



(22) Date de dépôt/Filing Date: 1999/04/06

(41) Mise à la disp. pub./Open to Public Insp.: 1999/11/12

(45) Date de délivrance/Issue Date: 2009/06/09

(30) Priorité/Priority: 1998/05/12 (US09/076,560)

(51) Cl.Int./Int.Cl. *C08F 4/646* (2006.01),
C08F 10/00 (2006.01), *C08F 10/02* (2006.01),
C08F 2/34 (2006.01), *C08F 4/02* (2006.01)

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(54) Titre : PROCESSUS DE TRAITEMENT AU MAGNESIUM ET A L'ALUMINIUM POUR LA FABRICATION D'UN
CATALYSEUR

(54) Title: MAGNESIUM ALUMINUM PROCESS FOR MAKING CATALYST

(57) Abrégé/Abstract:

The present invention provides a novel process for preparing a catalyst, preferably free of electron donor, useful in gas phase polymerization of olefins having a broad polydispersity. The catalyst is prepared by contacting a dehydrated silica support with a first alkylaluminum compound, a mixture of a second alkylaluminum compound and an alkylmagnesium compound, an organic chloride, and a source of titanium.



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MAGNESIUM ALUMINUM PROCESS FOR MAKING CATALYST**ABSTRACT OF THE DISCLOSURE**

The present invention provides a novel process for preparing a catalyst, preferably free of electron donor, useful in gas phase polymerization of olefins having a broad polydispersity. The catalyst is prepared by contacting a dehydrated silica support with a first alkylaluminum compound, a mixture of a second alkylaluminum compound and an alkylmagnesium compound, an organic chloride, and a source of titanium.

FIELD OF THE INVENTION

The present invention relates to supported Ziegler-Natta catalysts which are useful in olefin polymerization, and more particularly in the fluidized gas phase polymerization of alpha-olefins.

BACKGROUND OF THE INVENTION

10 Ziegler-Natta type catalysts are well known and have been used since the early 1950's. Generally the catalyst comprises a transition metal compound, typically titanium in the 3 or 4 valence state (e.g. TiCl_3 or TiCl_4) together with at least one activator, typically an aluminum compound such as a trialkyl aluminum (e.g. triethylaluminum (TEAL)) or an alkyl aluminum halide (e.g. diethylaluminum chloride (DEAC)) and the like. The catalysts may contain magnesium chloride which may be generated from a dialkyl
20 magnesium compound and active chloride. Typically, the catalysts are prepared in conjunction with an electron donor which tends to narrow the molecular weight distribution in the resulting polymer. A good description of these types of catalysts is contained in United States Patent 4,302,566 issued November 24, 1981 to Karol et al., assigned to Union Carbide Corporation. Karol teaches that it is essential to use an electron donor in
30 the preparation of the catalyst. The use of an electron donor has been eliminated from the catalysts of the present invention.

United States Patent 5,633,419 issued May 27, 1997 to The Dow Chemical Company discloses a supported Ziegler-Natta type catalyst or catalyst precursor. However, it is a limitation of the reference that the halide is used in the form of a hydrogen halide (e.g. HCl). The reference

teaches away from the subject matter of the present invention which is limited to the use of alkyl halides as the halide source. Additionally, the reference appears to teach the use of a support such as silica, which has been treated either thermally or chemically, but not both, which is contrary
5 to the method for preparing the support of the present invention.

European Patent Application 0 744 416 published November 27, 1996 in the name of BP Chemicals Limited (BP) teaches supported catalysts and catalyst precursors. The reference teaches that the support is reacted with either the aluminum compound or the magnesium
10 compound but not a concurrent treatment with a mixture of aluminum and magnesium (e.g. MAGALATM, a mixture sold by Akzo). The reference teaches against the addition of a second aluminum compound.

Additionally, in view of the examples, the BP patent strongly suggests that an electron donor needs to be used in the preparation of the catalyst, a
15 feature that has been eliminated from the present invention. This reference also teaches that the halogenating agent must be used in a molar ratio such that all of the Mg and Al compounds are converted to their respective halides, a limitation which is not put on the present invention. That is, in accordance with the present invention, there is an excess of
20 aluminum and magnesium over reactive halide so that not all of the aluminum and magnesium is precipitated.

BP patent EP 0 595 574 B1 granted in January 2, 1997 requires that the catalyst be prepared on a support treated with an organosilicon compound. The supports used in accordance with the present invention

are treated thermally and chemically (aluminum alkyls) but not with organosilicon.

BP patent EP 0 453 088 B1 granted in July 31, 1997 teaches that the catalyst be made on dehydrated silica and that the catalyst needs to be pre-polymerized to obtain a useful catalyst for the synthesis of linear low density polyethylene (LLDPE). The catalysts of the present invention
 10 do not need to be pre-polymerized to be useful for the polymerization of ethylene to LLDPE. The patent teaches about washing the catalyst to remove excess Mg compounds which is not relevant to our catalyst. This patent also teaches about the need for high Ti:(Mg+Al) ratios, a restriction which is removed in the present invention.

The present invention seeks to provide a supported Ziegler-Natta
 20 type catalyst which is prepared preferably in the absence of an electron donor, and provides a polymer having a broad molecular weight distribution. The present invention relates to supported Ziegler-Natta catalysts which are useful in olefin polymerization, and more particularly in the fluidized gas phase polymerization of alpha-olefins.

SUMMARY OF THE INVENTION

30 The present invention provides a process conducted in a hydrocarbon solvent at a temperature from 0°C to 100°C for preparing catalyst for the gas phase polymerization of alpha-olefins comprising:

- a. contacting a dehydrated silica support containing from 0.1 to 3 weight % aluminum having the formula $Al^1(R^1)_aX_b$ wherein each R^1 is independently selected from the group consisting of C_{1-10} alkyl

radicals, X is selected from the group consisting of Cl and Br, a and b are 0 or an integer from 1 to 3 provided the sum of $a+b=3$; with

- b. a mixture of an aluminum compound of the formula $Al^2(R^2)_nX_m$ wherein each R^2 is independently selected from the group consisting of C_{1-10} alkyl radicals, X is selected from the group consisting of Cl and Br, m and n are 0 or an integer from 1 to 3 provided the sum of $n+m=3$, and $Mg(R^3)_2$ wherein each R^3 is independently selected from the group consisting of C_{1-10} alkyl radicals wherein the molar ratio of $Mg:Al^2$ in said mixture is from 0.5:1 to 25:1 to provide from 0.25 to 8.0 weight % of Mg based on the weight of silica used, and contacting the resulting product with;
- c. carbon tetrachloride (CCl_4) or a secondary or tertiary alkyl halide of the formula R^4Cl wherein R^4 is selected from the group consisting of C_{3-6} alkyl radicals to produce a Cl:Mg molar ratio from 1:1 to 8:1 in the resulting product and contacting the resulting product with;
- d. a titanium compound of the formula $Ti(R^5)_y(Cl)_z$ wherein each R^5 is selected from the group consisting of C_{1-10} alkyl radicals and phenyl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical, y and z are 0 or an integer from 1 to 4 and the sum of $y+z=4$ to provide from 0.1 to 1.5 weight % of Ti based on the silica.

In a further embodiment of the present invention in the above process after step d there is added from 0 up to 0.3 mmol of electron donor per g of silica.

The present invention also provides a gas phase process for the polymerization, at a pressure from 10 to 500 psi, of a mixture comprising from 0 to 15 mole % of hydrogen, from 0 to 30 mole % of one or more C₃₋₈ alpha-olefins, from 15 to 100 mole % of ethylene and from 0 to 75 mole % of an inert gas such as N₂, conducted at a temperature from 50°C to 120°C in the presence of a catalyst as described above preferably in the absence of an electron donor.

The present invention further provides a polymer comprising from 0 to 15 mole % of one or more C₃₋₈ alpha-olefins, from 85 to 100 mole % of ethylene having a molecular weight (Mw) greater than 50,000 and a polydispersity (Mw/Mn) from 3.5 to 7 prepared according to the above process.

BEST MODE

The supports useful in accordance with the present invention typically comprise a substrate of alumina or silica having a pendant reactive moiety. The reactive moiety may be a siloxy radical or more typically is a hydroxyl radical. The preferred support is silica or alumina. The support should have a particle size from about 10 to 250 microns, preferably from about 30 to 150 microns. The support should have a large surface area typically greater than about 3 m²/g, preferably greater than about 50 m²/g, most preferably from 100 m²/g to 1,000 m²/g. The support will be porous and will have a pore volume from about 0.3 to 5.0 ml/g, typically from 0.5 to 3.0 ml/g. Supports, which are specifically designed to be an agglomeration of subparticles while useful, are not required.

It is important that the support be dried prior to the initial reaction with an aluminum compound. Generally the support may be heated at a temperature of at least 200°C for up to 24 hours, typically at a temperature from 500°C to 800°C for about 2 to 20 hours. The resulting support will be free of adsorbed water and should have a surface hydroxyl content from about 0.1 to 5 mmol/g of support, preferably from 0.5 to 3 mmol/g.

10 The first aluminum (Al^I) is deposited upon the support by contacting the support, preferably silica, with an anhydrous solution of an aluminum alkyl of the formula $Al^I(R^I)_aX_b$ wherein each R^I is independently selected from the group consisting of C_{1-10} alkyl radicals, preferably C_{1-6} alkyl radicals, X is selected from the group consisting of Cl and Br, preferably Cl and a and b are 0 or an integer from 1-3 provided the sum of $a+b=3$. Most
20 preferably, R^I is selected from the group consisting of methyl, ethyl and butyl radicals. Preferably, b is 0. From a commercial viewpoint, the most available compound is triethylaluminum (TEAL).

 The support is reacted with an aluminum compound such that the amount of aluminum on the support is from about 0.1 to about 3 weight %, preferably from about 0.5 to about 2 weight %, based on the weight of the
30 silica.

 The resulting treated support may then be reacted with the remaining components in the specified order.

 The second component in the catalyst is a mixture of an alkyl aluminum halide and a dialkyl magnesium compound.

The second aluminum component in the catalyst is of the formula $Al^2(R^2)_nX_m$ wherein each R^2 is independently selected from the group consisting of C_{1-10} alkyl radicals, preferably C_{1-6} alkyl radicals, X is selected from the group consisting of Cl and Br, preferably Cl and n and m are 0 or an integer from 1 to 3 provided the sum of $n+m=3$. Most preferably, R^2 is selected from the group consisting of methyl, ethyl and butyl radicals.

10 Preferably, m is 0. The second aluminum compound may be the same or different from the first aluminum compound. The amount of the second aluminum (e.g. Al^2) is such that it will provide from about 0.20 to 4.0 weight % of the catalyst based on the weight of the silica.

The magnesium component in the catalyst will have the formula $Mg(R^3)_2$ wherein each R^3 may be independently selected from the group consisting of C_{1-10} alkyl radicals, preferably C_{1-6} alkyl radicals. More
20 preferably, R^3 is selected from the group consisting of ethyl and butyl radicals. Some suitable magnesium compounds include dibutyl-magnesium and butyl-ethyl-magnesium. The magnesium is used in an amount to provide from 0.25 to 8.0 weight % based on the weight of the silica, preferably from 0.5 to 4.0 weight % based on the weight of the
30 silica. The molar ratio of $Mg:Al^2$ may range from 0.5:1 to 25:1, preferably from 0.5:1 to 16:1.

The halide in the catalyst is provided by CCl_4 or a secondary or tertiary halide of the formula R^4Cl wherein R^4 is selected from the group consisting of C_{3-6} alkyl radicals. Suitable chlorides include sec-butyl chloride, t-butyl chloride and sec-propyl chloride. The halide is added to

the support in a quantity of 2 to 30 weight %, preferably from 5 to 20 weight % based on the weight of the silica. The Cl:Mg molar ratio from 1:1 to 8:1, preferably from 1.5:1 to 6:1.

The titanium in the catalyst is provided by a compound of the formula $Ti(R^5)_yCl_z$ wherein each R^5 is independently selected from the group consisting of C_{1-10} alkyl radicals and phenyl radicals which are unsubstituted or substituted by a C_{1-4} alkyl radical, and y and z are 0 or an integer from 1 to 4 provided that the sum of $y+z=4$. Preferably, R^5 is selected from the group consisting of C_{2-6} alkyl radicals and phenyl and benzyl radicals. The titanium compound is added in an amount to provide from 0.1 to 1.5 weight % of titanium based on the weight of the silica. Preferably, the titanium is present in an amount from 0.25 to 1.0 weight % based on the weight of the silica. In one embodiment of the invention, y is 0.

The catalysts of the present invention will have: a molar ratio of total aluminum (Al^1+Al^2):Mg from 0.1:1 to 3:1, preferably from 0.4 to 3:1; preferably a molar ratio of halide (Cl) to $2Mg+3(Al^1+Al^2)$ from 0.25:1 to 4:1; an amount of organic halide from 0.2 to 5 mmol per g of silica; an amount of Mg from 0.1 to 3.5 mmol per g of silica; a total amount of aluminum to provide from 0.3 to 3.0 mmol of aluminum per g of silica; a molar ratio of titanium to aluminum and magnesium (e.g. $Ti:(Al+Mg)$) from 0.01:1 to 0.15:1 preferably from 0.02:1 to 0.085:1; an amount of Ti to provide from 0.02 to 0.32 mmol of Ti per g of silica; a molar ratio of Ti:Mg from 0.04:1 to 0.4:1.

The process to prepare the catalyst may be conducted at temperatures from 0°C to 100°C, typically at temperatures from 5°C to 80°C. The individual components (e.g. silica comprising aluminum compound, magnesium compound, second aluminum compound, halide (chloride) compound and titanium compound) are suspended or dissolved in a hydrocarbon medium. The solvent used in the preparation of the catalyst is an inert C₅₋₁₀ hydrocarbon which may be unsubstituted or substituted by a C₁₋₄ alkyl radical, such as a hydrocarbon that is inert with respect to the catalyst. Such solvents are known and include for example: pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha.

After each addition of a compound to the support, the resulting product may or may not be isolated. For example, the solvent is removed at least once prior to step d, and after step d. Thus, the two extreme cases are: the reactants may be reacted individually in sequence with drying between each reaction, or the reactants may be reacted in sequence with drying only after the last step. The catalyst obtained from the latter process tends to produce a polymer having a more rubbery or waxy feel than the polymer prepared using the same composition but with drying between each step. It is believed that the rubbery or waxy nature of the polymer reflects the amount of low molecular weight material (or "tail", i.e. polymer having a molecular weight (Mw) of less than about 15,000) in the polymer. The increase in the amount of low molecular weight material in a polymer affects the polydispersity. In a typical gas

phase polymerization, the low molecular weight portion of polymer tends to have more comonomer.

10 The drying steps may be conducted in a number of different manners. The drying step or steps may be conducted by maintaining the reactants at a temperature from 5°C to 80°C, preferably from 30°C to 80°C, by passing or purging a dry inert gas such as nitrogen through the reactants. The drying may also be conducted at a reduced pressure under vacuum at a temperature from 10°C to 80°C and at a pressure from 0.1 to 500 mm Hg (torr), preferably less than 400 torr (66.65 kPa, preferably less than 53.33 kPa).

20 The catalyst is recovered as a free flowing powder. The catalyst is then used in combination with a cocatalyst, typically an aluminum compound such as an aluminum alkyl, in the gas phase polymerization of a gaseous mixture comprising from 0 to 15 mole % of hydrogen, from 0 to 30 mole % of one or more C₃₋₈ alpha-olefins, from 15 to 100 mole % of ethylene, and from 0-75 mole % of an inert gas at a temperature from 50°C to 120°C, preferably from 75°C to about 110°C, and at pressures typically not exceeding 3447 kPa (about 500 psi), preferably not greater than 2414 kPa (about 350 psi). Preferably, the catalyst is used in the
30 absence of an electron donor. If present the electron donor may be used in amounts from 0 up to 0.3 mmol per g of silica. Suitable electron donors are well known to those skilled in the art and include tetrahydrofuran (THF), dimethyl formamide (DMF), ethyl acetate, methyl isobutyl ketone and the like.

The catalyst may be used in a fluidized bed gas phase reactor or in a stirred bed gas phase reactor. These processes are well known to those skilled in the art. A broad general description of these types of processes is set out in the paper "Gas Phase Ethylene Polymerization: Production Processes, Polymer Properties, and Reactor Modeling", by Tuyu Xie, Kim B. McAuley, James C. C. Hsu, and David W. Bacon, Ind. Eng. Chem. Res., 1994, 33, 449-479.

Generally, a monomer feed comprising at least ethylene and one or more C_{3-6} alpha-olefins is fed to a gas phase fluidized bed or stirred bed reactor. The monomer mixture optionally together with hydrogen and/or an inert gas are fed to the fluidized bed. In a fluidized bed reactor, the velocity of the gas is sufficient to suspend the bed in the fluid flow of monomer and other components. In a stirred bed reactor mechanical agitation serves to help suspend the bed. Generally a fluid bed reactor is vertical and a stirred bed reactor is horizontal. Concurrently with the monomers a cocatalyst and a supported catalyst are fed to the bed. The monomer passing over the catalyst polymerizes on the catalyst and in the pores of the catalyst causing the particle to increase in size and to break. The resulting particle of polymer on catalyst grows as it resides in the catalyst bed. In a stirred tank reactor the bed is stirred to a discharge section and leaves the reactor. In a fluidized bed the reactor typically has a narrower section to keep the fluid velocity sufficiently high to fluidize the bed. There is an expanded zone at the top of the reactor to reduce the speed of the gas passing through the reactor so the polymer/catalyst

particles fall back into the bed. The discharge is from the bed zone in the reactor.

In both the fluidized bed and stirred bed the polymer particles removed from the reactor are degassed to remove any volatile material
5 and the resulting polymer (with entrained catalyst) may then be further treated (e.g. stabilizers added and pelletized if necessary).

Typically the resulting polymer will comprise from 85 to 100 mole % of ethylene and from 0 to 15 mole % of one or more C₃₋₆ alpha-olefins. The polymer should have a molecular weight (weight average Mw) greater
10 than 50,000. The polymers prepared according to the present invention will have a polydispersity (Mw/Mn) from 3.5 to 7, preferably from 3.75 to 6.

The polymers may be compounded with the usual additives such as heat and light stabilizers (typically hindered phenol type stabilizers such as those sold by Ciba Geigy) and ultraviolet light stabilizers (such as the
15 hindered amine stabilizers sometimes referred to as HALS also sold by Ciba Geigy), processing aids such as the fluoroelastomers optionally in combination with waxes such as low molecular weight esters of polyethylene glycol (i.e. CarbowaxTM) as sold by 3M[®] and by DuPont[®].

The resulting polymers, depending on polymer properties, may be
20 used in a number of applications such as film, injection molding and rotomolding.

The present invention will now be illustrated by the following non-limiting examples.

Catalyst Synthesis

Support Preparation

Silica (200 g) was pre-dried at 150°C for a day prior to heating it to 200°C under a flow of air for 2 hours. After this time the air was turned off and nitrogen was slowly passed over the silica and the temperature was increased to 600°C for 6 hours. The oven was then turned off and the silica was allowed to cool to room temperature. The silica was then transferred to a reaction vessel and hexane (1 L) was added. With stirring, triethylaluminum (TEAL) (71.4 mL of a 25 weight % TEAL in n-hexane) was added over 10 minutes at room temperature. After stirring the slurry for 15 minutes at room temperature the solvent was removed under vacuum. After the silica reached a free-flowing state, it was dried thoroughly under a high vacuum (0.1 mm of Hg) at 60°C for 2 hours.

Catalyst Preparation

To a slurry of a prepared support (50 g) in pentane (300 mL) at 0°C was added MAGALA (81.2 g, 1.75 weight % Mg, 0.24 weight % Al in heptane) over 10 minutes. After the addition was complete, the cold bath was removed and the reaction mixture was stirred for 2 hours. After this time the solvent was removed at 45°C under a stream of dry, purified nitrogen. This procedure was repeated sequentially for the addition of t-butyl chloride (10.8 g diluted with 30 mL pentane) and finally TiCl₄ (1.4 g in 10 mL of pentane). After drying, the catalyst was stored in a glove box.

Polymerization of the Above Catalyst

In a 75 L stirred bed catalytic reactor at 88°C containing hydrogen, nitrogen, ethylene and hexene (as described in Table 1) the above catalyst was added at a rate of 0.40 g per hour. The Al, in the cocatalyst (TEAL):Ti ratio was maintained at approximately 40:1. Under these conditions an LLPDE was formed whose properties are shown in Table 1.

10

TABLE 1

C ₆ H ₁₂ /C ₂ H ₄ molar flow ratio	0.078
H ₂ /C ₂ H ₄ molar gas ratio	0.071
Nitrogen (mole %)	53.4
Activity (kg PE/g cat)	4.7
MI _{2.16}	0.69
MFR	36.7
Density (g/cc)	0.9191
Bulk density (lb/ft ³)	25.6

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Comparative Example

For comparative purposes the following catalyst was prepared. To a slurry of a prepared support (15 g) in pentane (150 mL) at 0°C was added dibutyl magnesium (Bu₂Mg) (17.7 mL, 1 M Bu₂Mg in heptane, 0.0177 mol) over 10 minutes. After the addition was complete, the cold bath was removed and the reaction mixture was stirred for 2 hours. After this time the solvent was removed at room temperature under vacuum. This procedure was repeated sequentially for the addition of t-butyl chloride (3.0 g diluted with 30 mL pentane, 0.0324 mol) and finally titanium

30

isopropoxide [Ti(i-PrO)₄] (0.62 g in 10 mL of pentane, 0.0022 mol). After drying, the catalyst was stored in a glove box.

In a 75 L stirred bed catalytic reactor at 88°C containing hydrogen, nitrogen, ethylene and hexene (as described in Table 2), the above catalyst was added at a rate of 0.67 g per hour. The Al, in the cocatalyst (TEAL):Ti ratio was maintained at approximately 40:1. Under these conditions an LLPDE was formed whose properties are shown in Table 2.

TABLE 2

C ₆ H ₁₂ /C ₂ H ₄ molar flow ratio	0.077
H ₂ /C ₂ H ₄ molar gas ratio	0.084
Nitrogen (mole %)	52.9
Activity (kg PE/g cat)	1.4
MI _{2.16}	0.45
MFR	32.9
Density (g/cc)	0.9268
Bulk density (lb/ft ³)	25.0

As is shown in the above examples, the catalyst of the present invention is more active (4.7 versus 1.4 kg PE/g cat) than the one based on Ti(i-PrO)₄. The catalyst of the present invention also produces a broader melt flow ratio [MFR] (36.7 versus 32.9), is more efficient in incorporating hexene (δ of 0.9191 with a C₆H₁₂/C₂H₄ ratio of 0.078 versus δ of 0.9268 with a C₆H₁₂/C₂H₄ ratio of 0.077) and has a better hydrogen response (MI 0.69 versus 0.45).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process conducted in a hydrocarbon solvent at a temperature from 0°C to 100°C for preparing a catalyst which is not prepolymerized for the gas phase polymerization of alpha-olefins comprising:
 - a. contacting a dehydrated silica support comprising from 0.1 to 3 weight % of Al, the source of aluminum being an aluminum compound of the formula $Al^1R^1_3$ wherein each R^1 is independently selected from the group consisting of methyl, ethyl and butyl radicals with;
 - b. a mixture of an aluminum compound of the formula $Al^2R^2_3$ wherein each R^2 is independently selected from the group consisting of methyl, ethyl and butyl radicals, and $Mg(R^3)_2$ wherein each R^3 is independently selected from the group consisting of ethyl and butyl radicals wherein the molar ratio of $Mg:Al^2$ in said mixture is from 0.5:1 to 16:1 to provide from 0.5 to 4.0 weight % of Mg based on the weight of the silica, on the resulting product; and contacting the resulting product with;
 - c. CCl_4 or a secondary or tertiary alkyl halide of the formula R^4Cl wherein R^4 is selected from the group consisting of C_{3-6} alkyl radicals to provide a molar ratio of $Cl:Mg$ from 1.5:1 to 6:1 in the resulting product; and contacting the resulting product with;
 - d. a titanium compound of the formula $Ti(R^5)_y(Cl)_z$ wherein each R^5 is selected from the group consisting of C_{2-6} alkyl radicals and benzyl and phenyl radicals, y and z are 0 or an integer from 1 to 4 provided

that the sum of $y+z=4$, to provide from 0.25 to 1.0 weight % of Ti based on the silica,

wherein said catalyst has a ratio, $(Al^1 + Al^2):Mg$ of from 0.1:1 to 3:1, an amount of organic halide from 0.2 to 5 mmol per g of silica, a total amount
5 of aluminum of from 0.3 to 3.0 mmol of aluminum per g of silica, and a molar ratio of Ti:Mg from 0.04:1 to 0.4:1.

2. The process according to claim 1, wherein y is 0.

10 3. The process according to claim 1, conducted in one reactor at a temperature from 5°C to 80°C with the removal of the solvent after step d at a temperature from 5°C to 80°C.

4. The process according to claim 3, wherein the removal of solvent is
15 conducted under vacuum from 0.1 to 500 mm of Hg at a temperature from 10°C to 80°C.

5. The process according to claim 3, wherein the removal of solvent is conducted at a temperature from 30°C to 80°C by passing a stream of
20 inert gas through said solvent.

6. The process according to claim 1, conducted in one reactor wherein the solvent is removed at least once prior to carrying out step d, and at least once after carrying out step d.

7. The process according to claim 6, wherein the removal of solvent is conducted under vacuum from 0.1 to 500 mm Hg at a temperature from 10°C to 80°C.
- 5 8. The process according to claim 6, wherein the removal of solvent is conducted at a temperature from 30°C to 80°C by passing a stream of inert gas through said solvent.
9. The process according to claim 2, conducted in one reactor wherein
10 the solvent is removed at least once prior to carrying out step d, and at least once after carrying out step d.
10. The process according to claim 1, further including adding after step d from 0 up to 0.3 mmol of an electron donor per g. of silica.