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(19)

(54) PROCESS FOR THE POLYMERISATION OF OLEFINS AND CATALYST THEREFOR

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LTD. a Japanese Company of 5—2 Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing a polyolefin. More particularly, it relates to a process for preparing a polyolefin by polymerizing an olenfin such as ethylene, propylene or butene-1, in the presence of a catalyst having high catalytic activity comprising an organoaluminum compound and a carrier supported catalytic component.

Heretofore, it has been proposed to use various carrier supported catalytic components for a polymerization of an olefin. For example, it has been proposed for the polymerization of α-olefins to use a solid catalytic component prepared by reacting a titanium halide on a carrier of a divalent metal hydroxychloride prepared using a divalent metal chloride and an oxide or a hydroxide, as in Japanese Patent Publication Nos. 13050/1968 and 5547/1969. However, when these catalysts are used, the stereospecific properties of the resulting polymers prepared by polymerizing an olefin, especially propylene or butene-1, are remarkably poor and the industrial value is low.

The present invention provides a process for preparing a polyolefin by polymerizing an olefin or a mixture of olefins in the presence of a catalyst system comprising an organoaluminum compound and a titanium-containing solid catalytic component prepared from (a) water and-or an alcohol, (b) a Grignard reagent and (c) a titanium tetrahalide, wherein the titanium-containing component is prepared by contacting the components (a), (b) or (c), or a reaction mixture of two or three of the said components with (d) one or more electron donors selected from amines, carboxylic acid amides, phosphines, phosphine oxides, phosphoric esters, phosphorous esters, phosphoric acid amides, ketones and carboxylic esters.

Using the process of the present invention it is possible to prepare a polyolefin having good stereo-specific properties and a high isotactic index which can be used without separating the catalyst residue because the high activity of the catalyst enables it to be used in small quantities.

The titanium-containing solid catalytic components used in the process of the present invention are prepared by contacting

(a) water and/or an alcohol (hereinafter referred to as the OH compound),
(b) a Grignard reagent,
(c) a titanium tetrahalide and
(d) a specific electron donor.

These components used in the preparation will be further illustrated.

(a) OH compound:

Water can be used in a liquid form by itself. It is preferable to use water by dissolving water in an ether solvent such as diethyl ether, dibutyl ether and tetrahydrofuran. Water can also be used in the form of steam. In this case, steam can be diluted with an inert gas such as nitrogen or argon.

Preferred OH compounds have the formula

$$R(OH)n$$

wherein n represents an integer of 1—6 and R represents a hydrocarbon moiety, preferably a hydrocarbon moiety having 1—35 carbon atoms or the formula

$$-(-CH_2CZ_2O-)_lH$$

wherein Z represents a hydrogen atom or an alkyl group having 1—6 carbon atoms and l represents an integer of 1—30.

The OH compounds include monohydric alcohols and polyhydric alcohols.

Monohydric alcohols include alkyl alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol, octyl alcohol, 2-ethylhexyl alcohol, nonyl alcohol and decyl alcohol; aralkyl alcohols such as benzyl alcohol and alicyclic alcohols such as cyclohexyl alcohol.

Polyhydric alcohols include alkylene glycols such as ethylene glycol, propylene glycol and butylene glycol; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; glycerol and pentaerythritol.

Besides the compound represented above—formula of R(OH)n, hydroxy—containing hydrocarbon polymers whose molecular weight is more than 500 can be used as the OH compound, such as polyvinyl alcohol or hydrolysed ethylene-vinylacetate copolymers.

The compound can be used with or without diluting with a diluent.

Suitable diluents include aromatic hydrocarbons such as benzene and toluene; saturated aliphatic hydrocarbons such as n-heptane or n-hexane, alicyclic hydrocarbons such as cyclohexane or methyl cyclohexane; and ethers such as diethyl ether and dibutyl ether.

It is preferable to use as the OH compound water and monohydric alcohols, especially water and the alkyl alcohols.

(b) Grignard reagents:

Grignard reagents have the formula

$$R^1MgX$$

wherein R^1 represents a hydrocarbon moiety and X represents a halogen atom.

Suitable hydrocarbon moieties R^1 include alkyl, aryl and aralkyl groups which have up to 20, preferably up to 10, carbon atoms, especially alkyl groups such as methyl, ethyl, propyl, butyl, amyl and hexyl groups; aryl groups such as phenyl; and aralkyl groups such as benzyl. Suitable halogen atoms X include chlorine, bromine and iodine atoms.

The Grignard reagent is usually used in an ether solution or an ether adduct. Suitable ethers include diethyl ether, dibutyl ether, dihexyl ether, dioctyl ether, tetrahydrofuran, tetrahydropyran, dioxane and diethyl thioether.

Suitable solvents beside the ether solvents include aromatic hydrocarbons such as benzene and toluene; heterocyclic compounds such as pyridine and thiophene.

(c) Titanium tetrahalides:

The titanium tetrahalides include titanium tetrachloride, tetrabromide and tetraiodide, and it is preferable to use titanium tetrachloride.

(d) Electron donors:

The electron donors are selected from amines, carboxylic acid amides, phosphines, phosphine oxides, phosphoric esters, phosphorous esters, phosphoric acid amides, ketones, and carboxylic esters. One or more electron donors can be used.

The carboxylic esters have hydrocarbon moiety which can have a substituent of an amino group or an alkoxy group such as amino acid esters.

Suitable electron donors include amines such as tetramethyl ethylenediamine and tetraethyl ethylenediamine; carboxylic acid amides such as benzoic acid amide and acetamide; phosphines such as tris (nonylphenyl) phosphine, triphenyl phosphine; phosphine oxides such as triethylphosphine oxide and triphenylphosphine oxide; phosphoric esters such as triethyl phosphate and tributyl phosphate; phosphorous esters such as triphenyl phosphite and tris (nonylphenyl) phosphite; phosphoric acid amides such as hexamethyl phosphoric acid tri-amide; carboxylic esters such as methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, phenyl benzoate, methyl p-methoxybenzoate, ethyl p-methoxybenzoate, propyl p-methoxybenzoate, methyl p-methylbenzoate, ethyl p-methylbenzoate, butyl m-methoxybenzoate, phenyl o-methoxybenzoate, methyl p-ethoxybenzoate, ethyl p-ethoxybenzoate, butyl p-methoxybenzoate, methyl p-ethylbenzoate, ethyl p-ethylbenzoate, butyl-p-ethoxybenzoate, methyl p-butoxybenzoate, ethyl p-butoxybenzonate, butyl p-butoxybenzoate, phenyl acetate, phenyl propionate, ethyl acrylate, methyl methacrylate, ethyl crotonate, propyl crotonate, butyl crotonate, ethyl cinnamate, propyl cinnamate, butyl cinnamate, dimethyglycine ethyl ester, dimethylglycine propyl ester, dimethylglycine butyl ester, diphenylglycine ethyl ester, diphenylglycine propyl ether, diphenylglycine butyl ester and ethyl p-dimethyl aminobenzoate, and ketones such as acetone, methyl ethyl ketone, benzophenone and acetophenone.

It is preferable to use carboxylic esters, especially ethyl benzoate, methyl p-methylbenzoate or ethyl p-methylbenzoate.

The electron donors can be used in a pure form and also by diluting with a diluent.

Suitable diluents include aromatic hydrocarbons such as benzene and toluene; saturated aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, n-octane, n-dodecane and liquid paraffin; alicyclic hydrocarbons such as cyclohexane and methyl cyclohexane; and ethers such as diethyl ether, dibutyl ether, tetrahydrofuran and tetrahydropyran.

In the process of the present invention, the four components (a), (b), (c) and (d) are contacted in suitable order to obtain the titanium-containing solid component.

The titanium tetrahalide as (c) component is preferably added to the reaction mixture produced by reacting the OH compound (a) with the Grignard reagent (b) or the reaction mixture produced by reacting the OH compound (a) with the Grignard reagent (b) and the electron donor (d).

Thus, it is preferable to contact the OH compound (a) with the Grignard reagent (b) before contacting both with the titanium tetrahalide (c).

The electron donor (d) is preferably used by adding it to the reaction mixture produced by reacting the OH compound (a) with the Grignard reagent (b) or the reaction mixture produced by reacting the OH compound (a) with the Grignard reagent (b) and the titanium tetrahalide (c).

The typical methods for contacting the components (a), (b), (c) and (d) are as follows:

1) The OH compound (a) is contacted with the Grignard reagent (b) to react them in the presence of the electron donor (d) and then, the titanium tetrahalide (c) is added to the reaction mixture.

2) The OH compound (a) is contacted with the Grignard reagent (b) to react them and the electron donor (d) is added and then the titanium tetrahalide (c) is added to the reaction mixture.

3) The OH compound (a) is contacted with the Grignard reagent (b) to react them and the titanium tetrahalide (c) is added to the reaction mixture and then the electron donor (d) is added to it.

4) The product obtained by contacting the OH compound (a) with the Grignard reagent (b) is simultaneously treated with the titanium tetrahalide (c) and the electron donor (d). The method 2) and 4) are preferable.

When the product obtained by reacting the OH compound (a) with the Grignard reagent (b) is a compound having the formula

$$Mg(OR^8)X.nE$$

wherein R^8 represents a hydrogen atom or a hydrocarbon moiety; X represents a

halogen atom; E represents an ether and n represents 0.4 to 25, in the methods 1) to 4), a catalyst having high catalytic activity can be obtained.

In the formula, R^8 represents hydrogen atom or hydrocarbon moiety having up to 20 carbon atoms, such as alkyl groups e.g. methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, nonyl and decyl groups; aryl groups e.g. phenyl; and aralkyl groups e.g. benzyl; X represents Cl, Br and I, especially Cl; E represents an ether which may be a polyether, glycol ether or dioxane and preferably has the formula $R^2—O—R^3$ wherein R^2 and R^3 respectively represent a hydrocarbon moiety having 1 to 30 carbon atoms and R^2 and R^3 can be bonded each other to form a ring such as dialkyl ethers e.g. diethyl ether, di-n-butyl ether, di-i-propyl ether, di-n-butyl ether, di-i-butyl ether, di-t-butyl ether, di-n-amyl ether, di-i-amyl ether, di-n-hexyl ether and di-n-octyl ether; diaryl ethers e.g. diphenyl ether and dibenzyl ether; diaralkyl ethers; alkylaryl ethers e.g. phenetole and anisole; alkyl cycloalkyl ethers e.g. methyl cyclohexyl ether, alkyl aralkyl ethers e.g. methyl benzyl ether; polyethers e.g. polyethyleneglycol alkyl ether, polypropyleneglycol alkyl ether, polyethyleneoxide and polypropyleneoxide; glycol ethers e.g. ethyleneglycol dimethyl ether and ethyleneglycol diethyl ether; propyleneoxide; cyclic ethers e.g. tetrahydrofuran, dioxane, 4-methyl-1,3-dioxane and tetrahydropyran, especially tetrahydrydrofuran; and n represents 0.4 to 10 especially 0.4 to 5.

Catalysts having high catalytic activity can be obtained using the compounds defined above.

The compounds can be prepared by adding a stoichiometric amount or excess of ether to a reaction product obtained by reacting the component (a) with the component (b), and reacting them at from room temperature to 100°C for 0.1 to 10 hours and separating excess ether by suitable manner such as heating, distillation under reduced pressure, extraction or washing. In the reaction, it is preferable to add an inert hydrocarbon solvent such as hexane and heptane.

The compounds can be also produced by preparing an ether solution or ether adduct of the component (b) and adding the component (a) to the ether solution or ether adduct, or adding the ether solution or ether adduct to the component (a) at near room temperature and then, reacting them at 50 to 200°C preferably 50 to 150°C for 0.1 to 10 hours and separating excess of the ether by a filtration or an evaporation from the reaction mixture. The amount of the ether in the starting materials is preferably present at at least a 0.3:1 molar ratio to Grignard reagent. The amount of the component (a) is usually in a range of 0.01 to 2, preferably 0.5 to 1.5 and especially 0.7 to 1.3 as a molar ratio of the OH compound to alkyl group in the Grignard reagent. When excess of the ether is separated after the reaction, the molar ratio of the complexed ether to the magnesium is generally more than 0.4:1 so as to prevent the separation of the complexed ether. Accordingly, when excess of tetrahydrofuran is separated by evaporation, the separation is preferably carried out at near room temperature.

Suitable methods of contacting the components to form the titanium-containing catalytic component will be illustrated by the cases 1) to 4).

1) The OH compound (a) and the Grignard reagent (b) are added to the electron donor (d) at −50 to 100°C, preferably −30°C to room temperature. The mixture is heated to 20 to 200°C, preferably 20 to 150°C especially 20 to 100°C to react them for 0.1 to 10 hours. It is preferable to prevent the reaction of the Grignard reagent with the electron donor before reacting the Grignard reagent with the OH compound. Accordingly, when the electron donor easily reacts with the Grignard reagent, it is preferable to mix the OH compound and the Grignard reagent at low temperature so that the reaction of the electron donor with the Grignard reagent does not occur but the reaction of the OH compound with the Grignard reagent can take place. The reaction mixture can be used without any separation. However, it is preferable to separate the reaction product as a solid by decantation, filtration, or vaporization of the solvent from the reaction mixture. When the separation of the reaction product is carried out by the decantation or the filtration to obtain the solid, the solid is washed with an inert hydrocarbon solvent and it is added to the titanium tetrahalide and the mixture is treated at 60 to 350°C for longer than 1 minute preferably 0.1 to 10 hours.

After the treatment the solid catalytic component is separated from the reaction mixture preferably at 50 to 140°C and washed with an inert hydrocarbon solvent.

Suitable inert hydrocarbon solvents include aromatic hydrocarbons such as benzene, toluene; saturated aliphatic hydrocarbons such as n-pentane, n-hexane,

n-heptane, n-octane, n-dodecane, liquid paraffin; alicyclic hydrocarbons such as cyclohexane, methyl cyclohexane, etc.

2) The Grignard reagent (b) is added to the OH compound (a) or vice versa at −50 to 100°C preferably −20°C to near room temperature to contact them. The reaction is performed at 20 to 200°C preferably 20 to 150°C especially 20 to 100°C for 0.1 to 10 hours. The resulting reaction mixture or the solid separated from the reaction mixture by a filtration, a decantation or an evaporation of the solvent, is admixed with the electron donor (d) or a solution thereof. The mixture is preferably treated at 60 to 200°C for longer than 0.1 hour preferably 0.1 to 10 hours especially 1 to 5 hours.

When toluene, xylene or kerosene is used as a diluent for the electron donor in the process, the operation is convenient because it can be treated at the boiling point thereof. It is also possible to treat the product at said temperature after adding the electron donor and distilling off the diluent to dry the product. The product is treated with the titanium tetrahalide (c) by the process (1). The conditions for treating with the titanium tetrahalide and separating and washing the product can be the same with those of the method 1).

3) the reaction of the OH compound with the Grignard reagent is performed as in the case of the method 2). The resulting reaction product is treated with the titanium tetrahalide as in the case of the method 1) and then, it is treated with the electron donor as the same with that of the process 2).

4) As in the process 2), the OH compound (a) is contacted with the Grignard reagent (b) and then, the titanium tetrahalide (c) and the electron donor (d) are simultaneously added to the product and the mixture is treated by the process 1). In this case, the complex can be previously formed by contacting the titanium tetrahalide (c) with the electron donor (d). In this operation, at any desired stage, a halogenation agent (e) such as a halogen-containing silicon compound can be added. The halogenation agent (e) is usually added to a product obtained by reacting the OH compound (a) with the Grignard reagent (b). This is usually done by adding simultaneously or separately in any order, the components (c), (d) and (e) to a product obtained by contacting the component (a) with the component (b), or adding simultaneously or separately in any order, the components (c) and (e) to a product obtained by contacting the component (a) with the component (b) in the presence of the component (d). Optionally, the electron donor (d) and the mixture is treated at the temperature below the decomposition temperature of the halogenating agent for longer than 0.1 hour preferably 0.1 to 1 hour.

The halogenation agents when used in the process of the present invention are usually chlorination, bromination or iodination agents. The known halogenation agents can be used.

Suitable halogenation agents include halogens such as chlorine, bromine and iodine: hydrogen halides such as hydrogen chloride, hydrogen bromide and hydrogen iodide; haloalkanes such as carbon tetrachloride, chloroform, dichloroethane, tetrachloroethane, methylene chloride, trichlene, methyl chloride, ethyl chloride,n-butyl chloride, n-octyl chloride; non-metallic oxyhalides such as sulfuryl chloride, thionyl chloride, nitrosyl chloride, phosphorus oxychloride, phosgene; non-metallic halides such as phosphorus trichloride, phosphorus pentachloride, halogen containing silicon compounds; halides of metal or ammonium such as aluminum halides, ammonium halides except titanium tetrahalides.

It is preferable to use a chlorination agent as the halogenation agent.

It is especially preferable to use a halogen containing silicon compound having the formula

$$R^4_n SiX_{4-n}$$

wherein R^4 represents a hydrocarbon moiety having 1 to 16 of carbon atoms or a halohydrocarbon moiety; X represents a halogen atom and $0 \leqq n \leqq 3$.
The typical R^4 is an alkyl group, a cycloalkyl group or an aryl group and the typical X is chlorine, bromine, iodine or fluorine atom.When n=0, the compounds are tetrahalosilanes having the formula

$$SiX_4$$

The halogen atoms can be the same or different.

Suitable tetrahalosilanes include tetrachlorosilane, tetrabromosilane, tetraiodosilane, tetrafluorosilane, trichlorobromosilane, trichloroiodosilane, trichlorofluorosilane, dichlorodibromosilane, dichlorodiiodosilane, dichlorodifluorosilane, chlorotribromosilane, chlorotriiodosilane, chlorotrifluorosilane, bromotriiodosilane, bromotrifluorosilane, dibromodiiodosilane, dibromodifluorosilane, tribromoidodosilane, tribromofluorosilane, iodotrifluorosilane, diiododifluorosilane, and triiodofluorosilane.

It is preferable to use tetrachlorosilane, tetrabromosilane, trichlorobromosilane, dichlorodibromosilane or chlorotribromosilane. It is optimum to use tetrachlorosilane.

When n=1 the compounds have the formula

$$R^4SiX_3$$

Suitable compounds having the formula

$$R^4SiX_3$$

include alkyl trichlorosilanes having C_1—C_{16} saturated alkyl group such as methyl trichlorosilane, ethyl trichlorosilane, n- and i- propyl trichlorosilanes, n-, i- and tert butyl trichlorosilanes, n- and i-amyl trichlorosilanes, n-hexyl trichlorosilane, n-heptyl trichlorosilane, n-octyl trichlorosilane, n-dodecyl trichlorosilane, n-tetradecyl trichlorosilane, n-hexadecyl trichlorosilane; unsaturated alkyl trichlorosilanes having C_1—C_4 unsaturated alkyl group such as vinyl trichlorosilane, isobutenyl trichlorosilane; haloalkyl or unsaturated haloalkyl trichlorosilanes such as chloromethyl trichlorosilane, dichloromethyl trichlorosilane, trichloromethyl trichlorosilane, (2-chloroethyl) trichlorosilane, (1,2-dibromoethyl) trichlorosilane, trifluoromethyl trichlorosilane and (vinyl-1-chloro) trichlorosilane; saturated or unsaturatd cycloalkyl trichlorosilanes such as cyclopropyl trichlorosilane, cyclopentyl trichlorosilane, cyclohexenyl trichlorosilane and 3-cyclohexenyl trichlorosilane; aryl or aralkyl trichlorosilanes such as phenyl trichlorosilane, 2-, 3- or 4-tolyl trichlorosilanes, and benzyl trichlorosilane; saturated alkyl or haloalkyl mixed trihalosilanes such as methyl difluorochlorosilane, methyl fluorodichlorosilane, ethyl difluorochlorosilane, ethyl fluorodichlorosilane, n- and i-propyl; fluorochlorosilane, n-butyl difluorochlorosilane, n-butyl difluorodichlorosilane, phenyl difluorochlorosilane, methyl dichlorobromosilane, ethyl dichlorobromosilane, methyl dichloioddosilane and (trifluoromethyl) difluorobromosilane.

When n=2, the compounds have the formula

$$R^4_2SiX_2$$

Suitable compounds include dialkyl dihalosilanes such as dimethyl dichlorosilane, diethyl dichlorosilane, di-n- and -i-propyl dichlorosilanes, di-n-, -i- and -tert-butyl dichlorosilanes, di-n- and -i-amyl dichlorosilanes, di-n-hexyl dichlorosilane, di-n-heptyl dichlorosilane and di-n-octyl dichlorosilane; dicycloalkyl dihalosilanes such as dicyclopentyl dichlorosilane, dicyclohexyl dibromosilane, dicyclohexyl diiodosilane, dicyclohexyl difluorosilane, and diaryl or diaralkyl dihalosilanes such as diphenyl dichlorosilane, di-2-, -3- or -4- tolyl dichlorosilane and dibenzyl dichlorosilane.

When n=3, the compounds have the formula

$$R^4_3SiX$$

Suitable compounds include trialkyl halosilanes such as trimethyl chlorosilane, triethyl chlorosilane, tri(n- and i-propyl) chlorosilanes, tri(n- and i-butyl) chlorosilanes, tri(n-hexyl) chlorosilane, tri(n-heptyl) chlorosilane, tri(n-octyl) chlorosilane, dimethyl (ethyl) chlorosilane, methyl (diethyl) chlorosilane; and triaryl or triaralkyl halosilanes such as triphenyl chlorosilane, tri(2-, 3- or 4-tolyl) chlorosilane, and tribenzyl chlorosilane.

It is preferable to use silicon tetrachloride, and mono- di- or tri- chlorosilanes having the formula in which R^4 is a methyl, ethyl or phenyl group.

It is possible to use several halogenation agents. It is also possible to treat with the halogenation agent in the presence of an inert solvent or gas.

Suitable inert solvents include aromatic hydrocarbons such as benzene and toluene, liquid saturated aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, n-octane, n-dodecane, liquid paraffin; alicyclic hydrocarbons such as cyclohexane and methyl cyclohexane.

The inert gases include nitrogen and argon gas.

The amounts of the components used in the process of the present invention are usually selected from the following ranges.

The molar ratio of the OH compound to alkyl group of the Grignard reagent is in a range of 0.01 to 2:1 preferably 0.5 to 1.5:1 especially 0.7 to 1.3:1.

When water is used as the OH compound, the ratio is preferably less than 1.0:1 because the precipitate having no free water can be obtained.

The molar ratio of the electron donor to the Grignard reagent is in a range of 0.01 to 10:1 preferably 0.1 to 2:1.

The molar ratio of the titanium tetrahalide to the Grignard reagent is in a range of 0.1 to 50:1 preferably 1 to 30:1.

The molar ratio of the halogenation agent to the Grignard reagent is in a range of 0.01 to 50:1 preferably 0.1 to 5:1.

When the compound having the formula

$$Mg(OR^8)X \cdot nE,$$

the titanium tetrahalide (c) and the electron donor (d) are contacted, the amounts of the components are selected from the following ranges.

The molar ratio of the electron donor to $Mg(OR^8)X$ in $Mg(OR^8)X \cdot nE$ is in a range of 0.2 to 10:1 preferably 0.4 to 4:1.

The molar ratio of the titanium tetrahalide to $Mg(OR^8)X$ in $Mg(OR^8)X \cdot nE$ is in a range of 0.1 to 50:1 preferably 1 to 30:1.

Thus, the pale yellowish brown solid having a titanium content of 0.01 to 20 wt.%, preferably 0.1 to 10 wt.%, especially 0.5 to 10 wt.% can be obtained by contacting the OH compound, the Grignard reagent, the titanium tetrahalide and the electron donor.

The solid catalytic component having high catalytic activity for a polymerization of an olefin to provide a high stereospecific polymer can be obtained by only washing the product with the hydrocarbon solvent. However, the solid catalytic component having higher catalytic activity can be obtained by washing with titanium tetrachloride.

When the titanium-containing solid catalytic component prepared by contacting the OH compound (a), the Grignard reagent (b), the titanium tetrahalide (c) and the electron donor (d) and washing the product with titanium tetrachloride is admixed with an organoaluminum compound to use for a polymerization of an olefin, high catalytic activity and high stereospecific property of the resulting polyolefin can be attained.

The washing operation can be carried out by adding titanium tetrachloride to the titanium containing solid catalytic component and keeping the mixture for 0.1 to 10 hours, preferably with stirring, and separating titanium tetrachloride from the titanium-containing solid catalytic component.

The washing operation can be carried out at near room temperature but is preferably carried out at an elevated temperature such as from 50° to the boiling point of titanium tetrachloride. It is preferable to separate the washing solution from the solid catalytic component at a temperature of 50 to 140°C. Accordingly, it is preferable to use a high temperature continuous extractor such as Soxhlet's extractor. The washing operation is quite effective in one step but is preferably repeated until providing a constant titanium content of the titanium-containing solid catalytic component. The titanium tetrachloride used in the washing operation can be by itself and also can be mixed with an inert hydrocarbon solvent.

Suitable inert hydrocarbon solvents include aromatic hydrocarbons such as benzene and toluene; saturated aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, n-octane, n-dodecane, liquid paraffin; alicyclic hydrocarbons such as cyclohexane and methyl cyclohexane.

The amount of titanium tetrachloride used for one washing step is not critical and is preferably at a molar ratio of titanium tetrachloride to the magnesium compound in the solid catalytic component of 1 to 30:1.

After the washing step with titanium tetrachloride, the solid catalytic component is washed with an inert hydrcarbon solvent. Suitable inert hydrocarbon

solvents used for the washing include the above-mentioned aromatic hydrocarbons, saturated alphatic hydrocarbons and alicyclic hydrocarbons.

In the polymerization of an olefin, the titanium-containing solid catalytic component is combined with an organoaluminum compound to form a catalyst system.

The organoaluminum compounds preferably have the formula

$$AlR^5_mX_{3-m}$$

wherein R^5 represents a C_1—C_8 alkyl group which can be the same or different and m represents 1 to 3 and X represents a halogen atom.

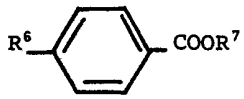
Suitable organoaluminum compound used as the auxiliary catalyst in the invention include trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum; dialkylaluminum monohalides such as dimethylaluminum monochloride, diethylaluminum monochloride; alkylaluminum sesquihalides such as methylaluminum sesquichloride, ethylaluminum sesquichloride; dialkylaluminum monoalkoxides such as diethylaluminum monoethoxide, diethylaluminum monomethoxide etc.

It is preferable to use the trialkylaluminum such as triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum or trioctylaluminum.

The molar ratio of the organoaluminum to Ti in the titanium-containing solid catalytic component is usually in a range of 1 to 500:1 preferably 1 to 100:1 and especially 2 to 50:1.

In the process of the present invention, the polymerization of an olefin is carried out in the presence of the catalyst system comprising the organoaluminum compound and the titanium-containing solid component, if necessary with a known additive for improving stereospecific property.

The additives can be electron donors such as the above-mentioned component (d) preferably carboxylic esters, phosphoric esters and phosphorous esters. It is most preferable to add the carboxylic esters having the formula



wherein R^6 and R^7 respectively represent C_1—C_{10} alkyl groups, because the polyolefins having high stereospecific property can be obtained in high polymerization activity.

Suitable carboxylic esters having the formula include methyl p-methylbenzoate, ethyl p-methylbenzoate, propyl p-methylbenzoate, butyl p-methylbenzoate, hexyl p-methylbenzoate, octyl p-methylbenzoate, methyl p-ethylbenzoate, ethyl p-ethylbenzoate, propyl p-ethylbenzoate, butyl p-ethylbenzoate, hexyl p-ethylbenzoate, octyl p-ethylbenzoate, methyl p-butylbenzoate, ethyl p-butylbenzoate, propyl p-butylbenzoate, butyl p-butylbenzoate, hexyl p-butylbenzoate, octyl p-butylbenzoate, methyl p-hexylbenzoate, ethyl p-hexylbenzoate, propyl p-hexylbenzoate, butyl p-hexylbenzoate, hexyl p-hexylbenzoate, octyl p-hexylbenzoate, methyl p-octylbenzoate, ethyl p-octylbenzoate, propyl p-octylbenzoate, butyl p-octylbenzoate, hexyl p-octylbenzoate and octyl p-octylbenzoate.

The benzoates having the formula wherein R^6 and R^7 represent C_1 to C_4 alkyl groups are especially effective.

The method of the addition of the additive is not limited. The additive can be added to the organoaluminum compound or the titanium-containing solid catalytic component or a mixture thereof.

The molar ratio of the additive to Ti in the titanium-containing solid catalytic component is in a range of 0.1—200 preferably 0.1 to 40 especially 1 to 10.

The olefins can be α-olefins such as ethylene, propylene or butene-1.

The polyolefins can be advantageously obtained by a homopolymerization, a random copolymerization or a block copolymerization with two or more monomers with the catalyst system of the invention. In the copolymerization, it is preferable to use less than 10 wt.% of a comonomer in the copolymer.

The catalyst system of the invention is preferably used in the homopolymerization of propylene or the copolymerization of propylene and another α-olefin.

In the process of the present invention, the homopolymerization or copolymerization can be carried out by a solution polymerization in an inert hydrocarbon or liquefied propylene, a slurry polymerization or a gaseous polymerization without any solvent. It is possible to add any additive as desired.

The polymerization is usually carried out at 20 to 100°C, preferably 50 to 80°C under a pressure from atmospheric pressure to 100 atm.

The molecular weight of the resulting polyolefin can be controlled by the presence of hydrogen in the polymerization zone.

As described in detail, in accordance with the process of the present invention, polyolefins having excellent stereospecific property can be easily obtained. Since the stereospecific property of the resulting polyolefin is remarkably high, the need for separation of amorphous polymer (atactic polymer) from the resulting polyolefin can be eliminated. The titanium-containing solid catalytic component used in the present invention has remarkably high polymerization activity. Accordingly, the step of removing the catalyst residue from the resulting polyolefin can be also eliminated.

The invention will be further illustrated by the following Examples which are provided herein for purpose of illustration only.

In the Examples and References, the isotactic index (I.I.) was given as a weight percent of solid residue after an extraction with boiled n-heptane for 6 hours by an improved Soxhlet extractor, and the melt index (MFI) was measured by ASTM D-1238.

Example 1.

(I) Preparation of titanium containing solid catalytic component:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 32 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2m mole/ml, was charged and 160 ml of ethyl ether solution containing 100 m mole of water was added dropwise to the solution at 25°C with vigorous stirring to form white precipitate. After the addition, the mixture was stirred at 25°C for 1 hour and the temperature was raised to 45°C and the mixture was further stirred for 1 hour. During the operation, ethyl ether was distilled off. The reaction mixture was dried under reduced pressure by distilling off the solvent to obtain 7.55 g of white powder. The atomic ratio of Cl/Mg of the resulting powder was 0.90.

Then, 20 ml of toluene solution containing ethyl benzoate at a concentration of 1 m mole/ml was added to the powder and after the addition, the mixture was heated at 110°C and stirred for 1.5 hours. Then, 220 ml of titanium tetrachloride was added and the mixture was heated to 130°C for 1 hour and the suspension of the reaction mixture was decanted without cooling it and the product was repeatedly washed with heptane until disappearing the symptom of chlorine in the washing solution to obtain a pale yellow solid catalytic component. The titanium content in the solid was 6.2 wt.%.

(II) Polymerization of propylene:

The polymerization of propylene was carried out using the catalyst component prepared by the process (I).

In a 1 litre four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.22 m mole of triethyl aluminum and 42.0 mg of the titanium containing solid catalyst prepared by the process of (I) were charged. The molar ratio Al/Ti was 4.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 16.0 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} given as K_{cat} = polymer (g)/$Ti_{cat.}$ component (g) × time (hr) × propylene pressure (Kg/cm²) was 317, and K_{TI} given as K_{TI} = polymer (g)/titanium (g) × time (hr) × propylene pressure (Kg/cm²) was 5,110 and the isotactic index (I.I) was 72.5 % and the melt index (MFI) was 2.2.

The results are shown in Table 1.

References 1 and 2:

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 1 except using magnesium

hydroxychloride prepared by preheating $MgCl_2 \cdot 6H_2O$ at 200°C for 20 hours and pulverizing it in a vibration mill for 72 hours and heating at 285°C in dry nitrogen gas in a quartz tube instead of the reaction product of water and chloro-n-butyl magnesium.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except varying the molar ratio of Al/Ti to 4 or 30. The results are shown in Table 1.

From the results, it was found that the polymerization activity and the isotactic index I.I. were remarkably different depending upon the solid carrier used for the preparation of titanium containing catalytic component.

TABLE 1

	Ti content in solid catalytic component (wt. %)	Al/Ti molar ratio	K		I.I. (%)
			K_{cat}	K_{Ti}	
Exp. -1	6.2	4	317	5110	72.5
Ref. -1	1.3	4	25	1920	45.3
Ref. -2	1.3	30	20	1540	41.5

As shown in Example 1 and References 1 and 2, when the catalyst of the present invention is used the polymerization activity is remarkably higher and the isomatic index of the resulting polyolefin is remarkably higher in comparison with those of the use of the catalysts prepared by using magnesium hydroxychloride in the same process. The fact shows that the magnesium compound produced by using water and Grignard reagent in the preparation of the titanium-containing solid catalytic component is different from the magnesium hydroxychloride. The X-ray diffractomatric diagram of the magnesium compounds of the invention has not diffraction peaks of magnesium hydroxychloride described in ASTM-24-726, and the fact shows that the magnesium compound is amorphous substrate.

Examples 2 to 3.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except varying the molar ratio of Al/Ti as shown in Table 2. The results are shown in Table 2.

TABLE 2

	A/Ti molar ratio	K		I.I (%)
		K_{cat}	K_{Ti}	
Exp. -2	8	310	5000	71.3
Exp. -3	15	265	4270	68.8

Example 4.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 1 except using 80 ml of tetrahydrofuran solution containing 100 m mole of water instead of the water containing ethyl ether.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using the catalytic component.

The results are shown in Table 3.

Example 5.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 1 except using 100 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 1 m mole/ml and 100 m moles of water instead of ethyl ether solution containing water.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using the catalytic component.

The results are shown in Table 3.

TABLE 3

	Ti content in solid catalytic component (wt. %)	K		I.I (%)
		K_{cat}	K_{Ti}	
Exp. -4	10.8	185	1710	75.3
Exp. -5	8.8	223	2530	70.2

Examples 6 to 7.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 1 except varying a molar ratio of ethyl benzoate/Mg as shown in Table 4.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using the catalytic component.

The results are shown in Table 4.

TABLE 4

	molar ratio ethylbenzoate/Mg	Ti content in cat. (wt. %)	K		I.I. (%)
			K_{cat}	K_{Ti}	
Exp. -1	0.2	6.2	317	5110	72.5
Exp. -6	0.8	8.8	280	3180	80.6
Exp. -7	1.0	10.4	61	590	90.5

Example 8.

The preparation of titanium-containing catalytic component was repeated in accordance with the process (I) of Example 1 except varying the amount of the toluene solution containing ethyl benzoate at a concentration of 1 m mole/ml from 20 ml to 80 ml, and adding 220 ml of titanium tetrachloride after decanting the suspension of the reaction mixture before washing it with heptane and stirring at 130°C for 1 hour and decanting again the suspension. The titanium content was 2.9 wt. %.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using 53.8 mg of the catalytic component and 0.22 m mole of triethyl aluminum to obtain 43.3 g of white powdery polypropylene. The polymerization activity of the catalyst K_{cat} was 671 and K_{Ti} was 23,140, and the isotactic index I.I. was 80.3 % and MFI was 3.0.

Examples 9 to 11.

The preparation of titanium-containing catalytic component was repeated in accordance with the process of Example 8 except washing two times after the treatment of titanium tetrachloride. The titanium content was 2.4 wt. %.

The polymerization of propylene was repeated in accordance with the process

of Example 8 except using the catalytic component and varying the molar ratio of Al/Ti as shown in Table 5.

The results are shown in Table 5.

TABLE 5

	Al/Ti molar ratio	K		I.I. (%)
		K_{cat}	K_{Ti}	
Exp. - 9	4	1400	58,330	65.4
Exp. - 10	8	1240	51,670	60.5
Exp. - 11	15	1080	45,000	60.0

Examples 12 to 14.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process of Example 8 except varying the molar ratio of ethyl benzoate/Mg as shown in Table 6.

The polymerization of propylene was repeated in accordance with the process of Example 8 except using the catalytic component.

The results are shown in Table 6.

Example 15.

The preparation of titanium-containing catalytic component was repeated in accordance with the process of Example 8 except varying the amount of the toluene solution of ethyl benzoate from 80 ml to 100 ml and heating the mixture at 110°C for 1.5 hours after the addition of the toluene solution of ethyl benzoate and washing the product with n-heptane and drying it before treating with titanium tetrachloride.

The polymerization of propylene was repeated in accordance with the process of Example 8 except using the catalytic component.

TABLE 6

	ethyl benzoate/Mg molar ratio	Ti content in cat (wt. %)	K		I.I. (%)
			K_{cat}	K_{Ti}	
Exp. - 12	0.2	2.8	817	29,180	47.5
Exp. - 13	0.5	3.0	720	24,000	68.9
Exp. - 14	1.0	3.4	135	3.970	92.5
Exp. - 15	1.0	3.0	705	23,500	60.5

Example 16.

In a 500 m four necked flask which was purged with dry nitrogen, 32 ml of d-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ ml was charged and the temperature was cooled to –20°C, and 100 m mole of ethyl benzoate was added dropwise whilst maintaining the temperature and stirring the mixture, and then, 160 ml of ethyl ether solution containing 100 m mole of water was added dropwise under maintaining at –20°C to form white precipitate. After the addition, the mixture was stirred at –20°C for 2 hours and heated to 45°C and further stirred for 1 hour. The supernatant liquid was decanted and the precipitate was washed with n-heptane and dried to obtain the solid and 220 ml of titanium tetrachloride was added and heated at 130°C for 1 hour, and the suspension of the reaction mixture was decanted without cooling, and the

precipitate was washed with n-heptane to obtain the solid catalytic, component having 6.3 wt. % of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using 40.0 mg of the solid catalytic component and 0.21 m mole of triethyl aluminum to obtain 14.0 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 292 and K_{TI} was 4,640 and the isotactic index I.I. was 72.8 % and MFI was 2.5.

Examples 17 to 20.

The preparation of the titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 1 except using various electron donors shown in Table 7 instead of ethyl benzoate.

The polymerization of propylene was repeated in accordance with the process (II) of Example 1 except using the catalytic components.

The results are shown in Table 7.

TABLE 7

	Electron donor	Ti content in cat. (wt. %)	K		I.I. (%)
			K_{cat}	K_{Ti}	
Exp. - 17	dimethyl glycine ethyl ester	9.8	180	1840	78.5
Exp. - 18	phenyl acetate	6.5	300	4620	70.5
Exp. - 19	tetramethyl ethylenediamine	10.5	194	1850	80.3
Exp. - 20	hexamethyl phosphoric triamide	9.6	165	1720	66.9

Example 21.

(I) Preparation of titanium containing solid catalytic component:

In a 500 ml four necked flask, which was purged with dry nitrogen gas, 150 ml of toluene, and 40 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium (n-C_4H_9MgCl) at a concentation of 2.5 m mole/ml were charged and 5.8 ml of ethanol (100 m mole) was added dropwise at 25°C with vigorous stirring. The molar ratio of EtOH/n-BuMgCl was 1.0. After the addition, the mixture was further stirred at 25°C for 1 hour, and heated to 80°C and further stirred for 1 hour. The reaction product was washed 5 times with each 150 ml of heptane and heptane was distilled off under a reduced pressure and the product was dried to obtain white powder of $(C_2H_5O)_{0.98}$ $MgCl_{0.93}$.

Then, 150 ml of toluene and 2.9 ml (20 m mole) of ethyl benzoate were added to the resulting powder at 25°C The atomic ratio of Mg/ ethyl benzoate was 0.2. After the addition, the mixture was heated to 110°C and stirred for 1 hour. The reaction mixture was dried under a reduced pressure to distil off toluene to obtain white powder. Then, 220 ml (2 mole) of titanium tetrachloride ($TiCl_4$) was added at 25°C with stirring. The molar ratio of $TiCl_4$/Mg was 20. After the addition, the mixture was heated at 130°C and stirred for 1 hour. Then, the suspension of the reaction mixture was decanted without cooling it and the residual solid was repeatedly washed with heptane until traces of chlorine disappeared the washing solution to obtain a pale yellow solid catalytic component. The titanium content in the solid was 2.4 wt. %.

(II) Polymerization of olefin:

The polymerization of olefin was carried out by using the catalytic component prepared by the process (I).

In a 1 litre four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.10 m mole of triethyl aluminum and 50.0 mg of the titanium-

containing solid catalyst prepared by the process of (I) were charged. The molar ratio of Al/Ti was 4.

Then, the mixture was heated to 70°C under stirring it and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 19.4 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 323 and K_{Ti} was 13,470 and the isotactic index (II) was 85.2% and MFI was 2.6.

Examples 22 to 26 and References 3 to 7.

The preparation of the catalytic component was repeated in accordance with the process (I) of Example 21 except using various alcohols instead of ethanol.

The polymerization of propylene was repeated in accordance with the process (II) of Example 21 except using the catalytic component.

The results are shown in Table 8 together with the results obtained without adding ethyl benzoate in the preparation of the catalytic component.

TABLE 8

	Preparation of Ti containing catalytic component			Results of polymerization		
	Type of alcohol	Addition of ethyl benzoate	Ti content (wt. %)	K_{cat}	K_{Ti}	I.I.
Exp. - 22	isopropanol	add	5.3	353	6660	89.1
Ref. - 3	,,	none	5.9	397	6730	43.2
Exp. - 23	n-butanol	add	3.6	365	10140	86.7
Ref. - 4	,,	none	4.1	421	10270	38.6
Exp. - 24	n-hexanol	add	4.0	321	8030	90.1
Ref. - 5	,,	none	6.7	382	5700	36.9
Exp. - 25	n-octanol	add	2.1	396	18860	87.6
Ref. - 6	,,	none	2.9	411	14170	58.6
Exp. - 26	n-decanol	add	3.6	295	8190	89.8
Ref. - 7	,,	none	5.2	350	6730	39.5

Example 27 to 30.

The preparation of the catalytic component was repeated in accordance with the process (I) of Example 21 except varying the molar ratio of ethyl benzoate/Mg. (EB/Mg).

The polymerization of propylene was repeated in accordance with the process (II) of Example 21 except using the catalytic component.

The results are shown in Table 9.

TABLE 9

	Preparation of Ti containing catalytic component			Results of polymerization		
	Type of alcohol	EB/Mg	Ti content (wt. %)	K_{cat}	K_{Ti}	I.I.
Exp. - 27	ethanol	0.4	3.1	330	10650	86.0
Exp. - 28	,,	0.6	3.2	305	9530	86.1
Exp. - 29	,,	0.8	5.8	227	3910	88.3
Exp. - 30	,,	1.0	8.9	72	810	93.1

Examples 31 to 37.

The preparation of the catalytic component was repeated in accordance with the process (I) of Example 21 except using various election donors shown in Table 10 instead of ethyl benzoate.

The polymerization of propylene was repeated in accordance with the process (II) of Example 21 except using the catalytic component.

The results are shown in Table 10.

TABLE 10

	Preparation of Ti containing catalytic component			Results of polymerization		
	Type of Electron donor (ED)	ED/Mg molar ratio	Ti content (wt. %)	K_{cat}	K_{Ti}	I.I.
Exp. - 31	methyl benzoate	0.2	3.0	305	10170	83.1
Exp. - 32	ethyl benzoate	,,	4.3	358	8330	84.5
Exp. - 33	phenyl acetate	,,	2.8	311	11110	85.8
Exp. - 34	dimethyl glucine ethyl ester	,,	4.1	301	7340	87.0
Exp. - 35	ethyl crotonate	,,	2.5	283	11320	90.4
Exp. - 36	hexamethyl phosphoric triamide	,,	6.8	185	2720	91.3
Exp. - 37	triphenyl phosphite	,,	7.1	163	2300	90.1

Example 38.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 150 ml of toluene and 32.3 ml of tetrahydrofuran solution containing chloro-n-butyl magnesium (n-C_4H_9MgCl) at a concentration of 3.1 m mole/ml were charged and cooled to −30°C, and 14.3 ml (100 m mole) of ethyl benzoate was added dropwise at −30°C under stirring and then 5.8 ml (100 m mole) of ethanol was added dropwise at −30°C with stirring to obtain a white precipitate. The molar ratio of ethyl benzoate/Mg was 1.0 and the molar ratio of ethanol/Mg was 1.0. After the addition, the mixture was stirred at −30°C for 3 hours and heated to 60°C and further stirred for 2 hours. The supernatant liquid was decanted and the precipitate was

washed 5 times with each 150 ml of heptane and dried under a reduced pressure to distil off heptane to obtain white powder.

Then, 220 ml (2 mole) of $TiCl_4$ was added to the powder at 25°C under stirring. The molar ratio of $TiCl_4$/Mg was 20. After the addition, the mixture was heated at 130°C and stirred at the temperature for 1 hour. The suspension of the reaction mixture was decanted without cooling it and the residual solid was washed 5 times with each 150 ml of heptane to obtain the solid catalytic component having 3.2 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 21 except using 40 mg of the catalytic component and 0.107 m mole of triethyl aluminum to obtain 12.7 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 265, and K_{TI} was 8,270 and the isotactic index I.I. was 82.5% and MFI was 3.1.

Example 39.

(I) Preparation of titanium containing solid catalytic component:

(I)-(A) Magnesium hydroxy-chloride- ether complex:

In a 500ml four necked flask which was purged with dry nitrogen gas, 87ml of tetrahydrofuran solution containing chloro-n-butyl magnesium at a concentration of 2.3 m mole/ml was charged and 150 ml of tetrahydrofuran solution containing 200 m mole of water was added dropwise at 25°C during 30 minutes with stirring, and the mixture was heated to 60°C and stirred for 1 hour and then, the product was washed 3 times with 250 ml volumes of n-heptane, and the solvent was removed at room temperature to obtain a white powder. The atomic ratio Cl/Mg of the powder was 0.93. The powder was dissolved in ethanol and the content of tetrahydrofuran was measured by gas chromatography. It was confirmed that the complex comprised 1.37 mole of tetrahydrofuran per 1 mole of magnesium (THF/Mg) in magnesium hydroxy chloride.

(I)-(B) Preparation of titanium containing solid catalyst:

2.2 g of the resulting powder was admixed with 23 ml of toluenene and 35.2 m mole of ethyl benzoate and the mixture was heated at 60°C for 2 hours and the product was washed with n-heptane and the solvent was destilled off under reduced pressure. Then, 28 ml of titanium tetrachloride was added to the residue and the mixture was heated at 130°C for 1 hour, and the product was washed 2 times with each 50ml of toluene and then, washed with n-heptane to obtain grey-green solid having 3.29 wt.% of the titanium content.

(II) Polymerization of propylene:

The polymerization of an olefin was carried out by using the catalytic component prepared by the process (I)-(B).

In a 500 ml four necked flask, 200 ml of n-heptane, 0.10 m mole of triethyl aluminum and 20 mg of the titanium-containing solid catalytic component prepared by the process (I)-(B) were charged. The mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 28 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 1167, K_{TI} was 35,000 and the isotactic index I.I. was 77.3%.

Reference 8:

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I)-(B) of Example 39 except using magnesium hydroxy-chloride prepared by heating $MgCl_2 \cdot 6H_2O$ at 200°C for 20 hours and pulverizing it for 72 hours by a vibration mill and heating it at 285°C in the presence of dry nitrogen gas in a quartz tube instead of the tetrahydrofuran complex of the reaction product of water and chloro-n-butyl magnesium.

The polymerization of propylene was repeated in accordance with the process (II) of Example 39.

The polymerization activity of the catalyst K_{cat} was 25 and K_{TI} was 1,920 and the isotactic index I.I. was 45.3%.

Examples 40 to 42.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I)-(B) of Example 39 except treating the tetrahydrofuran complex of magnesium hydroxy chloride obtained by the process (I)-(A) of Example 39 under reduced pressure or adding tetrahydrofuran in a toluene solvent so as to adjust the degree complexing of tetrahydrofuran (THF/Mg) as shown in Table 11.

The polymerization of propylene was repeated in accordance with the process (II) of Example 39.

The results are shown in Table 11.

TABLE 11

	THF/Mg	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. -40	0.42	957	25.0	71.1
Exp. -41	2.38	1266	42.8	69.8
Exp. -42	5.63	1248	41.3	70.3

Example 43.

The polymerization of propylene was carried out using the titanium-containing solid catalytic component obtained by the process (I)-(B) of Example 39.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 200 ml of n-heptane, 0.20 m mole of triethyl aluminum, 0.0310 m mole of ethyl benzoate and 26 mg of the titanium-containing solid catalytic component were charged.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 23.8 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 763 and K_{TI} was 23,200 and the isotactic index I.I. was 91.6%.

Example 44.

A 25 ml of titanium tetrachloride was added to 2.0 g of the reaction product of water and chloro-n-butyl magnesium obtained by the process (I)-(A) of Example 39 and the mixture was heated at 130°C for 1 hour and then, washed with n-heptane and 31.9 m mole of ethyl benzoate was added and the mixture was heated at 60°C for 1 hour and then, washed with n-heptane to obtain a solid catalytic component having a 3.02 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 39 except using the resulting catalytic component.

The polymerization activity of the catalyst K_{cat} was 938 and K_{TI} was 31,100 and the isotactic index I.I. was 79.1%.

Examples 45 to 49.

The preparation of the catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 39 except using various ethers shown in Table 12 instead of tetrahydrofuran in the process (I)-(A).

The results are shown in Table 12.

TABLE 12

	Ether	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. - 45	diethyl ether	993	31.9	72.3
Exp. - 46	di-n-butyl ether	1063	35.6	75.6
Exp. - 47	di-n-octyl ether	981	32.9	69.3
Exp. - 48	ethyleneglycol dimethyl ether	970	32.2	70.0
Exp. - 49	tetrahydropyran	1023	31.8	74.2

Examples 50 to 52.

The preparation of the catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 39 except using various electron donors shown in Table 13 instead of ethyl benzoate in the process (I)-(B).

The results are as follows.

TABLE 13

	Electron donor	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. - 50	phenyl acetate	966	33.5	70.2
Exp. - 51	ethyl cinnamate	891	29.7	68.3
Exp. - 51	tetramethyl ethylene diamine	822	24.8	64.1

Example 53.

(I) Preparation of titanium containing solid catalytic component:

(I)-(A) Magnesium ethoxychloride ether complex:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 43 ml of tetrahydrofuran solution containing chloro-n-butyl magnesium at a concentration of 2.3 m mole/ml was charged and then, 150 ml of tetrahydrofuran solution containing 100 m mole of ethanol was added dropwise at 25°C during 30 minutes with stirring, and the mixture was heated to 60°C and stirred for 1 hour and then, washed 3 times with 250 ml of n-heptane and the solvent was distilled off at the room temperature to obtain white powder. The atomic ratio of Cl/Mg of the powder was 0.93.

The powder was dissolved in ethanol and tetrahydrofuran in ethanol was analyzed by the gas chromatography analysis to confirm the fact that 1.3 mole of tetrahydrofuran per 1 mole of magnesium in the magnesium ethoxy chloride (THF/Mg) was complexed.

(I)-(B) Preparation of titanium containing solid catalytic component:

25 ml of toluene and 35.3 m mole of ethyl benzoate were added to 2.5 g of the resulting powder and the mixture was heated at 60°C for 2 hours and washed with n-heptane and the solvent was distilled off under reduced pressure. Then, 28 ml of titanium tetrachloride was added to the residue and the mixture was heated at 130°C for 1 hour and washed with n-heptane to obtain grey solid having a 3.0 wt.% titanium content.

(II) Polymerization of propylene:

The polymerization of propylene was carried out using the catalytic component prepared by the process (I)-(B).

In a 500 ml four necked flask which was purged with dry nitrogen gas, 200 ml of n-heptane, 0.10 m mole of triethyl aluminum and 20 mg of the titanium-containing solid catalyst prepared by the process of (I)-(B) were charged.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amont of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 14.8 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 617 and K_{Ti} was 20,560 and the isotactic index I.I. was 85.3%.

Examples 54 to 56.

The preparation of titanium-containing solid catalytic component was replaced in accordance with the process (I)-(B) of Example 54 except controlling the degree of complexing of tetrahydrofuran (THF/Mg) as shown in Table 14 by treating the tetrahydrofuran complex of magnesium ethoxychloride obtained by the process (I)-(A) under reduced pressure or by adding tetrahydrofuran.

The polymerization of propylene was repeated in accordance with the process (II) of Example 53.

The results are shown in Table 14.

TABLE 14

	THF/Mg	Ti content in cat. (wt. %)	K_{cat}	K_{Ti}	I.I. (%)
Exp. - 54	0.4	2.9	461	15,900	89.5
Exp. - 55	2.1	3.3	625	18.940	87.1
Exp. - 56	5.1	3.5	585	16,710	84.3

Example 57.

The polymerization of propylene was carried out by using the titanium containing solid catalytic component obtained in the process (I)-(B) of Example 53.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 200 ml of n-heptane, 0.15 m mole of triethyl aluminum 0.025 m mole of methyl p-methyl benzoate and 20 mg of the titanium-containing solid catalyst were charged.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmosphere pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 10.3 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 429 and K_{Ti} was 14,310 and the isotactic index I.I. was 93.5%.

Example 58.

A 20 ml of titanium tetrachloride was added to 2.0 g of the reaction product of ethanol and chloro-n-butyl magnesium obtained by the process (I)-(A) of Example 53 and the mixture was heated to 130°C for 1 hour and washed with n-heptane and then, 30 m mole of ethyl benzoate was added and the mixture was heated at 60°C for 1 hour and washed with n-heptane to obtain the solid catalytic component having a 2.9 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 53 except using the resulting catalytic component.

The polymerization activity of the catalyst K_{cat} was 510 and K_{Ti} was 17,590 and the isotactic index I.I. was 86.5%.

Example 59.

The mixture of 20 ml of titanium tetrachloride and 30 m mole of ethyl benzoate was added to 2.0 g of the reaction product of ethanol and chloro-n-butyl magnesium obtained by the process (I)-(A) of Example 53 and the mixture was

heated at 130°C for 1 hour and washed with n-heptane to obtain a solid catalytic component having a 3.2 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 53 except using the catalytic component.

The polymerization activity of the catalyst K_{cat} was 620 and K_{Ti} was 19,380 and the isotactic index I.I. was 85.1%.

Examples 60 to 62.

The preparation of the catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 53 except using various ethers shown in Table 15 instead of tetrahydrofuran in the process (I)-(A).

The results are shown in Table 15.

TABLE 15

	Ether	Ti content in cat.	K_{cat}	K_{Ti}	I.I.
		(wt. %)			(%)
Exp. - 60	diethyl ether	3.0	590	19,670	86.5
Exp. - 61	di-n-butyl ether	2.8	620	22,140	84.8
Exp. - 62	ethyleneglycol dimethyl ether	3.1	445	14,350	87.1

Examples 63 to 66.

The preparation of catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 53 except using various electron donors shown in Table 16 instead of ethyl benzoate in the process (I)-(B).

The results are shown in Table 16.

TABLE 16

	Electron donor	Ti content in cat.	K_{cat}	K_{Ti}	I.I.
		(wt. %)			(%)
Exp. - 63	methyl benzoate	2.9	510	17,590	89.3
Exp. - 64	methyl p-methyl benzoate	3.1	597	19,260	88.5
Exp. - 65	phenyl acetate	3.5	475	13,570	85.3
Exp. - 66	ethyl cinnamate	4.3	421	9,790	87.1

Examples 67 to 70.

The preparation of catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 53 except using various alcohols shown in Table 17 instead of ethanol in the process (I)-(B).

The results are shown in Table 17.

TABLE 17

	Alcohol	Ti content in cat.	K_{cat}	K_{Ti}	I.I.
		(wt. %)			(%)
Exp. -67	n-butyl alcohol	4.2	620	14,760	85.3
Exp. -68	n-hexyl alcohol	3.2	596	18,630	85.1
Exp. -69	n-decyl alcohol	2.9	683	23,550	84.2
Exp. -70	n-octyl alcohol	2.8	725	25,890	86.0

Example 71.

(I) Preparation of titanium containing solid catalytic component:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 3 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ml was charged and 150 ml of tetrahydrofuran solution containing 100 m mole of water was added dropwise at 25°C during 30 minutes with stirring and the mixture was heated to 60°C and further stirred for 1 hour. The white precipitate of the reaction product was washed with n-heptane and dried under a reduced pressure to distill off the solvent to obtain 7.8 g of dry powder. The atomic ratio of Cl/Mg of the powder was 0.92. Then, 18 ml of n-heptane was added to 1.00 g of the powder and 6.8 m mole of ethyl benzoate and 13.6 m mole of silicon tetrachloride were added to the solution and the mixture was stirred at 60°C for 1 hour, and then, the reaction product was washed 5 times with 100 ml volumes of n-heptane and the solvent was distilled off under a reduced pressure to obtain a white powder. The atomic ratio of Cl/Mg of the powder was 1.56. Then, 30 ml of titanium tetrachloride was added to the powder and the mixture was heated to 130°C to react them for 1 hour. After the reaction, the reaction product was washed twice with 100 ml volumes of toluene and further washed 3 times with 100 ml volumes of n-heptane to obtain a pale yellowish green solid catalytic component having a 2.8 wt.% titanium content.

(II) Polymerization of Olefin:

The polymerization of olefin was carried out by using the catalytic component prepared by the process (I).

In a liter four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.15 m mole of triethyl aluminum and 26 mg of the titanium-containing solid catalytic component prepared by the process (I) were charged. The molar ratio of Al/Ti was 9.9. Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added to methanol and the precipitate was separated and dried to obtain 31.1 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 998 and K_{Ti} was 35,600 and the isotactic index I.I. was 80.3% and MFI was 1.8.

The result is shown in Table 18.

Examples 72 to 77.

The preparation of titanium-containing solid catalystic component was repeated in accordance with the process (I) of Example 71 except using chlorosilanes shown in Table 18 instead of silicon tetrachloride.

The polymerization of propylene was repeated in accordance with the process (II) of Example 71.

The results are shown in table 18.

TABLE 18

	Si compound	Ti content in cat. (wt. %)	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. -71	$SiCl_4$	2.8	998	35.6	80.3
Exp. -72	$(CH_3)SiCl_3$	3.3	1011	30.6	75.0
Exp. -73	$(CH_3)_2SiCl_2$	4.1	1067	26.0	73.6
Exp. -74	$(CH_3)_3SiCl$	2.9	1462	50.4	71.9
Exp. -75	$C_6H_5SiCl_3$	3.8	1235	32.6	75.0
Exp. -76	$(C_6H_5)_2SiCl_2$	2.8	963	34.4	82.3
Exp. -77	$(C_6H_5)_3SiCl$	2.6	1132	43.5	80.9

Examples 78 to 80.

The polymerization of propylene was repeated in accordance with the process of Example 74 except using various electron donors shown in Table 19 instead of ethyl benzoate.

The results are shown in Table 19.

TABLE 19

	Electron donor	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I. (%)
Exp. -78	phenyl acetate	977	36.2	81.0
Exp. -79	ethyl cinnamate	865	26.2	72.8
Exp. -80	tetramethyl ethylenediamine	932	32.1	69.1

Example 81.

The polymerization of olefin was carried out by using the titanium-containing solid catalytic component of Example 74.

In a 1 liter four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.27 m mole of triethyl aluminum, 0.033 m mole of ethyl benzoate and 26 mg of the titanium-containing solid catalytic component were charged.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 26.8 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 859 and K_{Ti} was 29,600 and the isotactic index I.I. was 93.2%.

Example 82.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 32 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ml was charged and cooled to –20°C and 100 m mole of ethyl benzoate was added dropwise under stirring it, and then, 160 ml of ethyl ether solution containing 100 m mole of water was added dropwise at –20°C with stirring to form a white precipitate. After the addition, the mixture was stirred at –20°C for

2 hours and then, further stirred at 45°C for 1 hour. The supernatant liquid was decanted and the precipitate was washed with n-heptane and dried to obtain the solid. Then, 200 m mole of trimethyl chlorosilane was added and the mixture was treated at 60°C for 1 hour under stirring it and the product was washed with n-heptane and dried. Then, 220 ml of titanium tetrachloride was added to the product and the mixture was heated at 130°C for 1 hour and the product was washed with n-heptane to obtain the solid catalytic component having 3.56 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 71 but using 25.0 mg of the catalytic component and 0.12 m mole of triethyl aluminum to obtain 27.8 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 927 and K_{Tl} was 26,000 and the isotactic index I.I. was 73.8%.

Example 83.

In a 500 ml four necked flask which was purged with dry nitrogen gas, di-n-butyl ether solution containing 100 m moles of chloro-n-butyl magnesium was charged and ethyl ether solution containing 100 m mole of water was added dropwise at the room temperature under stirring it. After the addition, the mixture was stirred at the room temperature for 1 hour and further stirred at 45°C for 1 hour. The reaction mixture was washed with n-heptane and dried to obtain white powder. Then, 200 m mole of trimethyl chlorosilane was added to the powder and the mixture was stirred at 60°C for 1 hour and the product was washed with n-heptane and dried and then, 220 ml of titanium tetrachloride was added and the mixture was heated at 130°C for 1 hour. The product was washed with n-heptane and 20 m mole of ethyl benzoate was added and the mixture was heated at 60°C for 1 hour and the product was washed with n-heptane to obtain a solid catalytic component having 2.2 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 71 except using 25 mg of the resulting catalytic component and 0.08 m mole of triethyl aluminum to obtain 26.3 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 877 and K_{Tl} was 39,800 and the isotactic index I.I. was 76.3%.

Example 84.

In a 500 ml four necked flask which was purged with dry nitrogen gas, si-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 100 m mole was charged and an ethersolution containing 100 m mole of water was added dropwise at room temperature with stirring. After the addition, the mixture was stirred at the room temperature for 1 hour and further stirred at 45°C for 1 hour. The reaction mixture was washed with n-heptane and dried to obtain white powder. Then, 20 m mole of ethyl benzoate was added to the powder and the mixture stirred at 100°C for 1 hour and the product was washed with n-heptane and dried, and 200 m mole of silicon tetrachloride was added and the mixture was heated at 60°C for 1 hour and 220 ml of titanium tetrachloride was added and the mixture was heated at 130°C for 1 hour. The product was washed with n-heptane to obtain a solid catalytic component having 3.6 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 71 except using 23 mg of the catalytic component and 0.11 m mole of triethyl aluminum to obtain 33. 8 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 1225 and K_{Ti} was 34,000 and the isotactic index I.I. was 82.0%.

Example 86.

In a flask, 1.00 g of the hydrolyzed product of Grignard reagent obtained in Example 71 was admixed with 18 ml of n-heptane and 6.8 m mole of ethyl benzoate and the mixture was heated at 60°C for 1 hour and the product was washed 5 times with each 100 ml of n-heptane. The solvent was distilled off under reduced pressure and then, 13.6 m mole of dichlorodimethyl silane and 30 ml of titanium tetrachloride were simultaneously added and the mixture was heated at 60°C for 1 hour. Then, the product was washed with n-heptane to obtain the solid catalytic component having 2.4 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 71 except using 25 mg of the catalytic component and 0.090 m mole

of triethyl aluminum to obtain 28.5 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 950 and K_{Ti} was 39,600 and the isotactic index I.I. was 76.8%.

Example 86.

(I) Preparation of titanium-containing solid catalytic component:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 40 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 2.5 m mole/ml was charged and 150 ml of tetrahydrofuran solution containing 100 m mole of water was added dropwise at 25°C with vigorous stirring to form white precipitate. After the addition, the mixture was stirred at 50°C for 1 hour and then, the solvent was distilled off under reduced pressure to obtain 7.9 g of white solid powder. The atomic ratio of Cl/Mg of the powder was 0.98. Then, 4m mole of ethyl benzoate, 20 ml of n-heptane, 40 m mole of thionyl chloride were added to 1.54 g of the powder and the mixture was heated at 60°C for 2 hours and washed 5 times with each 100 ml of n-heptane and the solvent was distilled off to obtain white powder. The atomic ratio of Cl/Mag of the powder was 1.75. Then, 20 ml of titanium tetrachloride was added and the mixture was heated at 130°C for 1 hour and washed 7 times with each 100 ml of n-heptane to obtain a titanium-containing solid catalytic component having a 3.0 wt.% titanium content.

(II) Polymerization of Propylene:

The polymerization of olefin was carried out by using the catalytic component prepared by the process (I).

In a 1 liter four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.12 m mole of triethyl aluminum, and 35.0 mg of the titanium-containing solid catalyst prepared by the process of (I) were charged. The molar ratio of Al/Ti was 5.5.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under the atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 25.0 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 595 and K_{Ti} was 19,830 and the isotactic index I.I. was 85.6% and MFI was 1.6.

Example 87.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 86 but using phosphorous trichloride instead of thionyl chloride. The atomic ratio of Cl/Mg after the halogenation was 1.65, and the titanium content was 3.7 wt.%.

The polymerization of propylene was repeated in accordance with the process (II) of Example 86 except using the catalytic component.

The polymerization activity of the catalyst K_{cat} was 415 and K_{Ti} was 11,200 and the isotactic index I.I. was 78.2%.

Example 88.

20 ml of n-heptane and 4 m mole of ethyl benzoate were added to 1.54 g of the hydrolyzed product of the Grignard reagent obtained by the process of Example 86 and hydrogenchloride gas was introduced into the liquid phase at a rate of 10 liter/hour for 2 hours with stirring. The temperature was kept at 25°C. The supernatant was decanted and the precipitate was washed with n-heptane and dried to obtain a solid having an atomic ratio of Cl/Mg of 1.56. Then, 20 ml of titanium tetrachloride was added to it and the mixture was heated at 130°C for 1 hour and washed with n-heptane to obtain a solid catalytic component having a 4.1 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 87 except using 40.0 mg of the catalytic component and 0.24 m mole of triethyl aluminum to obtain 24.5 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 510 and K_{Ti} was 12,400 and the isotactic index I.I. was 84.5%.

Example 89.

The preparation of titanium-containing solid catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 86 except using 20 ml of carbon tetrachloride instead of thionyl chloride without using 20 ml of n-heptane and heating the mixture at the boiling point of carbon tetrachloride for 2 hours in the process (II).

The polymerization activity of the catalyst K_{cat} was 410 and K_{TI} was 10,300 and the isotactic index I.I. was 71.5%. The results are shown in Table 20.

Examples 90 to 93.

The preparation of the titanium-containing solid catalytic component and the polymerization of propylene were repeated in accordance with the process of Example 89 but using various halogenation agents shown in Table 20 instead of carbon tetrachloride.

The results are shown in Table 20.

TABLE 20

	Halogenation agent	Atomic ratio of Cl/Mg	Ti content in cat. (wt. %)	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. -89	CCl_4	1.52	4.0	410	10.3	71.5
Exp. -90	$CHCl_3$	1.40	3.6	400	11.1	73.3
Exp. -91	CH_2Cl_3	1.30	4.4	460	10.5	70.2
Exp. -92	$CH_3(CH_2)_3Cl$	1.32	4.8	380	7.9	75.0
Exp. -93	$CH_3(CH_2)_7Cl$	1.10	5.5	365	6.6	77.1

Example 94 to 96.

The polymerization of propylene was repeated in accordance with the process of Example 86 but using various electon donors shown in Table 21 instead of ethyl benzoate.

The results are shown in Table 21.

TABLE 21

	Electron donor	K_{cat}	$K_{Ti} \times 10^{-3}$	I.I.
Exp. -94	phenyl acetate	580	18.7	84.5
Exp. -95	ethyl cinnamate	590	17.9	88.5
Exp. -96	tetramethyl ethylene diamine	310	6.9	82.2

Example 97.

The polymerization of propylene was carried out by using the titanium containing solid component obtained in Examples 86 as follows.

In a 1 liter four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.263 m mole of triethyl aluminum, 0.033 m mole of ethyl benzoate and 35.0 mg of the catalytic component were charged.

Then, the mixture was heated at 70°C with stirring and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 12.0 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 285 and K_{Ti} was 9,500 and the isotactic index I.I. was 93.5%.

Example 98.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 32 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ml was charged and cooled to −20°C and 20 m mole of ethyl benzoate was added dropwise with stirring. Then, 160 ml of ethyl ether solution containing 100 m mole of water was added dropwise at −20°C to give a white precipitate. After the addition, the mixture was stirred at −20°C for 2 hours and then further stirred at 45°C for 1 hour. The supernatant was decanted and the precipitate was washed with n-heptane and dried to obtain the solid. Then, 200 m mole of thionyl chloride and 100 ml of n-heptane were added and the mixture was heated at 60°C for 1 hour with stirring, washed with n-heptane and dried. Then, 220 ml of titanium tetrachloride was added and the mixture was heated at 130°C for 1 hour and washed with n-heptane to obtain the solid catalytic component having a 3.3 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 86 but using 30.0 mg of the resulting catalytic component and 0.14 m mole of triethyl aluminum to obtain 18.5 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 514 and K_{Ti} was 15,600 and the isotactic index I.I. was 75.0%.

Example 99.

In a 500 ml four necked flask which was purged with dry nitrogen gas, di-n-butyl ether solution containing 100 m mole of chloro-n-butyl magnesium was charged and ethyl ether solution containing 100 m mole of water was added dropwise at the room temperature with stirring. After the addition, the mixture was stirred at room temperature for 1 hour and further stirred at 45°C for 1 hour. The reaction mixture was washed with n-heptane and dried to obtain white powder.

Then, 200 m mole of thionyl chloride was added and the mixture was stirred at 60°C for 1 hour, washed with n-heptane and dried. 220 ml of titanium tetrachloride was added and the mixture was stirred at 130°C for 1 hour and washed with n-heptane. Then, 20 m mole of ethyl benzoate was added and the mixture was heated at 60°C for 1 hour and washed with n-heptane to obtain a solid catalytic component having a 2.2 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 87 except using 25 mg of the catalytic component and 0.8 m mole triethyl aluminum to obtain 10.7g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 357 and K_{Ti} was 16,200 and the isotactic index I.I. was 84.6%.

Example 100.

In a 500 ml four necked flask which was purged with dry nitrogen gas, di-n-butyl ether solution containing 100 m mole of chloro-n-butyl magnesium was charged and ethyl solution containing 100 m mole of water was added dropwise at the room temperature with stirring. After the addition, the mixture was stirred at room temperature for 1 hour and further stirred at 45°C for 1 hour. The reaction product was washed with n-heptane and dried to obtain a white powder.

Then, 20 m mole of ethyl benzoate was added and the mixture was stirred at 100°C for 1 hour, washed with n-heptane and dried. Then, 80 m mole of thionyl chloride was added and the mixture was heated at 60°C for 1 hour and a further 220 ml of titanium tetrachloride was added and the mixture was treated at 130°C for 1 hour and washed with n-heptane to obtain the solid catalytic component having 4.2 wt.% of the titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 86 but using 33.0 mg of the resulting catalytic component and 0.15 m mole of triethyl aluminum to obtain 18.3 g of white powdery polypropylene.

The polymerization activity K_{cat} was 463 and K_{Ti} was 11,000 and the isotactic index I.I. index was 82.0%.

Example 101.

(I) Preparation of titanium containing solid catalytic component:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 150 ml of toluene and 40 ml of di-n-butyl ether solution containing n-butyl magnesium chloride at a concentration of 2.5 m mole/ml was charged and 5.8 ml (100 m mole) of ethanol was added dropwise at 25°C with vigorous stirring. The molar ratio of C_2H_5OH/n-BuMgCl was 1.0:1. After the addition, the mixture was stirred at 25°C for 1 hour and further stirred at 80°C for 1 hour. The reaction product was washed 5 times with each 150 ml of n-heptane and the heptane was distilled off under reduced pressure and the product was dried to obtain white powder. The formula of the powder was $(C_2H_5O)_{0.98}MgCl_{0.93}$.

Then, 150 ml of toluene, 2.9 ml (20 m mole) of ethyl benzoate and 200 m mole of thionyl chloride were added to the powder at 25°C. After the addition, the mixture was heated to 60°C and stirred at 60°C for 2 hours. Toluene was distilled off under reduced pressure and the product was dried to obtain white powder having an atomic ratio of Cl/Mg of 1.4:1.

Then, 220 ml (2 mole) of titanium tetrachloride was added at 25°C with stirring. The molar ratio of $TiCl_4$/Mg was 20. After the addition, the mixture was heated at 130°C and stirred at 130°C for 1 hour and then, the product was repeatedly washed with n-heptane until traces of chlorine disappeared to obtain pale yellowish titanium-containing solid catalytic component having a 2.8 wt.% titanium content.

(II) Polymerization of propylene.

The polymerization of propylene was carried out using the catalytic component prepared by the process (I).

In a 1 litre four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.20 m mole of triethyl aluminum and 50 mg of titanium-containing solid catalytic component prepared by the process (I) were charged. The molar ratio of Al/Ti was 7. Then, the mixture was heated to 70°C with stirring, and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 31.2 g of white powdery polypropylene.

The polymerization activity of the catalyst $K_{cat.}$ was 520 and K_{Ti} was 18,570 and the isotactic index I.I. was 88.2% and MFI was 2.8.

Examples 102 to 106.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 101 except using the halogenation agents shown in Table 22 instead of thionyl chloride.

The polymerization of propylene was repeated in accordance with the process (II) of Example 101.

The results are shown in Table 22.

TABLE 22

	Halogenation agent	Ti content in cat. (wt. %)	K_{cat}	K_{Ti}	I.I. (%)
Exp. - 103	PCl_3	2.5	509	20,360	88.9
Exp. - 104	HCl	2.3	480	20,870	91.3
Exp. - 105	CCl_4	3.1	510	16,450	90.8
Exp. - 106	$CHCl_3$	3.1	565	18,230	88.8
Exp. - 107	CH_2Cl_2	3.5	463	13,230	87.1

Example 107.

(I) Preparation of titanium containing solid catalytic component:

In a 500 ml four necked flask which was purged with nitrogen gas, 150 ml of toluene and 40 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 2.5 m mole/ml, was charged and 5.8 ml (100 m mole) of ethanol was added dropwise to the solution at 25°C with stirring. The molar ratio of C_2H_5OH/n-BuMgCl was 1.0:1. The temperature was raised to 80°C and the mixture was stirred at 80°C for 1 hour and the reaction product was washed with n-heptane and the solvent was distilled off under a reduced pressure to obtain dry white powder. The atomic ratio of Cl/Mg of the powder was 0.93. Then, 150 ml of toluene, 2.9 ml (20 m mole) of ethyl benzoate and 200 m mole of silicon tetrachloride were added to the powder and the mixture was heated at 60°C for 2 hours and the product was washed 5 times with 100 ml volumes of n-heptane and the solvent was distilled off under reduced pressure. The atomic ratio of Cl/Mg of the resulting white powder was 1.5:1. Then, 220 ml (2 mole) of titanium tetrachloride was added and the mixture was heated to 130°C for 1 hour. Then, the product was washed 5 times with each 100 ml of n-heptane to obtain pale yellowish green solid having a 2.8 wt.% titanium content.

(II) Polymerization of propylene

The polymerization of propylene was repeated in accordance with the process (II) of Example 102 except using the catalytic component to obtain 40.8 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 680 and K_{TI} was 24,290 and the isotactic index I.I. was 88.5% and MFI was 3.7.

Examples 108 to 111.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 107 except using the halogenation agents shown in Table 23 instead of silicon tetrachloride.

The polymerization of propylene was repeated in accordance with the process (II) of Examples 101.

The results are shown in Table 23.

TABLE 23

	Halogenation agent	Ti content in cat. (wt. %)	K_{cat}	K_{Ti}	I.I. (%)
Exp. - 108	CH_3SiCl_3	3.1	801	25,840	85.1
Exp. - 109	$(CH_3)_2SiCl_2$	2.9	705	24,310	86.5
Exp. - 110	$(CH)_3SiCl$	2.8	620	22,140	89.5
Exp. - 111	$(C_6H_5)SiCl_3$	3.5	631	18,030	88.3

Examples 112 to 115.

The preparation of the titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 107 but using the electron donors shown in Table 24 instead of ethyl benzoate.

The polymerization of propylene was repeated in accordance with the process (II) of Example 101.

The results are shown in Table 24.

TABLE 24

	Electron donor	Ti content in cat. (wt. %)	K_{cat}	K_{Ti}	I.I. (%)
Exp. - 112	methyl p-methyl benzoate	2.5	683	27,320	89.1
Exp. - 113	phenyl acetate	2.7	615	22,780	87.1
Exp. - 114	tetramethyl ethylenediamine	4.5	487	10,820	85.3
Exp. - 115	ethyl cinnamate	2.8	530	18,930	90.1

Examples 116 to 118.

The preparation of titanium-containing solid catalytic component was repeated in accordance with the process (I) of Example 107 but using the alcohols shown in Table 25.

The polymerization of propylene was repeated in accordance with the process (II) of Example 101.

The results are shown in Table 25.

TABLE 25

	Alcohol	Ti content in cat. (wt. %)	K_{cat}	K_{Ti}	I.I. (%)
Exp. - 116	n-butanol	2.3	580	25,220	90.3
Exp. - 117	n-hexanol	2.1	485	23,100	91.5
Exp. - 118	n-decanol	3.1	610	19,680	90 1

Example 119.

The polymerization of propylene was carried out by using the titanium-containing solid catalytic component obtained by the process (I) of Example 107 as follows.

In a 1 liter four necked flask which was purged with dry nitrogen gas, 500 ml of n-heptane, 0.322 m mole of triethyl aluminum, 0.058 m mole of methyl p-methylbenzoate and 50 mg of the titanium-containing solid catalytic component were charged. Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of i-propyl alcohol. The content was added into methanol and the precipitate was separated and dried to obtain 24.9 g of white powdery polypropylene. The polymerization activity of the catalyst, K_{cat} was 415, K_{Ti} was 14,820 and I.I. was 94.0%.

Example 120.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 32 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ml, was charged and 20 m mole of methyl p-methyl benzoate was added dropwise to the solution at −20°C with stirring and 100 m mole of ethanol was added dropwise at −20°C to the mixture with stirring to obtain a white precipitate. After the addition, the mixture was stirred at −20°C for 2 hours and further stirred at 45°C for 1 hour. The supernatant was decanted and the precipitate was washed with n-heptane and dried it and obtain a solid. Then, 200 m mole of thionyl chloride, and 100 m of n-heptane were added to the solid and the mixture was heated at 60°C for 2 hours with stirring and the product was washed with n-heptane and dried. Then, 220 ml of titanium tetrachloride was added to the

resulting solid, the mixture was heated at 130°C for 1 hour and the product was washed with n-heptane to obtain a solid catalytic component having a 3.4 wt.% titanium content.

The polymerization of propylene was repeated in accordance with the process (II) of Example 101 but using 50 mg of the resulting catalytic component and 0.28 m mole of triethyl aluminum to obtain 30.3 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 505 and K_{TI} was 14,850 and the isotactic index I.I. was 89.3%.

Example 121.

In a 500 ml four necked flask which was purged with dry nitrogen gas, di-n-butyl ether solution containing 100 m mole of chloro-n-butyl magnesium was charged and 100 m mole of ethanol was added dropwise at the room temperature with stirring. After the addition, the mixture was stirred at the room temperature for 1 hour and further stirred at 45°C for 1 hour and the reaction product was washed with n-heptane and dried to obtain white powder. Then 200 m mole of silicon tetrachloride was added, the mixture was stirred at 60°C for 1 hour and the product was washed with n-heptane and dried. Then, 220 ml of titanium tetrachloride was added, the mixture was heated at 130°C for 1 hour, the product was washed with n-heptane, 20 m mole of ethyl benzoate was added, the reaction mixture was heated at 60°C for 1 hour and the product was washed with n-heptane to obtain a solid catalytic having a 3.3 wt.% titanium compound.

The polymerization of propylene was repeated in accordance with the process (II) of Example 101 but using 50 mg of the catalytic component and 0.28 m mole of triethyl aluminum to obtain 24.8 g of white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 413 and K_{TI} was 12,530 and the isotactic index I.I. was 87.3%.

Example 122.

In a 500 ml four necked flask which was purged with dry nitrogen gas, di-n-butyl ether solution containing 100 m mole of chloro-n-butyl magnesium was charged and 100 m mole of butanol was added dropwise at the room temperature. After the addition, the mixture was stirred at the room temperature for 1 hour and at 45°C for 1 hour. The product was washed with n-heptane and dried to obtain a white powder. Then, 20 m mole of ethyl benzoate was added to the solid and the mixture was stirred at 90°C for 1 hour, then 80 m mole of thionyl chloride was added and the mixture was heated at 60°C for 1 hour, 220 ml of titanium tetrachloride was added the mixture was heated at 130°C for 1 hour and the product was washed with n-heptane to obtain a solid catalytic component having a 3.0 wt.% titanium content.

The polymerization of propylene repeated in accordance with the process (II) of Example 101 but using 55 mg of the catalytic component and 0.25 m mole of triethyl aluminum to obtain 29.2 g of white powdery polypropylene.

The polymerization activity of the catalyst K_{cat} was 486 K_{TI} was 16,220 and the isotactic index I.I. was 85.1%.

Example 123

(I) Preparation of titanium-containing solid catalytic component:

In a 500 ml four necked flask which was purged with dry nitrogen gas, 32 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 3.2 m mole/ml was charged and 150 ml of tetrahydrofuran solution containing 100 m mole of water was added dropwise at 25°C with stirring and the mixture was heated to 60°C and stirred at 60°C for 1 hour. The resulting white precipitate was washed with n-heptane and the solvent was distilled off under a reduced pressure to obtain 7.8 g of dry powder. The atomic ratio of Cl/Mg of the powder was 0.92. Then, 6.8 m mole of ethyl benzoate and 13,6 m mole of silicon tetrachloride were added to 18 ml of n-heptane solution containing 1.00 g of the powder, the mixture was heated at 60°C for 1 hour, the product was washed 5 times with 100 ml volumes of n-heptane and the solvent was distilled off under a reduced pressure to obtain white powder having an atomic ratio of Cl/Mg of 1.56. Then, 30 ml of titanium tetrachloride was added and the mixture was heated at 130°C for 1 hour. The product was washed twice with 100 ml volumes of toluene and further washed 3 times with 100 ml volumes of n-heptane to obtain a pale yellowish green solid having a 2.8 wt.% titanium content.

(II) Polymerization of olefin

The polymerization of propylene was carried out using the catalytic component obtained by the process (I) as follows.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 300 ml of n-heptane, 0.19 m mole of triethyl aluminum and 0.03 m mole of methyl p-tolulate and 30.1 mg of the titanium-containing solid catalytic component prepared by the process (I) were charged.

Then, the mixture was heated to 70°C with stirring and propylene gas was introduced under atmospheric pressure to perform the polymerization for 2 hours. The polymerization was stopped by adding a small amount of methanol. The content was added into methanol and the precipitate was separated and dried to obtain white powdery polypropylene.

The polymerization activity of the catalyst, K_{cat} was 392 and K_{TI} was 14,000 and the isotactic index I.I. was 95.8%.

Example 124.

(I) Preparation of titanium-containing solid catalytic component.

In a 500 ml four necked flask which was purged with dry nitrogen gas, 150 ml of toluene and 40 ml of di-n-butyl ether solution containing chloro-n-butyl magnesium at a concentration of 2.5 m mole/ml, were charged and 5.8 ml of ethanol was added dropwise to the solution at 25°C with vigorous stirring. The molar ratio of C_2H_5OH to n-BuMgCl was 1.0. After the addition, the mixture was stirred at 25°C for 1 hour, the temperature was raised to 80°c and the mixture was further stirred for 1 hour. The reaction product was washed 5 times with 150 m volumes of heptane and the reaction mixture was dried under a reduced pressure by distilling off n-heptane to obtain a white solid powder which was $(C_2H_5O)_{0.98}MgCl_{0.93}$.

Then, 150 ml of toluene and 2.9 m (20 m mole) of ethyl benzoate was added at 25°C. The molar ration of ethyl benzoate to Mg was 0.2. after the addition, the mixture was heated at 110°C and stirred for 1 hour. Then, toluene was distilled off from the reaction mixture under a reduced pressure to obtain white solid powder. Then, 220 m (2 mole) of titanium tetrachloride was added at 25°C with stirring. The molar ratio of $TiCl_4/Mg$ was 20. After the addition, the mixture was heated at 130°C and stirred at 130°C for 1 hour the supernatant of the suspension was decanted hot, and the product was repeatedly washed with n-heptane until traces of chlorine disappeared in the washing solution, to obtain a pale yellow solid catalytic component having a 2.4 wt.% titanium content.

Polymerization of olefin:

The polymerization of propylene was repeated in accordance with the process (II) of Example 123 but using the solid catalytic component obtained by the process (I).

The polymerization activity of the catalyst, K_{cat} was 250 and K_{TI} was 10,400 and the isotactic index I.I. of 92.4%.

WHAT WE CLAIM IS:—

1. A process for preparing a polyolefin by polymerizing an olefin or a mixture of olefins in the presence of a catalyst system comprising an organoaluminum compound and a titanium-containing solid catalytic component prepared from (a) water and/or an alcohol, (b) a Grignard reagent and (c) a titanium tetrahalide, wherein the titanium-containing component is prepared by contacting the components (a), (b) or (c), or a reaction mixture of two or three of the said components with (d) one or more electron donors selected from amines, carboxylic acid amides, phosphines, phosphine oxides, phosphoric esters, phosphorous esters, phosphoric acid amides, ketones and carboxylic esters.

2. a process according to claim 1 wherein propylene is polymerized.

3. A process according to claim 1 wherein there is polymerized a mixture of propylene and another α-olefin.

4. A process according to any preceding claim wherein component (d) is a carboxylic ester.

5. A process according to any preceding claim wherein the titanium-containing solid catalytic component is prepared by adding simultaneously or separately in any order the component (c) and the component (d) to the product obtained by contacting the component (a) with the component (b).

6. A process according to claim 1 wherein the titanium containing solid catalytic component is prepared by adding the component (c) to a product obtained by contacting the component (a) with the component (b) in the presence of the component (d).

7. A process according to any one of claims 1 to 4 wherein the titanium-containing solid catalytic component is prepared by adding the component (d) to a product obtained by contacting the component (a) with the component (b) and then adding the component (c) to the mixture.

8. A process according to any one of claims 5 to 7 wherein the contacting of component (a) with component (b) is carried out in the presence of an ether.

9. A process according to any one of claims 5 to 8 wherein the product of the reaction between component (a) and (b) is a compound having the formula

$$Mg(OR^8)X.nE$$

wherein R^8 represents hydrogen atom or a hydrocarbon moiety having up to 20 carbon atoms; X represents a halogen atom; E represents an ether; and n represents 0.4 to 25.

10. A process according to any one of claims 1 to 4 wherein the components (a), (b), (c) or (d), or the reaction mixture of two or three or four components thereof is contacted with (e) a halogenation agent other than a titanium tetrahalide.

11. A process according to claim 10 wherein the titanium-containing solid catalytic component is prepared by adding simultaneously or separately in any order, the components (c), (d) and (e) to a product obtained by contracting the component (a) with the component (b).

12. A process according to claim 10 wherein the titanium-containing solid catalytic component is prepared by adding simultaneously or separately in any order, the components (c) and (e) to a product obtained by contacting the component (a) with the component (b) in the presence of the component (d).

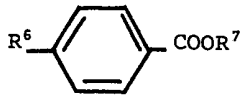
13. A process according to any one of claims 10 to 12 wherein the halogenation agent (e) is a halogen containing silicon compound having the formula

$$R_n^4SiX_{4-n}$$

wherein R_4 represents a hydrocarbon moiety having 1 to 16 carbon atoms or a halohydrocarbon moiety; X represents a halogen atom and $O \leqq n \leqq 3$.

14. A process according to any preceding claim wherein the titanium-containing solid catalytic component is further treated with titanium tetrachloride.

15. A process according to any preceding claim wherein a compound having the formula



wherein R^6 and R^7 respectively represent C^1—C^{10} alkyl groups, is added as an additive together with the titanium-containing solid catalytic component and the organoaluminum compound, in the polymerization reaction mixture.

16. A process according to claim 1 substantially as herein described with reference to the Examples.

17. A polyolefin made by a process according to any preceding claim.

18. A process for preparing a titanium-containing solid catalytic component from (a) water and/or an alcohol, (b) a Grignard reagent and (c) and a titanium tetrahalide, which process comprises contacting the component (a), (b) or (c), or a reaction mixture of two or three of the said components with (d) one or more electron donors selected from amines, carboxylic acid amides, phosphines, phosphine oxides, phosphoric esters, phosphorous esters, phosphoric acid amides, ketones and carboxylic esters.

19. A process according to claim 18 substantially as herein described with reference to the Examples.

20. A titanium-containing solid catalytic component prepared by a process according to claim 18 or claim 19.

21. A catalyst comprising a titanium-containing solid catalytic component according to claim 20 and an organo aluminum compound.

22. A catalyst system according to claim 21 substantially as herein described with reference to the Examples.

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