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(54) Catalysts for polymerizing α-olefins

(57) A catalyst for polymerization of α-olefins is obtained by reacting a trivalent metal halide with a hydroxide, an oxide, a carbonate of a divalent metal, a double compound containing any of these compounds or a hydrate of a compound containing a divalent metal, thereby to produce a solid product (I); reacting the solid product (I) with one or more electron donor compounds and one or more electron acceptor compounds separately or simultaneously and each in from one to ten steps but using $TiCl_4$ as an acceptor at least in one step, thereby to obtain a solid product (II); and then combining an organoaluminium compound and an electron donor with the solid product (II). The catalyst permits control of the molecular weight distribution to a narrower range, and can give a higher yield and a higher crystallinity of polymer product.

SPECIFICATION

Catalysts for polymerizing α-olefins

This invention relates to catalytic processes for producing α-olefin polymers, to catalysts for use in such polymerization, and to methods for producing the catalysts.

In particular, the invention is concerned with catalysts for the production of α-olefin polymers having a narrow molecular weight distribution and a high crystallinity, and in high yield.

The α-olefin polymerizations and α-olefin polymers to which the present invention relates include not only homopolymerizations and homopolymers of α-olefins but also copolymerizations and copolymers with other α-olefin copolymerizable monomers.

Various α-olefin polymerization processes have been proposed in which an electron-donor is used as one component of the catalyst. For example, there are those processes in which an electron donor is added as one component to a component such as $MgCl_2$ (anhydrous), a solid containing Mg—Cl bond, magnesium carbonate, an oxide or a hydroxide of a metal of the II or VIII group of the periodic table or the like as a carrier.

We ourselves have developed catalysts for polymerizing ethylene or α-olefins including ethylene. Our catalysts have a transition metal compound carried, in one of various ways, on a solid product obtained by reacting a trivalent metal halide with a divalent metal compound.

For example, we have put forward (1) a method in which a transition metal compound is reacted with the above-mentioned solid product in the presence of an aromatic compound (Japanese patent publication Nos. 10849 of 1972, 13609 of 1972, 16782 of 1974, etc); (2) a method in which a transition metal compound is reacted with a product obtained by reacting the above-mentioned solid product with a polysiloxane or an electron donor (Japanese patent publication No. 13827 of 1977 and Japanese patent application No. 127750 of 1977); (3) a method in which reaction is carried out by adding to the above-mentioned solid product, a polysiloxane or an electron-donor compound and a transition metal compound, either simultaneously or by adding a complex of a polysiloxane with a transition metal compound or a complex of an electron-donor with a transition metal compound (Japanese patent publication No. 21246 of 1978, No. 21247 of 1978, No. 32031 of 1978, etc) and (4) a method in which an electron donor or an electron acceptor is reacted with the above-mentioned solid product in a plurality of steps (Japanese patent application No. 101960 of 1978). We have also proposed a method in which an additive such as a titanium alkoxide, silicone oil, a polyethylene glycol dialkyl ether or the like is added (Japanese patent publication No. 13609 of 1972, No. 13772 of 1972, etc).

We have engaged in research work on the improvement of these prior inventions and have unexpectedly found that superior catalytic effectiveness can be attained if a solid product (II) comprising a reaction product between a trivalent metal halide and a divalent metal compound, an electron donor and an electron acceptor which includes titanium tetrachloride, is used in combination with an organoaluminium compound and an electron donor.

The present invention resides in a method for producing an α-olefin polymerization catalyst, which method comprises reacting a trivalent metal halide (A) with a divalent metal compound (B) which is a hydroxide, an oxide or a carbonate of a divalent metal, a double compound containing such a compound or a hydrate of a compound containing a divalent metal, thereby to produce a solid product (I); reacting the solid product (I) with an electron donor (C) comprising one or more electron donor compounds and with an electron acceptor (D) comprising titanium tetrachloride and one or more other electron acceptor compounds, thereby to produce a solid product (II), the electron donor (C) and electron acceptor (D) being reacted separately or simultaneously with said solid product (I) and in from one to ten steps; and then combining said solid product (II) with an organoaluminium compound (E) and an electron donor (C′).

The catalyst ingredients used in the method of the present invention are as follows:

(A) Trivalent metal halide
(B) Divalent metal compound (a hydroxide, an oxide, a carbonate of a divalent metal, a double compound containing any of these compounds or a hydrate of a compound containing a divalent metal)
(C) An electron donor
(D) An electron acceptor
(E) An organoaluminum compound
(C′) An electron donor

Preferred methods for preparing the catalyst of the present invention will now be described:

The solid product (I) is obtained by reacting a trivalent metal halide (A) with a divalent metal compound (B).

The trivalent metal halide (A) is suitably aluminium trichloride (anhydrous), aluminium tribromide (anhydrous), ferric trichloride (anhydrous), etc.

Preferred divalent metal compounds (B) include hydroxides such as $Mg(OH)_2$, $Ca(OH)_2$, $Zn(OH)_2$ $Mn(OH)_2$ and the like; oxides such as MgO, CaO, ZnO, MnO and the like; double oxides containing a divalent metal oxide such as $MgAl_2O_4$, Mg_2SiO_4, Mg_6MnO_8 and the like; divalent metal carbonates and double carbonates containing a divalent metal carbonate such as $MgCO_3$, $MnCO_3$ and $MgCO_3.CaCO_3$; hydrates of halides such as $SnCl_2.2H_2O$, $MgCl_2.nH_2O$ ($n = 1$ to 6), $NiCl_2.6H_2O$, $MnCl_2.4H_2O$, $KMgCl_3.6H_2O$; hydrates of double compounds consisting of a halide and a hydroxide such as $MgCl_2.nMg(OH)_2.mH_2O$ ($n = 1$ to 3, $m = 1$ to 6); hydrates of a double oxide such as $3\ MgO.2SiO_2.2H_2O$; hydrates of a double compound consisting of a carbonate and a hydroxide such as $3MgCO_3.Mg(OH)_2.3H_2O$; or hydrates of a hydroxide-carbonate containing a divalent metal such as $Mg_6Al_2(OH)_{14}CO_3.4H_2O$. Of these, divalent metal compounds (B) containing magnesium are most preferred.

Convenient methods for producing the solid compounds (I) include (1) a method in which a trivalent metal halide (A) and a divalent metal compound (B) are reacted while being milled in milling apparatus such as a ball mill, a vibrating mill or the like, (2) a method in which a trivalent metal halide (A) and a divalent metal compound (B) are milled and mixed and then reacted on heating; and the like methods. The ratio of the amount of divalent metal compound (B) to trivalent metal halide (A) will usually be 0.1 to 20 mol of divalent metal compound (B) per 1 mol of trivalent metal halide (A). In the case of reaction carried out under milling, it will normally be performed at a temperature in the range from room temperature (about 20°C) to 500°C, for a time of 5 to 100 hours for a ball mill and 10 minutes to 50 hours for a vibrating mill. In the case of heating after milling, milling is normally carried out for 5 to 100 hours for a ball mill and 10 minutes to 50 hours for a vibrating mill and then heating is carried out at a temperature from room temperature to 500°C for 10 minutes to 50 hours. The solid product thus obtained is a solid product (I).

The solid product (I) is then reacted with an electron donor (C) and an electron acceptor (D).

The electron donor compounds used in the present invention include organic compounds containing oxygen, nitrogen, sulphur or phosphorus.

Suitable electron donor compounds include for example ester (of general formula R^1COOR^2, wherein R^1 and R^2 in this and the following formulae are usually hydrocarbyl groups such as alkyl groups, aryl groups or the like); alcohols (R^2OH); ethers (R^1—O—R^2); aldehydes (R^1CHO), fatty acids (R^1COOH); ketones (R^1COR^2); nitriles (R^1CN); amines ($R^1_nNH_{n-3}$ wherein $n = 1, 2$ or 3, and also alcoholamines and cyclic amines); isocyanates (R^1NCO); azo-compounds (R^1—N=N—R^2); phosphines $R^1_nPR^2_{3-n}$ wherein $n = 1, 2$ or 3); phosphites [$P(OR^1)_3$]; phosphinites [$R^1P(OR^2)_2$]; thioethers [$R^1_mSR^2_{2-m}$ wherein $m = 1$ or 2); thioalcohols (R^1SH), and the like. Furthermore, polysiloxanes can also be used as electron donor compounds. Of these examples of electron donors, esters, alcohols, ethers, ketones, phosphines, and polysilxanes are preferred with esters most preferred.

Concrete examples of electron donor compounds include alcohols such as methanol,e thanol, propanol, butanol, pentanol, hexanol, octanol, phenol, cresol, xylenol, ethylphenol, naphthol and the like; ethers such as diethyl ether, di-*n*-propyl ether, di-*n*-butyl ether, di-isoamyl ether, di-*n*-pentyl ether, di-*n*-hexyl ether, di-*n*-octyl ether, di-*i*-octyl ether, ethylene glycol monomethyl ether, diphenyl ether, tetrahydrofuran, anisole, diphenyl ether and the like; esters such as ethyl acetate, butyl formate, amyl acetate, vinyl butyrate, vinyl acetate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl benzoate, 2-ethylhexyl benzoate, methyl toluylate, ethyl toluylate, 2-ethylhexyl toluylate, methyl anisate, ethyl anisate, propyl anisate, ethyl cinnamate, methyl naphthoate, ethyl naphthoate, propyl naphthoate, butyl naphthoate, 2-ethylhexyl naphthoate, ethyl phenylacetate and the like; aldehydes such as acetaldehyde, benzaldehyde and the like; fatty acids such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, tartaric acid, acrylic acid, maleic acid, benzoic acid and the like; ketones such as methyl ethyl ketone, methyl isobutyl ketone, benzophenone and the like; nitriles such as acetonitrile; amines such as methylamine, diethylamine, tributylamine, triethanolamine, pyridine, aniline, dimethylaniline and the like; isocyanates such as phenylisocyanate, toluylisocyanate and the like; azo-compounds such as azobenzene and the like; phosphines such as ethylphosphine, triethylphosphine, tri-*n*-butylphosphine, tri-*n*-octylphosphine, triphenylphosphine and the like; phosphites such as dimethylphosphite, di-*n*-octylphosphite, tri-*n*-butylphosphite, triphenylphosphite; phosphinites such as ethyldiethylphosphinite, ethyldibutylphosphinite, phenyldiphenylphosphinite and the like; thioethers such ad diethyl thioether, diphenyl thioether, methyl phenyl thioether, ethylene sulphide, propylene sulphide and the like; and thioalcohols such as ethylthioalcohol, *n*-propylthioalcohol, thiophenyl and the like.

As polysiloxanes, chain or cyclic siloxane polymers with a chain represented by the general formula $\text{-}\!\!\left[Si(R^3)(R^4)O\right]\!\!\text{-}_p$ (wherein p is from 3 to 10,000; and R^3 and R^4 represent the same or different substituents on silicon) can be used, but especially those polysiloxanes wherein R^1 and R^2 are each one or more of a hydrogen atom, a hydrocarbyl radical such as alkyl, aryl or the like, a halogen atom, an alkoxy group, an aryloxy group, or a carboxylic group, thus including polysiloxanes wherein subchains are connected and distributed in a molecule in various ratios. Polysiloxanes in which each R^3 and R^4 is a hydrocarbyl group are particularly appropriate. As concrete examples, there are alkylsiloxane polymers e.g. a lower polymer such as octamethyltrisiloxane, hexahexylcyclotrisolxane or octaethylcyclotetrasiloxane and alkylsiloxanes such as dimethylpolysiloxane, ethylpolysiloxane, or methylethylpolysiloxane; arylsiloxane polymers such as diphenylpolysiloxane; alkylarylsiloxane polymers such as diphenyloctamethyltetrasiloxane or methylphenylpolysiloxane. Alkylhydrogensiloxane polymers or haloalkylisiloxane polymers or haloarylsiloxane polymers, wherein R^3 is hydrogen or halogen and R^4 is a hydrocarbyl group such as an alkyl, aryl or the like group, can also be mentioned. Further polysiloxanes wherein R^3 and/or R^4 is an alkoxy or an aryloxy group or a fatty acid residue, are also useful. As for the viscosity of the polysiloxane, a value at 25°C in the range of from 10 to 10,000 centistokes, preferably from 10 to 2,000 centistokes, is suitable.

The electron donor compounds can be used in the form of a mixture.

As well as the $TiCl_4$, the electron acceptor compounds for use in the present invention include other halides of elements of the groups III to VIII of the periodic table. For example, $AlCl_3$ (anhydrous), $SiCl_4$, $SnCl_2$, $SnCl_4$, $ZrCl_4$, PCl_3, VCl_4, $SbCl_5$, SCl_2, $MnCl_2$, $FeCl_2$, $NiCl_2$ and the like can be employed. The electron acceptor compounds can also be used in the form of a mixture. Of the electron acceptor compounds, $AlCl_3$ (anhydrous), $SiCl_4$, $SnCl_2$ and $SnCl_4$ are preferred.

When the solid product (I) is reacted with an electron donor compound and/or an electron acceptor compound, a solvent can be used. A solvent can be used also for washing after the reaction. Suitable solvents include hydrocarbons such as *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *i*-octane, *n*-nonane, *n*-decane or the like; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene or the like; and halogenated hydrocarbons such as carbon tetrachloride, chloroform, dichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrabromide, chlorobenzene, orthodichlorobenzene or the like.

The reaction of (I) with electron donor and/or acceptor compounds can be carried out in suspension in the presence or absence of a solvent (hereinafter sometimes referred to as a suspension reaction) or the reaction can be carried out simultaneously with milling by using a mill such as a vibrating mill, ball mill or the like (hereinafter sometimes referred to as a milling reaction). Suspension and milling reactions can be combined.

When more than one electron donor compound is used as electron donor (C), they can be used in the mixed state. For a reaction in which an electron donor is used in more than one step, the electron donor compounds can be used in each step in the mixed state or separately.

In the present invention, titanium tetrachloride, is always used as an electron acceptor compound. When the electron acceptor (D) includes other electron acceptor compounds, they can be used in the form a mixture. Moreover, when the reaction with (D) is carried out in a plurality of steps, electron donor compounds can be used in each step in the form of a mixture or separately.

The reaction with (D) is carried out in one or a plurality of steps, and titanium tetrachloride is used in at least one step. When $TiCl_4$ is being used in a step, it is preferable to use it alone, but it is possible to use a mixture with other electron acceptor compounds, the amount of titanium tetrachloride being 20% by weight or more in the mixture. As such, when titanium tetrachloride is referred to in the following discussion of the reaction involving (D), we include the above-mentioned mixtures as well as titanium tetrachloride alone.

The reaction of solid product (I) with an electron donor (C) with an electron acceptor (D) is performed in up to ten steps. For reaction of (C) or (D) with (I), there should preferably be up to 5 steps. When reaction is carried out in more than 10 steps, the effectiveness attained is less. The steps can use different materials i.e. C_1, C_2 . . ., and D_1, D_2 . . ., or can involve repetition using the same materials. As for the order of addition or reaction of the three substances to be reacted, various kinds could be mentioned, but as some representative examples, the following methods can be given:

(1) As for methods for reacting (C) and (D) with a solid product (I) in respective single steps, there are the following modes:

(1—1) A method in which the three reactants, solid product (I), (C) and (D), are added and reacted in any desired order.

(1—2) A method in which a solid product (I) is reacted with a reaction product between (C) and (D).

(1—3) A method in which (C) is reacted with a solid product (I) and then (D) is reacted.

(2) As for methods in which, when (C) and (D) are reacted with a solid product (I) and either one or both of (C) and (D) are reacted in two or more steps, there are the following modes (where the subscripts indicate generally that the electron donor (C) or the electron acceptor (D) is made up of more than one compound or mixture of compounds, and wherein each subscript identifies a specific component which is a compound or mixture of compounds):

(2—1) A method in which (C) is reacted with a solid product (I) and then (D) is reacted in two steps or more;

(2—2) A method in which (C_1) is reacted with a solid product (I) and then (C_2) and (D) are reacted according to a method (1);

(2—3) A method in which (D_1) is reacted with a solid product (I) and then (C) and (D_2) are reacted according to a method (1);

(2—4) A method in which (C_1) and (D_1) are reacted with a solid product (I) according to a method (1) and then (D_2) is reacted in one or more steps;

(2—5) A method in which coexistent (C_1) and (C_2) are reacted with a solid product (I), or stepwise (C_1) and then (C_2) are reacted with the solid product (I), then (D_1) is reacted and then (D_2) is reacted in one or more steps;

(2—6) A method in which (C_1) is reacted with a solid product (I), (C_2) is reacted, and then (C_3) and

(D) are reacted according to the method (1); and

(2—7) A method in which (C_1) and (D_1) are reacted with a solid product (I) according to a method (1), and then (C_2) and (D_2) are reacted according to a method (1).

Of the reaction modes, the more preferable are (2—1), (2—4) or (2—5). For the modes (2—4) and (2—5), the case where $SiCl_4$ is used as (D_1) and $TiCl_4$ is used as (D_2) is most preferable.

With regard to the reaction state, a milling reaction is most preferable for reacting $SiCl_4$ as (D_1), either singly for the mode (2—5) or together with (C) for the mode (2—4), and a suspension reaction is most preferable for reacting $TiCl_4$ as (D_2). It is best if the number of reaction steps for (D_2) is one or two.

Where the reaction is performed in steps, it is to be noted as a general practice that unreacted compounds or unwanted reaction products are removed at the end of each step after termination of reaction. If the greater part of the material to be removed is in the form of a liquid, either by itself or by virtue of dissolution in a solvent employed in the step, then removal can be effected by a process such as decantation, filtration or evaporation to dryness. Moreover even if no solvent is used in the reaction it may be possible to add a solvent to dissolve the material to be removed, and thereby permit processes such as decantation etc to be used. In such cases, the removal of unreacted compounds or unwanted reaction products is not a strict requirement. Accordingly, if an amount of (C) or (D) used in a reaction is small and unreacted compounds and unwanted products are almost absent or slight, the shift to a next step can be made directly, thus omitting the removal operation. For the mode (1—2), the reaction product between (C) and (D) can be obtained by mixing (C) and (D) and a solid product (I) added even when unreacted products, etc are present.

The amount used in each step of electron donor or electron acceptor at the time of their reaction with a solid product (I) is preferably in the range of 1 to 5,000g per 100g of the solid product (I). Solvent for each step is preferably in the range of 0 to 5,000 ml per 100g of the solid product (I).

As for the reaction conditions, it is preferable that the reaction temperature is in the range of 0 to 500°C, more preferably 20°—200°C. The preferred range of reaction time varies according to the reaction state, e.g. one minute to 10 hours for a reaction carried out in suspension, 5 to 200 hours for reaction in a ball mill and 10 minutes to 50 hours for reaction in a vibrating mill. The reaction product between (C) and (D) in the mode (2—1), can be obtained by mixing them both at a temperature from room temperature (about 20°C) to 150°C for one minute or more.

The product thus obtained by the reaction of (I) with (C) and (D) is referred to as solid product (II).

The solid product (II) is extracted preferably by subjecting reaction liquid to distillation under sub-atmospheric or atmospheric pressure to remove unreacted (C) and (D) or to filtering-off or decantation, followed by washing with a solvent and drying, after completion of reaction. Alternatively, the crude solid product (II) is subjected to repeated washings with a solvent after decantation, and used in the next reaction in the suspension state with added solvent.

The solid product (II) is combined with an organoaluminium compound (E) and an electron donor (C).

The organoaluminium compounds of use in the present invention include trialkylaluminiums such as trimethylaluminium, triethylaluminium, tri-*n*-propylaluminium, tributyaluminium, tri-*i*-butylaluminium, tri-*n*-hexylaluminium, tri-*i*-hexylaluminium, tri-2-methylpentylaluminium, tri-*n*-octylaluminium, tri-*n*-decylaluminium, etc; dialkylaluminium monohalides such as diethylaluminium monochloride, di-*n*-propylaluminium monochloride, di-*i*-butylaluminium monochloride, diethylaluminium monofluoride, diethylaluminium monobromide, diethylaluminium monoiodide, etc.; alkylaluminium dihalides such as ethylaluminium dichloride, *i*-butylaluminium dichloride; alkylaluminium hydrides such as diethylaluminium hydride; and alkylaluminium sesquihalides such as methylaluminium sesquichloride, ethylaluminium sesquichloride. In addition, alkoxyalkylaluminiums such as monoethoxydiethylaluminium, diethoxymonoethylaluminium, etc. can also be used.

The electron donor (C′) to be combined with a solid product (II) can selected from the same compounds as those described in the context of the preparation of the solid product (II) for electron donor (C).

The amounts of organoaluminium compound (E) and electron donor (C′) will be sufficient if (E) is in the range of 50 to 5,000g and (C′) is in the range of 2 to 2,000g per 100g of the solid product (II).

There are various methods for combining (III), (E) and (C). For example, there are methods (1) in which (E), (C′) and solid product (II) are mixed simultaneously; (2) in which (E) and (C′) are mixed and then solid product (II) is added; (3) in which (E) and solid product (II) are mixed and then (C′) is added; (4) in which (C′) and solid product (II) are mixed and then (E) is added; and the like methods. Of these methods, the methods (1), (2) or (3) are preferable. After a mixing or addition, it is possible directly to carry out a next addition or the use as a polymerization catalyst. However, standing with stirring is often carried out before polymerization in order to improve catalyst performance. For the above-mentioned methods, particularly good results are obtained in this case when a method (1) or (2) is being used.

The temperature at the time of the above-mentioned mixing or addition of (E), (C′) and a solid product (II) will be most suitable if it is in the range of 0 to 100°C. The elapse of time from the mixing of two substances till the addition of the remaining substance is preferably in the range of zero seconds (i.e. simultaneous) to 50 hours.

The catalyst thus obtained can be used for producing α-olefin polymers.

The α-olefins applied in the polymerization process of the present invention include ethylene, propylene, butene-1, hexene-1, heptene-1, octene-1, decene-1 and other straight chain monoolefins; 4-methyl-pentene-1, 2-methyl-pentene-1, 3-methyl-butene-1, and other branched chain monolefins; butadiene, isoprene, chloroprene and other diolefins; styrene; and the like. These can be subjected not only to homopolymerizations but also to copolymerization with other α-olefins e.g. propylene with ethylene, butene-1 with ethylene, propylene with butene-1, etc.

The polymerization reaction can be carried out in a hydrocarbon solvent such as *n*-hexane, *n*-heptane, *n*-octane, benzene, toluene or the like. Besides this, it can be carried out in the α-olefin itself e.g. liquefied propylene or liquefied butene-1, without using a solvent. In practice, a polymerization temperature in the range of room temperature (about 20°C) to 200°C, a polymerization pressure in the range of atmospheric (0 Kg/cm^{2}G) to 50 Kg/cm^{2}G, and a time of 5 minutes to 10 hours are usually used. An appropriate amount of hydrogen can be added in order to control the molecular weight during polymerization.

One effect attainable in polymerization processes of the present invention is the fact that the molecular weight distribution can be controlled to be in a narrow range. Namely, as expressed by Mw/Mn wherein Mw is the weight average molecular weight and Mn is the number average molecular weight), the distribution can be controlled to be in the range of 3.5 to 7.0. Accordingly, when a shaped article having an especially small strain is desired in the processing of injection moulding or when characteristic properties which depend upon molecular weight distribution, e.g. flow characteristic properties of molten polymer, impact strength, characteristic properties of torsion, tear, strength, surface gloss, etc are desired to be controlled in a most preferable combination, the present invention shows particular effectiveness.

A second effect of the present invention is the capability of producing polymers of higher crystalinity from α-olefins. For example, in the production of propylene polymer, the crystalline polypropylene (as *n*-hexane-insoluble polymer) can amount to 98%.

While retaining the above-mentioned superior effectiveness, the present invention enables one to obtain a high yield of polymer per solid product (II) or per transition metal. Namely, the yield of α-olefin polymer per solid product (II) is high, and in particular in the polymerization of propylene, it reaches up to 1×10^4 to 2×10^4g of polymer/g of solid product (II) under usual polymerization conditions. Typically, no colouration and no degradation of the physical properties of polymers occur and such adverse effects as rusting of the mould at the time of shaping of polymers are not observed, even if the step of removal of remaining catalyst, i.e. the ash-removal step, is omitted. Further the transition metal is utilized with an extremely higher efficiency and in case of polymerization of propylene, the efficiency reaches up to 1×10^4 to 1×10^6g of polymer/g of transition metal atom.

The following Examples embodying the invention are given by way of illustration but not by way of limitation. Comparative Examples are also given.

EXAMPLE 1

(1) Preparation of solid product (II)

Aluminium trichloride (anhydrous) (130g) and magnesium hydroxide (58g) were reacted while being milled at 250°C for 3 hours in a vibrating mill, whereby reaction occurred with accompaniement of generation of hydrogen chloride gas. After completion of heating, cooling was carried out in nitrogen stream and a solid product (I) was obtained.

Into a vibrating mill, 100 g of the solid product (I) and 22 g of ethyl cinnamate were charged and reacted while being milled at 40°C for 5 hours. Thereafter 35 g of titanium tetrachloride was charged and reaction was carried out while being milled for another 20 hours. After completion of reaction, reaction product was washed twice each with 500 ml portion of n-hexane in a dry box the atmosphere of which had been replaced with nitrogen to obtain dried solid product (II).

(2) Preparation of propylene polymer

After replacement of the atmosphere of a stainless steel reaction tube having an inner volume of 1.5 l with nitrogen, 1 l of n-hexane, 342 mg of triethylaluminum, 45 mg of ethyl anisate and 18 mg of the solid product (II) were charged in this order within a period of one minute. After addition of 75 ml hydrogen, polymerization reaction was carried out under a partial pressure of propylene of 12 Kg/cm^{2}G, at 60°C for 5 hours. After completion of the polymerization reaction, 50 ml of methanol was introduced into the reaction vessel to stop the polymerization reaction. The contents were poured on a Buffner's funnel, rinsed three times each with 500 ml of n-hexane and separated into a n-hexane-insoluble polymer (isotactic polypropylene) and a n-hexane-soluble polymer (atactic polypropylene) each of which was dried to obtain polymers. There were obtained 182 g of isotactic polypropylene and 3.7 g of atactic polypropylene. Polymer yield per 1 g of solid product (II) was 10,111 g of isotactic propylene and isotactic index which is expressed by a following formula was 98.0.

$$\frac{\text{amount of isotactic polymer (g)}}{\text{amount of isotactic polymer (g)} + \text{amount of atactic polymer (g)}} \times 100$$

(3) Measurement of molecular weight distribution

By using a gel permeation chromatographic apparatus (GPC 200 type manufactured by Waters Co., Ltd.) and o-dichlorobenzene as a solvent, a propylene polymer was dissolved and measurement of molecular weight distribution was carried out at a concentration from 0.1 to 0.5%, a temperature of 140°C and a flow velocity of 1 ml/min. (the same procedure was used hereinafter). As the result, $\overline{Mw}/\overline{Mn}$ of propylene polymer obtained in Example 1 was 4.0.

COMPARATIVE EXAMPLE 1

By using the solid product (II) obtained in Example 1, polymerization reaction was carried out as in Example 1 without adding ethyl anisate at the time of polymerization of propylene. The molecular weight distribution was $\overline{Mw}/\overline{Mn} = 8.2$. Other results are summarized in Table 1.

EXAMPLE 2

To 20 g of the solid product (I) obtained in Example 1, 3.7 g of ethyl benzoate was added and reaction was carried out while being milled in a ball mill (diameter 100 mm, inner volume 785 ml, 80 balls having a diameter of 10 mm) at 40°C for 80 hours, thereafter 20 g of the reaction product was suspended in 139 g of titanium tetrachloride, and then reaction was carried out at 60°C for 3 hours. After completion of reaction, the product was filtered off in a dry box, washed three times each with 150 ml portion of n-hexane to obtain a solid product (II). By using said solid product (II), polymerization of propylene was carried out as in Example 1.

EXAMPLE 3

Aluminium trichloride (anhydrous) (60 g) and hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) (20 g) were reacted in a ball mill while being milled and heated at 80°C for 80 hours to obtain a solid product (I).

To 20 g of the solid product (I), 3 g of titanium tetrachloride was added and reacted in a ball mill at 130°C for 30 minutes, then unreacted titanium tetrachloride was removed under reduced pressure, then 2.5 g of a complex of tetrahydrofuran and titanium tetrachloride (2:1) was added and then reaction was carried out while being milled at 50°C for 48 hours to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 4

Aluminium trichloride (anhydrous) (133 g) and magnesium carbonate (98 g) were subjected to milling reaction while being heated in a ball mill at 180°C for 48 hours to obtain a solid product (I). To 20 g of the solid product (I), 5 g of a complex of ethyl phenylacetate and titanium tetrachloride (1:1) were added and milling reaction was carried out in a ball mill at 30°C for 72 hours to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 5

The solid product (I), (20 g) obtained in Example 4, was suspended in 100 ml of toluene and 12 g of methyl p-toluylate was added. After reaction at 100°C for 30 minutes, filtering-off and drying were carried out. Then 20 g of the resulting solid was suspended in 500 g of titanium tetrachloride and reaction was carried out at 120°C for one hour. After completion of reaction, a product was filtered off, washed three times each with 150 ml of n-hexane portion, and dried to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 6

Aluminium trichloride (anhydrous) (120 g) and magnesium oxide (40 g) were reacted while being milled in a vibrating mill at 120°C for 48 hours to obtain a solid product (I). Said solid product (I) (20 g), anisole (10 g) and titanium tetrachloride (100 ml) were added and reacted in the suspension state at 160°C for 2 hours. Thereafter filtering-off, three time washing each with 150 ml n-hexane portions, and drying were applied to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 7

After 20 g of the solid product (I) obtained in Example 6, 3 g of silicon tetrachloride and 3.0 g of ethyl benzoate were reacted while being milled in a ball mill at 40°C for 48 hours, 7 g of titanium tetrachloride was introduced and further milling and reacting were carried out at 40°C for 48 hours. Thereafter washing was carried out three times in a dry box each with 150 ml portion of n-hexane to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 8

Ferric trichloride (anhydrous) (60 g) and aluminum-magnesium oxide ($MgAl_2O_4$) (70 g) were reacted in a vibrating mill at 320°C for 5 hours to obtain a solid product (I).

Said solid product (I) (20 g) was suspended in 180 ml of toluene, 10 g of ethanol was added to the suspension, and after reaction at 30°C for one hour, an operation consisting of addition of 150 ml of toluene and decantation, was repeated twice to turn the total volume to 180 ml by toluene. Then 8 g of benzophenone was added and after reaction at 60°C for 30 minutes, decantation was carried out and 150 ml of toluene was added. After decantation and turning the total volume to 60 ml, 170 g of titanium tetrachloride and 20 ml of di-n-butyl ether were added and reaction was carried out at 130°C for one hour to obtian a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 9

A material (40 g) obtained by heating aluminum trichloride (anhydrous) (60 g) and hydromagnesite ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) at 100°C for 2 hours, was milled and reacted in a vibrating mill at 250°C for one hour to obtain a solid product (I).

Into 200 ml of n-hexane, 20 ml of methylhydrogenpolysiloxane, and 50 g of the above-mentioned solid product (I) were introduced and reacted in the state of suspension at 40°C for one hour. Then the resulting product was filtered off, washed with n-hexane and dried. Resultant dried solid (20 g), methyl p-toluylate (2 g) and titanium tetrachloride (6 g) were charged in a ball mill. After milling reaction was carried out at 80°C for 20 hours, a subatmospheric pressure was held at 80°C for 2 hours to remove unreacted material and to obtain a solid product (II).

Polymerization of propylene was carried out as in Example 1 by using said solid product (II).

EXAMPLE 10

Polymerization of propylene was carried out as in Example 1 except that the solid product (II) obtained in Example 7 was used and 50 mg of methyl p-toluylate was used in place of ethyl anisate.

EXAMPLE 11

Aluminum trichloride (anhydrous) (133 g) and magnesium oxide (40 g) were milled in a ball mill for 24 hours, then heated at 120°C for 2 hours. After cooling, a further milling was carried out for 10 hours to give a solid product (I).

Ethyl benzoate (12 g) and silicon tetrachloride (4.5 g) were mixed and reacted at room temperature (20°C) in advance. Resultant product and 40 g of the solid product (I) were milled and reacted in a ball mill at 35°C for 48 hours. Resultant powdery material (20 g) was suspended in 180 g of titanium tetrachloride. After reaction at 80°C for 2 hours a supernatant liquid was removed by decantation, 180 g of titanium tetrachloride was added and reaction was carried out at 80°C for one hour. After reaction, an operation consisting of addition of 150 ml of n-hexane and removal by decantation was repeated twice and a solid product (II) was obtained by filtering a product off and drying it.

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 12

Cumyl alcohol (2 g) and ethyl benzoate (5 g) were reacted with 20 g of the solid product (I) obtained by the operation same with that of Example 11, while they were milled in a ball mill at 40°C for 48 hours. Then 9 g of silicon tetrachloride was added and subjected to milling reaction in a ball mill for 24 hours. The resultant powdery material (20 g) was suspended in 240 g of titanium tetrachloride and reaction was carried out at 100°C for 2 hours. After reaction, a supernatant liquid was removed by decantation, an operation consisting of adding 150 ml of n-hexane and removal of supernatant liquid was repeated twice and a solid product (II) was obtained by filtering a product off in a dry box and drying it.

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 13

Methyl benzoate (12 g) was reacted with 40 g of the solid product (I) obtained in the operation same with that of Example 11 while they were milled in a ball mill at 30°C for 24 hours. Then 15 g of silicon tetrachloride was added and milling reaction was carried out for another 48 hours to obtain powdery material, 20 g of which was suspended in 350 g of titanium tetrachloride and reaction was carried out at 80°C for 2 hours. The resulting supernatant liquid was removed by decantation, 200 ml of tetrachloroethylene was added and decantation was carried out. Further an operation consisting of adding 200 ml of n-hexane and carrying out decantation was repeated twice and after distilling-off of n-hexane under subatmospheric pressure, a solid product (II) was obtained.

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 14

The solid product (I) (40 g) obtained according to the operation same with that of Example 11 and isopropyl benzoate (16 g) were reacted while being milled in a ball mill at 45°C for 48 hours. Resultant powder (20 g) was suspended in 190 g of titanium tetrachloride and after reaction at 70°C for 4 hours, reaction liquid was removed by filtering-off to give a solid which was suspended again in 220 g of titanium tetrachloride and reacted at 90°C for one hour. The reaction liquid was removed by decantation. After twice repeating an operation consisting of addition of 250 ml n-hexane and decantation, a solid product (II) was obtained by distilling-off n-hexane under reduced pressure.

Polymerization of propylene was carried out as in Example 1 by using the solid product (II).

EXAMPLE 15

The solid product (II) (13 mg) obtained in Example 11, triethylaluminum (230 mg) and methyl p-toluylate (60 mg) were suspended in 500 g of liquefied propylene, 90 ml of hydrogen was added, and polymerization reaction was carried out at a polymerization temperature of 65°C under a pressure of 26.5 Kg/cm^{2}G for 3 hours. After completion of polymerization reaction, remaining propylene was removed to give 148 g of propylene polymer.

The results of Example 1~15 and Comparative example 1 are shown in Table 1. From these results, it can be seen that the method of the present invention is particularly superior in the values of $\overline{Mw}/\overline{Mn}$ and isotactic index.

TABLE 1

Results of Polymerisation of Propylene

	Content of titanium atom (mg/g) in solid product (II)	Polymer yield (g)		Isotactic index	$\overline{Mw}/\overline{Mn}$	MFR*
		per g. solid product (II)	per g.titanium atom			
Example 1	20.8	15,400	7.4×10^5	98.0	4.0	6.8
Comparative example 1	,,	19,200	9.2×10^5	96.0	8.2	5.4
Example 2	22.0	12,400	5.6×10^5	97.1	3.9	6.2
,, 3	35.0	16,700	4.8×10^5	96.9	4.2	6.2
,, 4	27.0	12,800	4.7×10^5	97.5	4.5	5.8
,, 5	30.2	13,200	4.4×10^5	97.0	4.0	5.4
,, 6	32.0	11,800	3.7×10^5	97.2	4.8	4.9
,, 7	28.0	18,100	6.5×10^5	98.0	4.0	4.8
,, 8	22.3	10,900	4.9×10^5	96.9	4.2	7.1
,, 9	29.4	16,500	5.6×10^5	97.5	4.1	6.5
,, 10	20.8	17,100	8.2×10^5	97.0	4.0	6.0
,, 11	19.0	14,800	7.8×10^5	98.0	4.3	6.1
,, 12	22.0	12,400	5.6×10^5	98.1	3.9	5.8
,, 13	16.0	13,200	8.3×10^5	97.1	4.2	4.9
,, 14	18.0	14,300	7.9×10^5	97.3	4.1	3.8
,, 15	19.0	11,380	6.0×10^5	97.0	4.2	6.1

*Melt Flow Rate, according to ASTM D–1238(L).

EXAMPLE 16

Triisobutyl aluminum (430 mg) and isobutyl alcohol (20 mg) were mixed in 1 l of n-hexane and allowed to stand for 10 minutes. The solid product (II) (12 mg) obtained in Example 2 was added and polymerization reaction was carried out under a hydrogen partial pressure of 6 Kg/cm^{2}G and an ethylene partial pressure of 7 Kg/cm^{2}G, at 85°C for 5 hours. The results are shown in Table 2.

EXAMPLE 17

Polymerization reaction of ethylene was carried out as in Example 16 after adding 380 mg of triethylaluminum, 10 mg of dimethylpolysiloxane and 8 mg of the solid product (II) obtained in Example 4 in this order within a period of one minute.

EXAMPLE 18

Polymerization of ethylene was carried out as in Example 16 after simultaneously adding 520 mg of tri-n-octylaluminum, 80 mg tri-n-octylphosphine and 15 mg of the solid product (II) obtained in Example 6.

COMPARATIVE EXAMPLE 2

Polymerization of ethylene was carried out as in Example 18, but without using tri-n-octylphosphine in the operation of Example 18.

EXAMPLE 19

Tri-n-butylaluminum (380 g), diphenyl ether (20 mg) and the solid product (II) (25 mg) obtained in Example 7 were added to a polymerization vessel, and after continuously feeding 480 g of butene-1 at 70°C for 4 hours, polymerization reaction was carried out for 2 hours. After completion of reaction, the solvent was distilled off to obtain 290 g of polybutene.

EXAMPLE 20

Copolymerization of propylene-ethylene was carried out by using the solid product (II) obtained in Example 1.

The solid product (II) obtained in Example 1 (10 mg), of triethylaluminum (420 mg) and ethyl p-toluylate (40 mg) were added to a polymerization vessel, 80 ml of hydrogen was introduced and polymerization reaction was carried out at a partial pressure of propylene of 10 Kg/cm^{2}G for 4 hours and a polymerization temperature of 60°C while ethylene was fed 8 times each in 10 g portion at an interval of 30 minutes. After reaction, propylene-ethylene copolymer was obtained as in Example 1. The yield of polymer per 1 g of the solid product (II) was 14,300 g (polymer) and isotactic index was 94.0.

EXAMPLE 21

Copolymerization of propylene-butene-1 was carried out as in Example 20.

An operation was carried out to copolymerize propylene-butene-1 as in Example 20 except that butene-1 was used in an amount of 20 g in place of ethylene in Example 20. The yield of polymer per 1 g of the solid product (II) was 12,300 g (polymer) and isotactic index was 95.0.

COMPARATIVE EXAMPLE 3

Polymerization of butene-1 was carried out as in Example 19 but without using diphenyl ether, in Example 19.

COMPARATIVE EXAMPLE 4

Copolymerization of propylene-ethylene was carried out as in Example 20 but without using ethyl p-toluylate in Example 20.

COMPARATIVE EXAMPLE 5

Copolymerization of propylene-butene-1 was carried out as in Example 20 but without using ethyl p-toluylate in Example 21.

The results of Examples 16∼21 and Comparative examples 2∼5 are shown in Table 2. Even in case of homopolymerization of α-olefins other than propylene, and copolymerization thereof with propylene, the superiority of the present invention can be noted.

TABLE 2

Results of Preparation of Polymers

	Content of titanium atom (mg/g) in solid product (II)	Polymer yield (g)		Isotactic index	$\overline{M}w/\overline{M}n$	MFR
		per g.solid product (II)	per g.titanium atom			
Example 16	22.0	18,200	8.3×10^5	—	3.6	4.1
,, 17	27.0	16,300	6.0×10^5	—	4.0	4.3
,, 18	32.0	19,400	6.1×10^5	—	3.8	5.2
Comparative example 2	32.0	22,400	7.0×10^5	—	8.0	4.5
Example 19	28.0	11,600	4.1×10^5	—	5.2	
,, 20	20.8	14,300	6.9×10^5	94.0	4.8	5.2
,, 21	,,	12,300	5.9×10^5	95.0	4.9	4.8
Comparative example 3	28.0	13,800	4.9×10^5	—	9.5	
,, 4	20.8	17,400	8.4×10^5	90.0	9.0	4.5
,, 5	20.8	15,300	7.4×10^5	91.0	8.8	6.2

In the specification of our application No. 7914909 of 30th April 1977 we describe the preparation and use of catalysts which are similar to those of the present invention. The reader is referred to this prior specification for further disclosure of techniques and procedures applicable to the present invention.

CLAIMS

1. A method for producing an α-olefin polymerization catalyst, which method comprises reacting a trivalent metal halide (A) with a divalent metal compound (B) which is a hydroxide, an oxide, or a carbonate of a divalent metal, a double compound containing such a compound or a hydrate of a compound containing a divalent metal, thereby to produce a solid product (I); reacting the solid product (I) with an electron donor (C) comprising one or more electron donor compounds and with an electron acceptor (D) comprising titanium tetrachloride and one or more other electron acceptor compounds, thereby to produce a solid product (II), the electron donor (C) and electron acceptor (D) being reacted separately or simultaneously with said solid product (I) and in from one to ten steps; and then combining said solid product (II) with an organoaluminium compound (E) and an electron donor (C').

2. A method according to Claim 1 wherein the solid product (I), the electron donor (C) and the electron acceptor (D) are mixed and reacted in a desired order to obtain the solid product (II).

3. A method according to Claim 1 wherein a reaction product between the electron donor (C) and the electron acceptor (D) is further reacted with the solid product (I) to obtain the solid product (II).

4. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid product (I) first with the electron donor (C) and then with the electron acceptor (D).

5. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid product (I) first with the electron donor (C) and then with the electron acceptor (D) in one or more steps.

6. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid product (I) with an electron donor component (C_1) and then with another electron donor component (C_2) and an electron acceptor (D).

7. A method according to Claim 1 wherein the product (II) is obtained by reacting the solid product (I) with an electron acceptor component (D_1) and then with an electron donor (C) and another electron acceptor component (D_2).

8. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid product (I) with an electron donor (C) and an electron acceptor component (D_1) and then with another electron acceptor component (D_2) in one or more steps.

9. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid compound (I) with two coexistent electron donor components (C_1) and (C_2), then with an electron acceptor component (D_1), and then with another electron acceptor component (D_2) in one or more steps.

10. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid compound (I) with an electron donor component (C_1), then with another electron donor component (C_2), then with an electron acceptor component (D_1), and then with another electron acceptor component (D_2) in one or more steps.

11. A method according to Claim 1 wherein the solid product (II) is obtained by reacting the solid compound (I) with an electron donor component (C_1), then with another electron donor component (C_2), then with another electron donor component (C_3) and with an electron acceptor (D).

12. A method according to any preceding claim wherein the amount of electron donor (C) or electron acceptor (D) reacted in a step with the solid product (I) is 1 to 5,000g per 100g of the solid product (I).

13. A method according to any preceding claim wherein at least one step of the reaction of the solid product (I) with the electron donor (C) and electron acceptor (D) is carried out in 0 to 5000ml of solvent per 100g of the solid product (I).

14. A method according to any preceding claim wherein at least one step of the reaction of the solid product (I) with the electron donor (C) and electron acceptor (D) is carried out at a temperature from 0° to 500°C.

15. A method according to any preceding claim, wherein reaction of the electron acceptor (D) with the solid product (I) is carried out as a milling reaction with $SiCl_4$ as an electron acceptor component (D_1) and then reaction is carried out as a suspension reaction using $TiCl_4$ as electron acceptor component (D_2) in one or more steps.

16. A method according to any preceding claim, wherein an organo-aluminium compound (E) in an amount of 50 to 5,000g and an electron donor (C') in an amount of 2 to 2,000g are combined with 100g of a solid product (II).

17. A method according to any preceding claim wherein organoaluminium compound (E), electron donor (C) and solid product (II) are combined by simultaneous mixing.

18. A method according to any of Claims 1 to 16 wherein organoaluminium compound (E) is mixed with an electron donor (C') and then solid product (II) is added to complete the combination.

19. A method according to any of Claims 1 to 16 wherein organoaluminium compound (E) and solid product (II) are mixed and then electron donor (C') is added to complete the combination.

20. A method according to any preceding claim, wherein the trivalent metal halide (A) is $AlCl_3$ (anhydrous) or $FeCl_3$ (anhydrous).

21. A method according to any preceding claim, wherein the divalent metal compound (B) is MgO, $Mg(OH)_2$, $MgCO_3$, $MgAl_2O_4$ (aluminiummagnesium oxide), $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ (hydrotalcite), $3MgCO_3.Mg(OH)_2.3H_2O$ (hydromagnesite), $3MgO.2SiO_2.2H_2O$ or $Mg_6Al_2(OH)_{14}CO_3.4H_2O$.

22. A method according to any preceding claim wherein the electron donor (C) or (C′) is an ester (R^1COOR^2, wherein R^1 and R^2 are alkyl or aryl having 1 to 20 carbon atoms), an alcohol (R^1OH, wherein R^1 is as defined), an ether (R^1—O—R^2, wherein R^1 and R^2 are as defined) a ketone (R^1COR^2, wherein R^1 and R^2 are as defined), an amine ($R^1_nNH_{n-3}$ wherein $n = 1, 2$ or 3 and R^1 is as defined, or a alcoholamine, or cyclic amine), a phosphine ($R^1_nPR^2_{3-n}$ wherein $n = 1, 2$ or 3 and R^1 and R^2 are as defined) or a polysiloxane ($-\!\!\left[\mathrm{Si}(R^3)(R^4)O\right]\!\!-_p$ wherein R^3 and R^4 are hydrogen, hydrocarbyl, halogen, alkoxy, aryloxy, or fatty acid residue and $p = 3$ to 10,000).

23. A method according to any preceding claim, wherein the electron acceptor (D) includes $AlCl_3$ (anhydrous), $SiCl_4$, $SnCl_2$ or $SnCl_4$.

24. A method according to any preceding claim, wherein the organoaluminium compound (E) is an trialkylaluminium, a dialkylaluminium monohalide, an alkylaluminium dihalide, an alkylaluminium hydride, an alkylaluminium sesquihalide or an alkoxyalkylaluminium.

25. A method for producing an α-olefin catalyst, the method being substantially as hereinbefore described in any of the Examples.

26. A catalyst for producing α-olefin polymers which catalyst is obtained by reacting a trivalent metal halide with a hydroxide, an oxide, a carbonate of a divalent metal, a double compound containing any of these compounds or a hydrate of a compound containing a divalent metal compound, thereby to produce a solid product (I); reacting with said solid product (I) one or more electron donor compounds and one or more electron acceptor compounds in a separate manner or a simultaneous manner and each in one step or in a plurality of up to ten steps, titanium tetrachloride being used as an acceptor compound in at least step, thereby to obtain a solid product (II); and then combining an organoaluminium compound and an electron donor with the solid product (II).

27. A catalyst according to Claim 26 wherein $AlCl_3$ (anhydrous) or $FeCl_3$ (anhydrous) is used as the trivalent metal halide; MgO, $Mg(OH)_2$, $MgCO_3$, $MgAl_2O_4$ (aluminium-magnesium oxide), $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ (hydrotalcite) or $3MgCO_3.Mg(OH)_2.3H_2O$ (hydromagnesite) is used as the divalent metal compound; an ester (R^1COOR^2, wherein R^1 and R^2 are alkyl or aryl having 1 to 20 carbon atoms), an alcohol (R^1OH, wherein R^1 is as defined), an ether (R^1—O—R^2, wherein R^1 and R^2 are as defined), a ketone (R^1COR^2, wherein R^1 and R^2 are as defined), an amine ($R^1_nHN_{n-3}$ wherein $n = 1, 2$ or 3 and R^1 is as defined above) an alcoholamine, a cyclic amine, a phosphine ($R^1_nPR^2_{3-n}$ wherein $n = 1, 2$ or 3 and R^1 is as defined) or a polysiloxane ($-\!\!\left[\mathrm{Si}(R^3)(R^4)O\right]\!\!-_p$ wherein R^3 and R^4 are hydrogen, hydrocarbyl, alkoxy, aryloxy or fatty acid and $p = 3$ to 10,000) is used as an electron donor; $TiCl_4$ and optionally $AlCl_3$ (anhydrous), $SiCl_4$, $SnCl_2$ or $SnCl_4$, is used as the electron acceptor; and a trialkylaluminium, a dialkylaluminium monohalide, an alkylaluminium dihalide, an alkylaluminium hydride, and alkylaluminium sesquihalide or an alkoxalkylaluminium is used as the organoaluminium compound.

28. A process for polymerization of an α-olefin in which a catalyst is employed which is a catalyst produced by a method according to any of Claims 1 to 25 or which is a catalyst as claimed in Claim 26 or 27.

29. A process according to Claim 28 wherein the α-olefin is ethylene, propylene, butene-1, hexene-1, 4-methyl-pentene-1, 2-methyl-pentene-1, or 3-methyl-butene-1.

30. Poly(α-olefin) manufactured by a process as claimed in Claim 28 or 29.

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