoboric acid in water or hydrofluoric acid, can also
be used. In this case, the water must be removed before catalyst preparation. In most cases, it is preferred to use solid fluorinating agents such as ammonium hexafluorotitanate, ammonium hexafluorosilicate, ammonium fluoborate and magnesium fluoborate. These complex salts can be
60 dry mixed with the silica or alumina and the combination can then be heated to above the decomposition temperature of the complex salt to initiate the fluorinating reaction. Among these compounds, ammonium fluoborate is preferred. The heating can be done in a fluidized bed if desired. 60

The solid oxide can vary in particle size, surface area, and pore volume. Porous silicas of
65 different surface areas are very suitable for this invention, for example, Davison Chemical 65

Company grades 952, 951 and 561D. These grades and similar silica materials fluidize readily and are well suited to the fluid bed treatment described above. Very finely divided, nonporous silicas made from silicon tetrachloride can also be used for this invention. These materials are available in several grades with trade-names Aerosil and Cab-O-Sil. Such silicas do not satisfactorily fluidize under normal conditions, consequently for Aerosil and Cab-O-Sil silicas the use of liquid fluorinating agents is preferred. Likewise, the use of liquid fluorinating agents is preferred for very dense silica materials such as the Glas Shot® of the Cataphote Corporation. Diatomaceous silicas can also be used in this invention.

The fluorinating agent reacts primarily with the surface of the silica so that only small changes in the particle size, pore volume, and surface area of the silica result. In this invention, the amount of combined fluorine per unit surface area of the silica must be controlled. After treatment, the silica should contain less than about 2×10^{-4} g of chemically bonded fluorine per square meter of silica surface area. Preferably, the amount of bonded fluorine is 1.2×10^{-4} g to 1.5×10^{-4} g per square meter. In the case of Davison grade 952 silica, the amount of ammonium fluoborate dry mixed with the silica should be less than about 7 wt.%, preferably 4-6 wt.%. In the decomposition of ammonium fluoborate, hydrogen fluoride and boron trifluoride are formed. Both react with silica.

In catalysts where the silica is fluorinated Davison grade 952 silica, the amount of titanium is about 6 wt.% or less of the total catalyst weight. The preferred titanium range is 4-5 wt.%. If other solid oxides of different surface areas are used, the maximum and preferred amounts change in proportion to the surface area.

2. Treatment with a Magnesium Alkyl Compound or Complex

Particles of the inorganic oxide material after their treatment with a fluorine compound and heat treatment are initially reacted with an organomagnesium compound or complex of the general formulas MgR_2 or $(MgR_2)_m(AlR'_3)_n$ in which R and R' are the same or different alkyl groups and the ratio m/n is within the range of about 0.5 to about 10, and preferably between about 2 and 10.

The alkyl groups R bonded to the magnesium atom may be the same or different, and each has between 2 and 12 carbon atoms. When the R groups are identical, it is preferred that each have at least 4 carbon atoms, and are preferably butyl or hexyl groups. The alkyl groups R' are preferably ethyl groups.

The reaction between the magnesium compound and the inorganic oxide particles treated with the fluorine containing compound is carried out in a solvent, preferably at room temperature for convenience. The catalyst-forming reactions may be carried out at higher or lower temperatures, if desired.

The amount of the magnesium-aluminum complex is chosen such that the total number of moles of magnesium and aluminum is between about 0.1 and 10 times the number of moles of transition metal, the amount of which is chosen with reference to the weight of inorganic oxide, as is described below. It is preferred that magnesium be present in equimolar ratio to the transition metal compound.

The magnesium-aluminum complex is known in the art, as disclosed in Aishima et al. 4,004,071 (January 18, 1977) at col. 2, 11. 34-40 and col. 3, 11. 30-36. The complex is readily prepared according to the teachings of Ziegler et al., "Organometallic Compounds XXII: Organomagnesium-Aluminum Complex Compounds", *Annalen der Chemie*, Vol. 605, pages 93-97 (1957).

3. Transition Metal Compound

After the fluorinated inorganic oxide particles are completely reacted with the organomagnesium alkyl compound or complex, a selected halogen-containing transition metal compound is reacted with the resulting hydrocarbon insoluble reaction product to form an active solid catalyst component. The catalyst-forming reaction is carried out in a solvent, preferably a hydrocarbon, and preferably at room temperature.

The transition metal compound is selected from those of the general formula $Tr(OR)_aX_{4-a}$ or $TrOX_3$ wherein Tr is titanium, vanadium or zirconium, R is an alkyl group of less than about 20 carbon atoms, X is a halogen atom and a is zero or an integer less than 4. Suitable transition metal halides include $TiCl_4$, $Ti(OR)Cl_3$, $Ti(OR)_2Cl_2$, $Ti(OR)_3Cl$, $VOCl_3$, VCl_4 , $ZrCl_4$ and others commonly used in conventional Ziegler catalysts.

For optimum reactivity, the transition metal is added to the inorganic oxide-magnesium compound reaction product in equimolar ratio to the total magnesium and aluminum present. For each mole of organo-magnesium compound, the number of moles of transition metal should equal m + n.

The ratio of transition metal compound with respect to the inorganic oxide material may vary over a relatively wide range, although it has been found that the best results are obtained with a transition metal content of between about 0.25 and 2.0 mmoles per mmole of active surface

hydroxyl and oxide groups on the inorganic oxide material. Preferably, between 0.6 and 2.5 mmoles of transition metal compound should be added to the reaction mixture per gram of inorganic oxide material.

5 4. Solvent Removal 5

After formation of the solid catalyst component by reaction of the transition metal compound with the inorganic oxide-magnesium compound reaction product, the solvent present in the catalyst-forming reaction must be removed under an inert atmosphere. For example, solvent removal may be by evaporation at a temperature between about 90°C and 100°C under a nitrogen atmosphere for from about 1/2 to 10 hours, or until dry. If desired, the solvent can be removed by filtration or centrifuging and the catalyst may be subjected to repeated solvent extractions. In this invention, however, simple evaporation is preferred. 10

Solvent removal is necessary to insure that product polymer is formed in small particles suitable for a particle form process rather than in sheets, fibers or chunks which rapidly foul the reactor and decrease reaction efficiency. 15

After solvent removal, the catalyst may advantageously be added to a solvent for reaction therein, as in the particle form polymerization process. The solvent added to the catalyst may be the same solvent used in the catalyst forming reaction, if desired, or may be any other suitable solvent. The catalyst exhibits no loss in activity due to addition to solvent. 20

20 5. Cocatalyst 20

The catalyst prepared as described above is active in the presence of an alkyl aluminum cocatalyst. Trialkyl aluminum compounds such as triisobutyl aluminum (TIBAL) are preferred cocatalysts. The alkyl aluminum compound is fed to the polymerization reaction zone separately from the solid catalyst component. 25

The proportion of cocatalyst to solid catalyst component may be varied, depending on the transition metal concentration in the solid catalyst component. In the case of TIBAL, excellent results have been obtained with as low as 4.6 mmole cocatalyst per gram of solid catalyst component. 30

30 6. Reaction Conditions 30

The particle form reaction system is characterized by the introduction of monomer to an agitated catalyst-solvent slurry. The solvent, typically isobutane, may be the solvent in which the catalyst preparation reaction is carried out. This type of reaction is best carried out in a closed vessel to facilitate pressure and temperature regulation. Pressure may be regulated by the addition of nitrogen and/or hydrogen to the vessel. Addition of the latter is useful for regulation of the molecular weight distribution and average molecular weight of product polymer, as is well known in the art. 35

Particle form polymerization of ethylene with the catalyst of this invention is best carried out at about 105°C to 110°C at a pressure of between 35 and 40 atmospheres. In gas phase polymerization, the temperature may range from less than about 85°C to about 100°C with a pressure as low as about 20 atmospheres. Copolymers may be produced by either process by addition of propylene, butene-1, hexene-1 and similar alpha olefins to the reactor. Production of copolymers of relatively low density is preferably carried out at temperatures from about 60°C to 45 78°C. 45

In the alcohol modification of this catalyst many commonly available alcohols can be used. Primary aliphatic liquid alcohols are preferred, and ethyl alcohol, propyl alcohol, and n-butyl alcohol are the most convenient. The dry alcohol can be combined with the fluorinated silica before or after the solid oxide is reacted with the organomagnesium compound. The molar ratio of alcohol to the organomagnesium compound can be as high as about 10, but generally a ratio of 0.5 to 2.0 is sufficient to effect a desirable increase in melt index by enhancing the transfer reaction with hydrogen. 50

The following examples are given by way of illustration only.

55 Example 1 55

The effect of using ammonium fluoborate as the fluorinating agent was demonstrated in a series of polymerization reactions, all conducted at 215°F in isobutane with 50 psig hydrogen added and ethylene as required to maintain the total pressure at 550 psig. Triisobutyl-aluminum was used as a cocatalyst at 9.2 millimoles per gram of solid catalyst component. The solid catalyst component was prepared from Davison Chemical Company grade 952 silica. 60

Different samples of the silica were dry mixed with different amounts of ammonium fluoborate and the mixtures were heated at 600°C for five hours with nitrogen fluidization. A portion of each silica sample was made into a catalyst as follows. A known weight was added to a dry, N₂-purged flask and stirred under flowing N₂ for one hour or more at room temperature. A solution in heptane of a dibutyl magnesium-triethyl-aluminum complex was then added. The combina- 65

tion was stirred for thirty minutes at room temperature, then titanium tetrachloride in an amount equimolar to the dibutyl magnesium was added. The reaction mixture was stirred for 30 minutes under flowing N_2 , then the solvent was evaporated by heating at 90–95°C. After the solvent was evaporated, portions of the free flowing catalyst were tested as described. The reactivities of the catalyst are shown in the table below. It can be clearly seen that treatment with the fluorinating agent at 2.5 and 5.0 per cent increases the reactivity substantially. However, at 7 per cent the effect of the fluorinating agent is deleterious.

10 TABLE 1

NH ₄ BF ₄ wt.% of Silica	Catalyst Reactivities; g/g of Catalyst per hr. Titanium—Weight Per Cent of Total Catalyst		
	4.2	4.6	6.1
0	1260	1520	4400
1	1160	—	6600
2.5	—	2900	6800
5.0	3700	4700	9900
7.0	Dead	—	3000–5000 (Unstable Catalyst)

Example 2

Another series of catalysts was prepared using Davison 952 silica which had been treated with 2.5 wt.% ammonium fluoborate as described in Example 1. The catalyst preparation procedure was the same as described in Example 1 except that the ratio of dibutyl magnesium to titanium tetrachloride was 0.8, and n-butyl alcohol was added to some of the catalysts. The alcohol was added to the silica just before the addition of the dibutyl magnesium complex solution. After the solvent was evaporated, the catalysts were tested in polymerization reactions at 215°F with 50 and 100 psig of added hydrogen. The results given in Table II show that the melt index of the particle form polyethylene produced increases with increased amounts of n-butyl alcohol. The titanium content of these catalysts was about 5.5 wt.% on a solvent-free basis.

40 TABLE II

{n-BuOH} {Bu ₂ Mg}	H ₂ , psig	Reactivity g/g cat./hr.	Melt Index
0.36	50	2754	1.2
1.0	50	2244	1.6
2.0	50	2187	4.1
0	100	2782	3.6
0.36	100	1154	7.25
1.0	100	1554	12.7
2.0	100	1000	14.7

Example 3

This example shows that the fluorided silica can be treated with the organomagnesium compound before the alcohol modifier is added.

A quantity of Davison Chemical Company grade 952 silica was mixed with a quantity of dry ammonium fluoborate which was 5% of the silica weight. The mixture was heated in a fluidized bed with nitrogen flow for 3 hours at about 600°C. After cooling the fluorided silica was kept dry. A 14.8 g quantity of this was added to a dry flask under flowing nitrogen. After 30 minutes, 62.8 ml of an 8.9 wt.% solution of dibutyl magnesium-triethylaluminum complex in heptane was added. The approximate formula of the complex was $(Bu_2Mg)_{6.1}Et_3Al$. After mixing 4.06 ml of n-butyl alcohol was added dropwise with constant stirring. Following this 40 ml of

hexane was added and the mixture was stirred for 30 minutes. A 2.4 ml volume of titanium tetrachloride was added, and after another 30 minutes of stirring at room temperature under nitrogen flow, the flask was put into an oil bath at 90°C. The flask was kept in the bath until the solvents were evaporated and a free-flowing powder remained.

- 5 A portion of this catalyst was tested in particle form polymerization as described in Example 1. 5
The reactivity was found to be 1520 g/g cat./hr. and the melt index was 2.4.
All parts and percentages herein are by weight.
Abbreviations used herein to identify chemical ingredients and product characteristics include:
- 10 HLMI – high load melt index 10
MI – melt index (ASTM D-1238 52T)
R_p – rheological dispersity
TIBAL – triisobutyl aluminum
- 15 CLAIMS 15
1. A method of preparing an olefin polymerization and copolymerization catalyst which is active in the presence of an alkyl aluminium cocatalyst, which method comprises:
(a) treating particles of silica and/or alumina with a fluorine compound with simultaneous or subsequent heating to a temperature of from 50°C to 700°C so as to complete the reaction and expel by-products, 20
(b) reacting the particles from step (a) in the presence of a hydrocarbon solvent with a compound or complex of the formula (MgR₂)_m(AlR'₃)_n or MgR₂, wherein R and R' are alkyl groups and m/n is from 0.5 to 10, so as to obtain a reaction mixture containing a first reaction product which is insoluble in the hydrocarbon solvent, and
25 (c) reacting the first reaction product in the reaction mixture from step (b) with a halogen-containing transition metal compound to form a second reaction product, the transition metal compound having the formula Tr(OR'')_aX_{4-a} or TrOX₃, wherein Tr is a transition metal selected from titanium, vanadium, and zirconium, R'' is an alkyl group having 1–20 carbon atoms, X is a halogen atom, and a is zero or an integer less than 4.
- 30 2. A method according to claim 1, in which from 0.6 to 5.0 mmoles of the transition metal compound is present per gram of silica and/or alumina. 30
3. A method according to claim 1, in which from 0.25 to 2.0 mmoles of the transition metal compound is present per mmole of active hydroxyl and oxide groups present on the silica and/or alumina.
- 35 4. A method according to any of claims 1 to 3, in which the transition metal compound is added in equimolar ratio to the total magnesium and aluminium present in the first reaction product. 35
5. A method according to any of claims 1 to 4, in which m/n is from 2 to 10.
6. A method according to any of claims 1 to 5, in which the transition metal compound is
40 TiCl₄, Ti(OR'')Cl₃, Ti(OR'')₂Cl₂, Ti(OR'')₃Cl, VOCl₃, VCl₄ or ZrCl₄. 40
7. A method according to any of claims 1 to 6, in which R has from 2 to 12 carbon atoms.
8. A method according to any of claims 1 to 7, in which R is butyl, R' is ethyl, and m/n is about 6.5.
9. A method according to any of claims 1 to 8, in which the fluorine compound is a gaseous
45 fluorinating agent which is reactive with the silica and/or alumina. 45
10. A method according to claim 9, in which the reaction is conducted by fluidizing the silica and/or alumina particles with an inert gas containing an effective amount of the gaseous fluorinating agent at a temperature and for a time sufficient to combine fluorine with the particles.
- 50 11. A method according to any of claim 1 to 10, in which the fluorinated particles obtained in step (a) are treated with a dry alcohol before step (b). 50
12. A method according to any of claims 1 to 10, in which the particles are treated with a dry alcohol after step (b).
13. A method according to claim 11 or 12, in which the alcohol is a liquid primary aliphatic
55 alcohol. 55
14. A method according to any of claims 11 to 13, in which the molar ratio of the alcohol to the organomagnesium compound used in step (b) is up to 10.
15. A method according to claim 14, in which the molar ratio is from 0.5 to 2.0.
16. A method of preparing an olefin polymerization and copolymerization catalyst which is
60 active in the presence of an alkyl aluminium cocatalyst according to claim 1, substantially as herein described in any of the Examples. 60
17. An olefin polymerization and copolymerization catalyst which is active in the presence of an alkyl aluminium cocatalyst, prepared by the method claimed in any of the preceding claims.
18. A method of polymerizing or copolymerizing one or more 1-olefins, which comprises
65 polymerizing the olefin(s) under polymerizing conditions in the presence of a catalyst as claimed 65

in claim 17 and an alkyl aluminium cocatalyst.

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