

SOLID CATALYST COMPONENT
FOR USE IN POLYMERIZATION OF α -OLEFINS

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This invention relates to a solid catalyst component for use in the polymerization of α -olefins.

5 More particularly, this invention relates to a solid catalyst component for use in the polymerization of α -olefins, which is quite excellent in catalytic activity and stereospecificity and improved in resistance to grinding, characteristics of particles and convenience
10 in handling.

As a general process for producing a polymer of α -olefin such as propylene and butene-1, the use of the so-called Ziegler-Natta catalyst consisting of
15 a compound of transition metal belonging to Group IV-VI of the periodic table and an organometal compound belonging to Group I-III of the periodic table is well known.

In such a production process, however, an amorphous polymer is formed as a by-product in addition to
20 a highly stereospecific α -olefin polymer having a high industrial value.

The amorphous polymer is low in industrial utilizability and exercises a very adverse influence upon mechanical properties of the α -olefin polymer when the

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1 polymer is processed into film, fiber and others and put
to use.

Further, formation of the above-mentioned
amorphous polymer causes a loss of starting monomer and
5 makes it indispensably necessary to provide an apparatus
for removing the amorphous polymer, which is quite
disadvantageous from the industrial point of view.

Accordingly, if a process entirely free from
formation of such an amorphous polymer or a process for
10 forming only a slight quantity of amorphous polymer is
discovered, it will be quite advantageous.

On the other hand, in such a polymerization
process as above, catalyst residue remains in the
resulting α -olefin polymer, which makes troubles in
15 various points such as stability, processability, etc. of
the α -olefin polymer. Thus, it is necessary to provide
an apparatus for removing the catalyst residue and
stabilizing the polymer.

This fault can be overcome by increasing the
20 catalytic activity expressed by the weight of formed
 α -olefin polymer per unit weight of catalyst. By this
increase, the apparatus for removing catalyst residue
becomes unnecessary and production cost of α -olefin
polymer can be reduced.

25 The present inventors previously proposed a
process which comprises treating, with an ester compound,
an ether compound and titanium tetrachloride, a solid
product obtained by reducing an alkoxytitanium compound.

- 1 with an organomagnesium compound in the presence of an
organic silicon compound having Si-O bond [U.S. Patent
4,672,050, JP-A-1-319508].

The catalyst obtained according to this
5 process could overcome the above-mentioned fault in
stereospecificity and catalyst activity.

The solid catalyst component obtained by the
above-mentioned process is usually dried until it reaches
a fluidizable state and thereafter put to use, for the
10 reason of convenience for use, in many cases.

As a drier used for drying powdery materials,
various driers have been proposed. For example, as
material-standing and material-conveyance type driers;
vacuum box type drier, freeze dried box type drier,
15 ordinary pressure drum drier, vacuum drum drier, vertical
drier, cylindrical drier and band drier can be
referred to. As material-agitation type driers; ventila-
tion rotary drier, ventilation agitation drier, fluidized
bed drier, cylindrical agitation drier, multi-stage disc
20 drier and grooved agitation drier can be
referred to. Further, as hot air conveyance type driers,
spray drier, air stream drier and the like can be referred
to. A variety of driers constituted of combination of
these driers are also used. In the case of a solid
25 catalyst component for olefin polymerization which must be
handled in an inert gas and made free from organic solvent
by a drying process, there are often used driers in which
ventilation and agitation are combined such as ventilation

1 rotary drier, ventilation agitation drier, gas stream
drier and fluidized bed drier, with consideration of
safety, convenience in handling and cost.

5 However, a solid catalyst component obtained by
the above-mentioned process has a problem that fine powder
is formed by friction between particles in the process of
drying treatment accompanied by powder flow. Such a solid
catalyst component containing fine powder deteriorates the
particle size distribution of the resulting α -olefin
10 polymer which copies the shape of the solid catalyst
component, and thereby forms a fine powdery polymer.
Further, the fine powder agglomerates in the course of
polymerization to clog the lines of polymer-producing
apparatus and makes it impossible to produce a polymer
15 stably. Accordingly, elimination of such a fine powder
from the solid catalyst component will bring about a great
merit.

As a technique for improving the crushability of
solid catalyst component, there has been disclosed a
20 method which comprises preliminarily polymerizing an
olefin in the presence of a solid catalyst component and
thereby preventing the formation of fine powder at the
time of supplying a slurry of the solid catalyst component
into polymerization reactor by means of a circulating pump

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[JP-A- 57-

151602]. However, such a method has a problem that the
solid catalyst component comes to coexist with an organo-
aluminum compound during the period from completion of

1 preliminary polymerization to its feeding into polymeriza-
tion reactor and, during this period of storage, its
activity is deteriorated with the lapse of time. Further,
there has been disclosed a method
5 [JP-A- 63-89509] which comprises
inserting a step of preliminary polymerization of α -olefin
into the step of synthesizing a solid-catalyst component
and thereafter treating the catalyst component with a
titanium compound to obtain a solid catalyst component in
10 order to prevent the pulverization of the particles of
solid catalyst component in the course of synthesizing the
solid catalyst component. However, even if such a method
is applied to the technique previously proposed by the
prior arts [U.S. Patent 4,672,050,
15 JP-A- 1-319508], the
preliminarily polymerized polymer dissolves into solvent
at the time of treating the solid catalyst component with
a titanium compound and filtration cannot be effected
satisfactorily or the remaining organoaluminum compound
20 reacts with the titanium compound to form an undesirable
compound decreasing the polymerization activity and
stereospecificity.

In view of the above-mentioned state of things,
25 the problem to be solved by this invention or the object
of this invention is to provide a process for producing a
solid catalyst component for use in the polymerization of

1 α -olefin having so high a catalytic activity and a
stereospecificity as to make it unnecessary to remove
catalyst residue and amorphous polymer, which is improved
in crush resistance, particle characteristics and
5 convenience to handle.

Thus, this invention relates to a solid catalyst
component for use in the polymerization of α -olefins
obtained by reducing a titanium compound represented by
general formula $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$ wherein R^1 represents a
10 hydrocarbon group having 1 to 20 carbon atoms, X repre-
sents a halogen atom, and n represents a number satisfying
 $0 < n \leq 4$, with an organomagnesium compound in the
presence of an organic silicon compound having a Si-O bond
to obtain a solid product, treating the solid product with
15 an ester compound, thereafter treating it with a mixture
of an ether compound and titanium tetrachloride or a
mixture of an ether compound, titanium tetrachloride and
an ester compound to obtain a trivalent titanium compound-
containing solid catalyst precursor, and treating the
20 solid catalyst precursor with a small quantity of an
olefin in the presence of an organoaluminum compound.

By adopting the process of this invention, the
above-mentioned object and particularly an improvement of
the solid catalyst particle in crush resistance can be
25 achieved.

Fig. 1 is a particle size distribution curve of

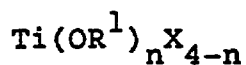
1 polypropylene powder, wherein the dotted line illustrates
a particle size distribution curve of polypropylene powder
obtained in Example 1, and the solid line illustrates a
particle size distribution curve of the polypropylene
5 powder obtained in Comparative Example 1.

Fig. 2 is a flow chart diagram for facilitating
understanding of this invention. The flow chart is
nothing more than a typical example of the embodiments of
this invention, and this invention is by no means limited
10 thereby.

Next, this invention will be explained below
more concretely.

(a) Titanium Compound

15 The titanium compound used in this invention is
represented by the following general formula:



wherein R^1 represents a hydrocarbon group having 1 to 20
carbon atoms, X represents a halogen atom, and n
represents a number satisfying $0 < n \leq 4$.

20 Concrete examples of R^1 include alkyl groups
such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl,
amyl, isoamyl, hexyl, heptyl, octyl, decyl and dodecyl;

1 aryl groups such as phenyl, cresyl xylyl and
naphthyl; cycloalkyl groups such as cyclo-
hexyl. and cyclopentyl; allyl groups such as
propenyl ; and aralkyl groups such as benzyl.

5 Among them, alkyl groups having 2 to 18
carbon atoms and aryl groups having 6 to 18 carbon atoms
are preferable, and straight chain alkyl groups having 2
to 18 carbon atoms are particularly preferred. It is also
possible to use two or more kinds of titanium compounds
10 different in OR^1 .

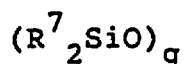
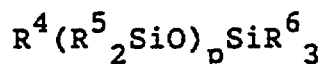
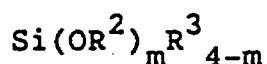
Examples of the halogen atom represented by X
include chlorine, bromine and iodine. Among them,
chlorine give a particularly good result.

The value of n in the general formula
15 $Ti(OR^1)_nX_{4-n}$ is a value satisfying $0 < n \leq 4$, preferably
 $2 \leq n \leq 4$, and particularly preferably $n = 4$.

As the method for synthesizing the titanium
compound represented by general formula $Ti(OR^1)_nX_{4-n}$
($0 < n \leq 4$), well known methods can be used. For example,
20 a method of reacting $Ti(OR^1)_4$ and TiX_4 at a predetermined
ratio, or a method of reacting TiX_4 with a predetermined
quantity of the corresponding alcohol can be used.

(b) Organic Silicon Compound Having Si-O Bond

The organic silicon compound having Si-O bond
25 used in synthesizing the solid catalyst component of this
invention is represented by the following general formulas:



- 1 where R^2 represents a hydrocarbon group having 1 to 20 carbon atoms, R^3 , R^4 , R^5 , R^6 and R^7 each represents a hydrocarbon group having 1 to 20 carbon atoms or a hydrogen atom, m represents a number satisfying $0 < m \leq 4$,
 5 p represents an integer of 1 to 1,000, and q represents an integer of 2 to 1,000.

Concrete examples of the organic silicon compound include tetramethoxysilane, dimethyldimethoxysilane, tetraethoxysilane, triethoxyethylsilane,
 10 diethoxydiethylsilane, ethoxytriethylsilane, tetraisopropoxysilane, diisopropoxydiisopropylsilane, tetrapropoxysilane, dipropoxydipropylsilane, tetrabutoxysilane, dibutoxydibutylsilane, dicyclopentoxydiethylsilane, diethoxydiphenylsilane, cyclohexyloxytrimethylsilane,
 15 phenoxytrimethylsilane, tetraphenoxysilane, triethylxyphenylsilane, hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, octaethyltrisiloxane, dimethylpolysiloxane, diphenylpolysiloxane, methylhydropolysiloxane, and phenylhydropolysiloxane.

20 Among these organic silicon compounds,

- 1 alkoxy silane compounds represented by general formula
 $\text{Si}(\text{OR}^2)_m \text{R}^{2}_{4-m}$ are preferable, wherein m preferably
satisfies $1 \leq m \leq 4$. Among them, tetraalkoxy silane
compounds wherein $m = 4$ are particularly preferable.

5 (c) Organomagnesium Compounds

- Next, the organomagnesium compound used in this
invention may be any forms of organomagnesium compounds,
so far as they have a magnesium-carbon bond. Among them,
Grignard compounds represented by general formula R^8MgX ,
10 wherein R^8 represents a hydrocarbon group having 1 to 20
carbon atoms and X represents a halogen, and dialkyl- or
diaryl-magnesium compounds represented by general formula
 $\text{R}^9\text{R}^{10}\text{Mg}$, wherein R^9 and R^{10} each represents a hydrocarbon
group having 1 to 20 carbon atoms, are particularly
15 preferable. In these formulas, R^8 , R^9 and R^{10} may be
identical or different one another and each represents an
alkyl, aryl, aralkyl or alkenyl group having 1 to 20
carbon atoms such as methyl, ethyl, propyl, isopropyl,
butyl, sec-butyl, tert-butyl, amyl, isoamyl, hexyl, octyl,
20 2-ethylhexyl, phenyl and benzyl.

- Concrete examples of the Grignard compound
include methylmagnesium chloride, ethylmagnesium chloride,
ethylmagnesium bromide, ethylmagnesium iodide, propyl-
magnesium chloride, propylmagnesium bromide, butyl-
25 magnesium chloride, butylmagnesium bromide, sec-butyl-
magnesium chloride, sec-butylmagnesium bromide, tert-
butylmagnesium chloride, tert-butylmagnesium bromide,

1 amylmagnesium chloride, isoamylmagnesium chloride,
phenylmagnesium chloride, phenylmagnesium bromide and the
like. Concrete examples of the compound represented by
 $R^9R^{10}Mg$ include diethylmagnesium, dipropylmagnesium,
5 diisopropylmagnesium, dibutylmagnesium, di-sec-butyl-
magnesium, di-tert-butylmagnesium, butyl-sec-butyl-
magnesium, diamylmagnesium, and diphenylmagnesium.

As the solvent used in the synthesis of the
above-mentioned organomagnesium compounds, etheral
10 solvents such as diethyl ether, dipropyl ether, diiso-
propyl ether, dibutyl ether, diisobutyl ether, diamyl
ether, diisoamyl ether, dihexyl ether, dioctyl ether,
diphenyl ether, dibenzyl ether, phenetole, anisole,
tetrahydrofuran and tetrahydropyran can be
15 referred to. Hydrocarbon solvents such as hexane,
heptane, octane, cyclohexane, methylcyclohexane, benzene,
toluene and xylene and mixtures of an etheral
solvent and a hydrocarbon solvent are also usable.
Preferably, the organomagnesium compound is used in the
20 form of a solution in a solution of ether compound. As
the ether compound used for this purpose, ether compounds
having 6 or more carbon atoms in one molecule and ether
compounds having a cyclic structure can be referred to.

From the viewpoint of catalytic activity, it is
25 particularly preferable to use a Grignard compound
represented by R^8MgCl in the form of a solution in an
ether compound.

1 It is also possible to use the above-mentioned
organomagnesium compound in the form of a hydrocarbon-
soluble complex with an organometallic compound. Examples
of said organometallic compound include organic compounds
5 of Li, Be, B, Al and Zn.

(d) Ester Compounds

The ester compounds which can be used in this
invention are esters of mono- and poly-valent carboxylic
acids, which include aliphatic carboxylic esters, olefinic
10 carboxylic esters, alicyclic carboxylic esters and
aromatic carboxylic esters.

Concrete examples of the ester compound include
methyl acetate, ethyl acetate, phenyl acetate, methyl
propionate, ethyl propionate, ethyl butyrate, ethyl
15 valerate, methyl acrylate, ethyl acrylate, methyl
methacrylate, ethyl benzoate, butyl benzoate, methyl
toluate, ethyl toluate, ethyl anisate, diethyl succinate,
dibutyl succinate, diethyl malonate, dibutyl malonate,
dimethyl maleate, dibutyl maleate, diethyl itaconate,
20 dibutyl itaconate, monoethyl phthalate, dimethyl
phthalate, methyl ethyl phthalate, diethyl phthalate,
dipropyl phthalate and diphenyl phthalate.
phthalate, diisobutyl phthalate, diheptyl phthalate,
dioctyl phthalate, diphenyl phthalate and the like.

25 Among these ester compounds, olefinic carboxylic
esters, such as methacrylic esters and maleic esters, and
phthalic esters are preferable, and phthalic diesters are

1 particularly preferable.

(e) Ether Compounds

Next, as the ether compound used in this invention, dialkyl ethers such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diamyl ether, diisoamyl ether, dineopentyl ether, dihexyl ether, dioctyl ether, methyl butyl ether, methyl isoamyl ether and ethyl isobutyl ether are preferable. Among them, dibutyl ether and diisoamyl ether are particularly
10 preferable.

(f) Organoaluminum Compounds

The organoaluminum compound used in this invention has at least one aluminum-carbon bond in one molecule. Typical examples of the organoaluminum compound.
15 are those represented by the following general formulas:



wherein R^{11} , R^{12} , R^{13} , R^{14} and R^{15} each represents a hydrocarbon group having 1 to 20 carbon atoms, Y represents halogen, hydrogen or an alkoxy group, and γ represents a number satisfying $2 \leq \gamma \leq 3$.

20 Concrete examples of the organoaluminum compound

1 include trialkylaluminums such as triethylaluminum,
triisobutylaluminum and trihexylaluminum;
dialkylaluminum hydrides such as diethylaluminum hydride
diisobutylaluminum hydride; mixtures of
5 trialkylaluminum and dialkylaluminum halide; mixtures of
trialkylaluminum and alkylaluminum alkoxide; and
alkylalumoxanes such as tetraethyldialumoxane and tetra-
butyldialumoxane.

Among these organoaluminum compounds, trialkyl-
10 aluminums, mixtures of trialkylaluminum and dialkyl-
aluminum halide, and alkylalumoxanes are preferable, and
among them triethylaluminum, triisobutylaluminum, a
mixture of triethylaluminum and diethylaluminum chloride,
and tetraethyldialumoxane are particularly preferable.

15 (g) Olefins

The olefins used in this invention for treatment
of solid catalyst precursor are those having 2 to 20
carbon atoms. Concrete examples of the olefin include
ethylene, propylene, butene-1, pentene-1, hexene-1,
20 3-methylbutene-1, 3-methylpentene-1, 4-methylpentene-1,
octene-1, decene-1, and dodecene-1. Among these
olefins, those having 2 through 8 carbon atoms are
preferable, and those having 2 through 5 carbon atoms are
particularly preferable.

25 (h) Electron Donors

When a solid catalyst precursor is treated with

1 a small quantity of olefin in the presence of organo-
aluminum compound in this invention, the treatment may be
carried out in the presence of an electron donor, if
desired. Said electron donor is selected from the group
5 consisting of organic silicon compounds having Si-OR^{16}
bond wherein R^{16} represents a hydrocarbon group having 1
to 20 carbon atoms or a Si-N-C bond, aromatic carboxylic
ester compounds and sterically hindered amines.

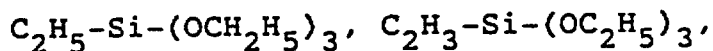
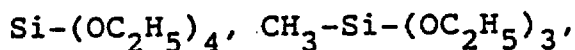
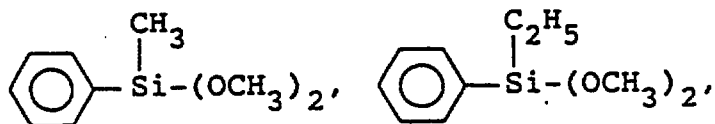
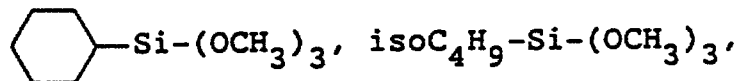
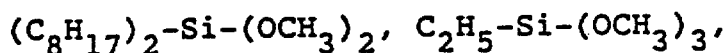
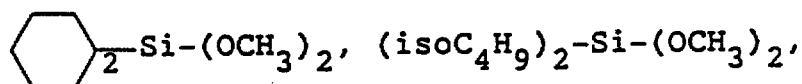
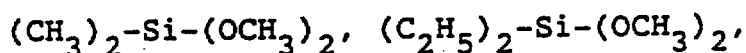
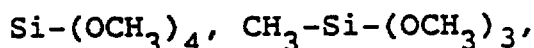
As the organic silicon compound, alkoxy silane
10 compounds represented by general formula $\text{R}^{17}_t\text{Si}(\text{OR}^{16})_{4-t}$
wherein R^{17} and R^{16} each represents a hydrocarbon group
having 1 to 20 carbon atoms and t represents a number
satisfying $0 \leq t \leq 3$ are preferably used.

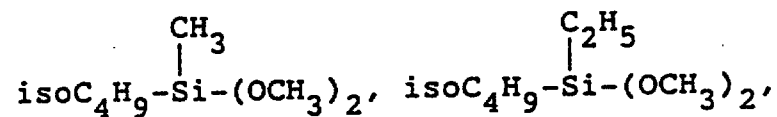
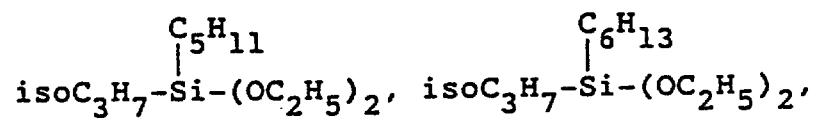
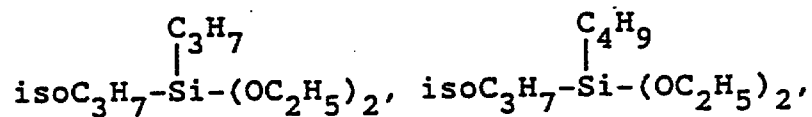
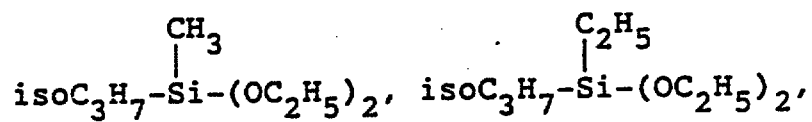
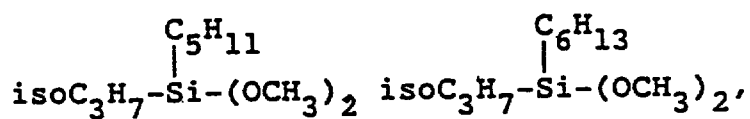
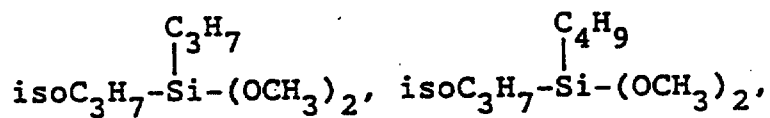
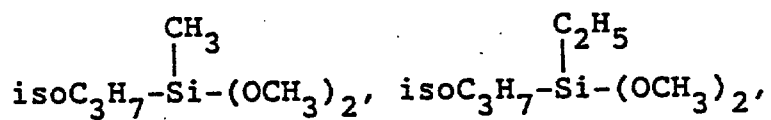
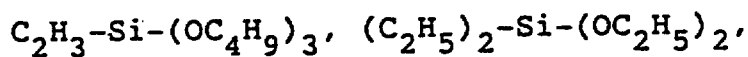
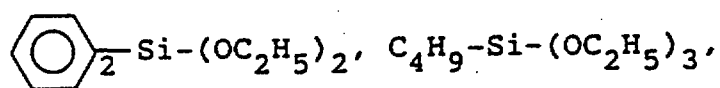
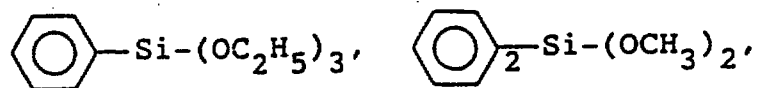
As the aromatic carboxylic ester compound,
15 methyl benzoate, ethyl benzoate, propyl benzoate,
isopropyl benzoate, butyl benzoate, phenyl benzoate,
methyl toluylate, ethyl toluylate, methyl anisate, ethyl
anisate, monoethyl phthalate, dimethyl phthalate, methyl
ethyl phthalate, diethyl phthalate, dipropyl phthalate,
20 diisopropyl phthalate, dibutyl phthalate, diisobutyl
phthalate, diheptyl phthalate, dioctyl phthalate and diphenyl
phthalate can be referred to.

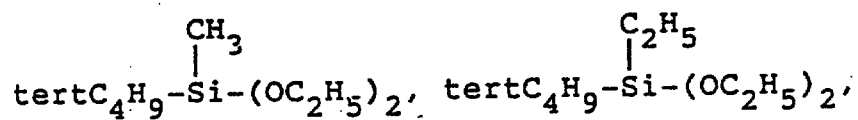
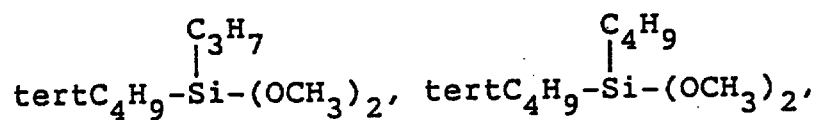
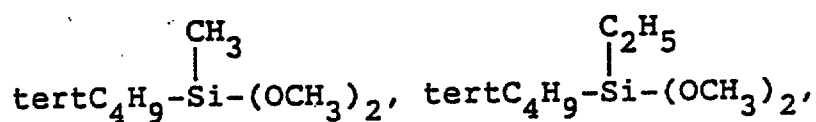
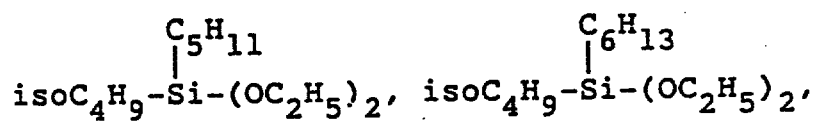
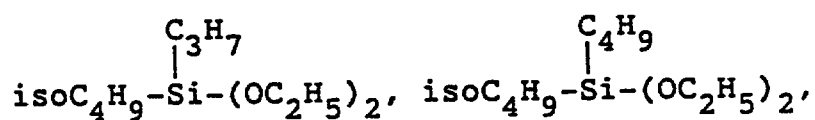
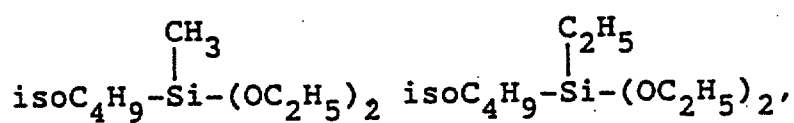
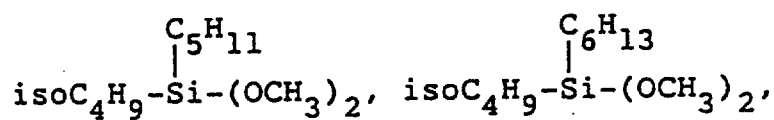
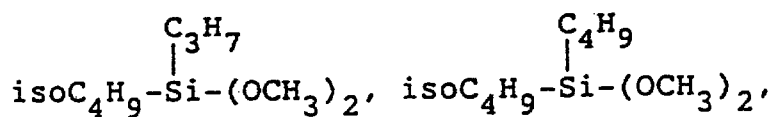
As the sterically hindered amine, 2,6-substi-
tuted piperidines, 2,5-substituted pyrrolidines, and
25 substituted methylenediamine compounds such as
 N,N,N',N' -tetramethylmethylenediamine can be
referred to.

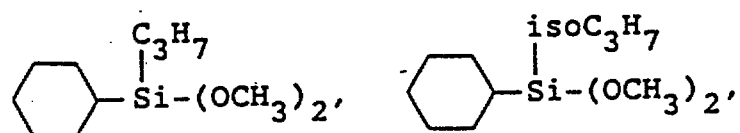
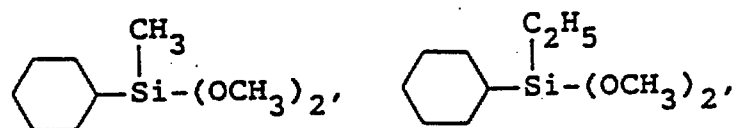
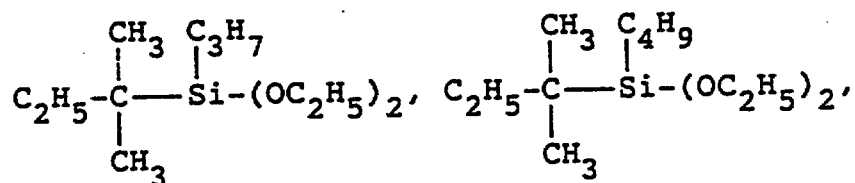
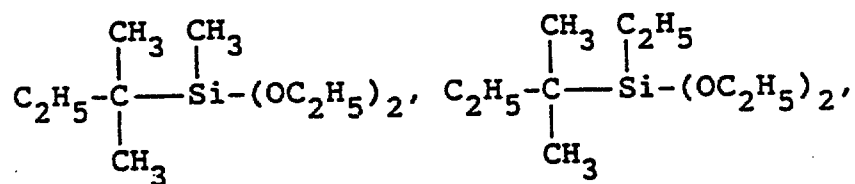
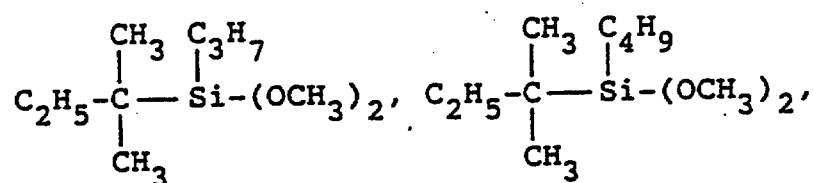
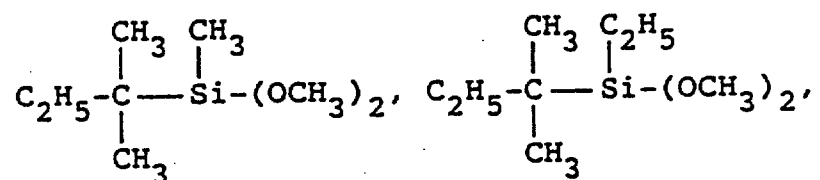
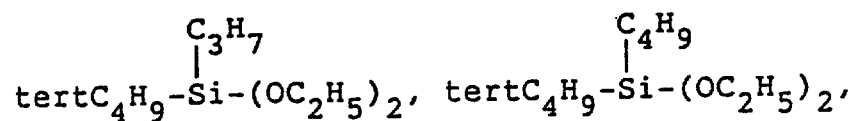
1. Among these electron donors, alkoxysilane compounds represented by general formula $R^{17}_t Si(OR^{16})_{4-t}$ and 2,6-substituted piperidines give a particularly good result.

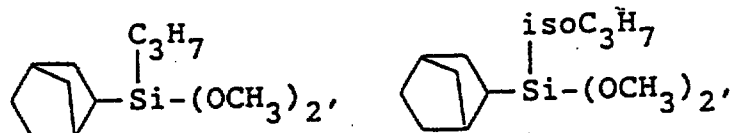
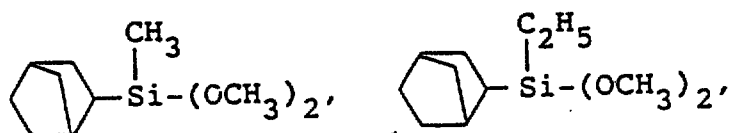
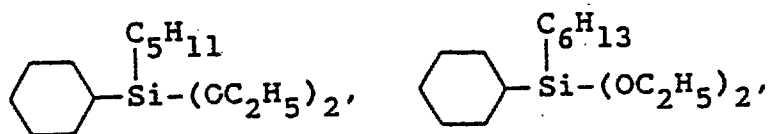
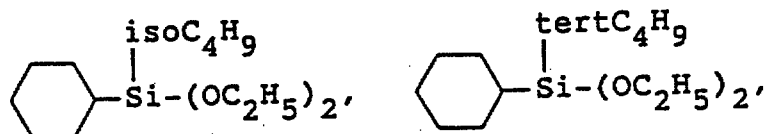
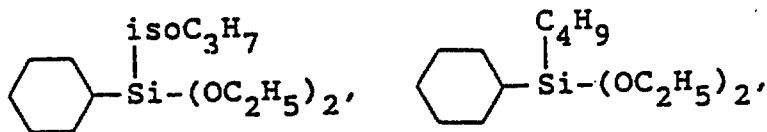
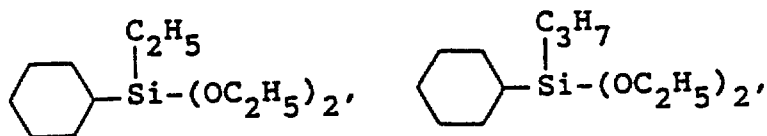
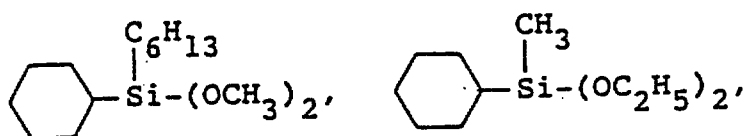
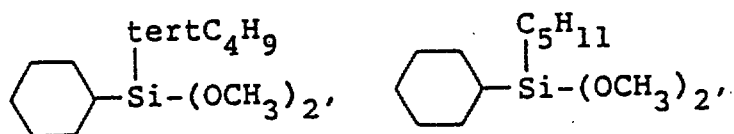
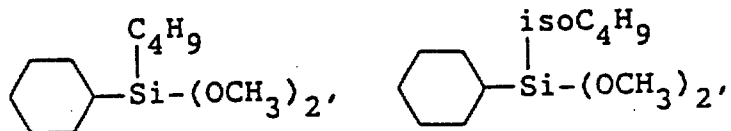
5 Concrete examples of said alkoxysilane compound include the followings:

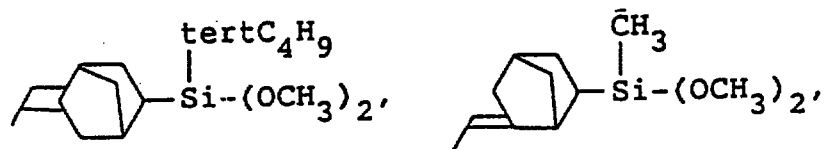
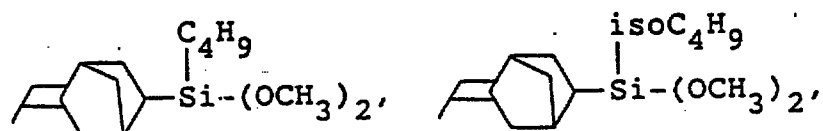
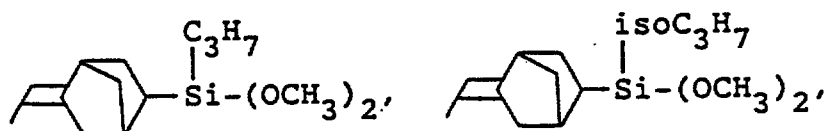
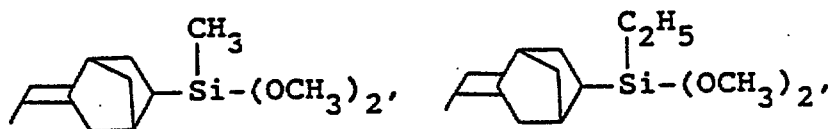
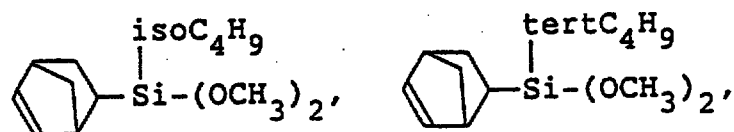
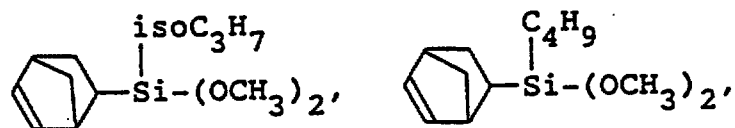
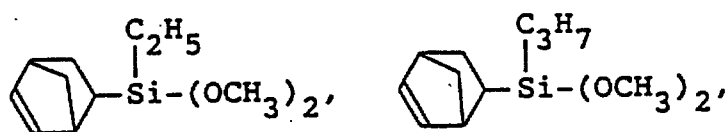
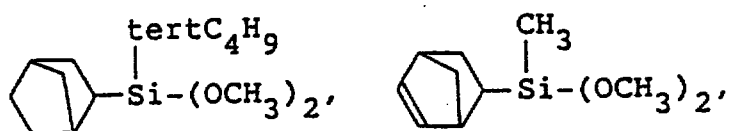
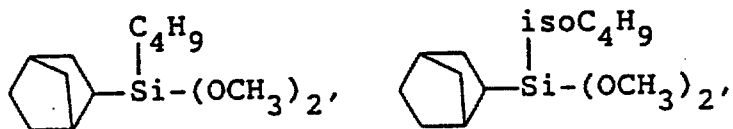


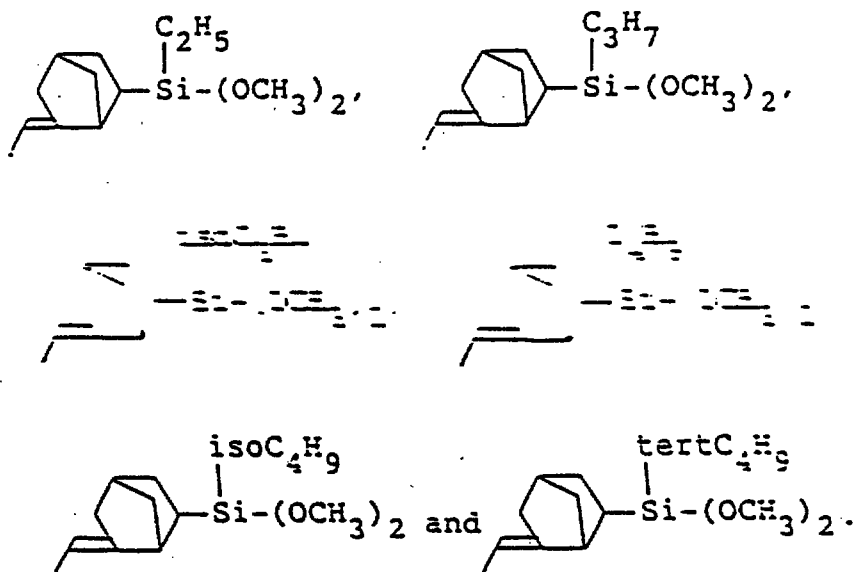












1

Examples of the 2,6-substituted piperidine include 2,2,6,6-tetramethylpiperidine.

(i) Synthesis of Solid Catalyst Component

5 The solid catalyst component of this invention is synthesized by reducing a titanium compound with an organomagnesium compound in the presence of an organic silicon compound to form a solid product, treating the solid product first with an ester compound and subsequent-

10 ly with a mixture of an ether compound and titanium tetrachloride or with a mixture of an ester compound, an ether compound and titanium tetrachloride to form a trivalent titanium compound-containing solid catalyst precursor, and then treating the latter with a small

15 quantity of olefin in the presence of an organoaluminum compound.

The synthetic reactions are all performed in an

1 atmosphere of inert gas such as nitrogen, argon or the like or in an atmosphere of an olefin.

As the method for reducing a titanium compound with an organomagnesium compound, a method which comprises
5 adding an organomagnesium compound to a mixture of a titanium compound and an organic silicon compound or an inverse method which comprises adding a mixture of a titanium compound and an organic silicon compound to a solution of an organomagnesium compound may both be
10 adopted. Of these two methods, the method of adding an organomagnesium compound to a mixture of titanium compound and organic silicon compound is more preferable from the viewpoint of catalytic activity.

Preferably, the titanium compound and the
15 organic silicon compound are used in the form of a solution or a dilution in an appropriate solvent.

As said solvent, aliphatic hydrocarbons such as hexane, heptane, octane and decane, aromatic hydrocarbons such as toluene and xylene,
20 alicyclic hydrocarbons such as cyclohexane, methylcyclohexane and decaline and ether compounds such as diethyl ether, dibutyl ether, diisooamyl ether and tetrahydrofuran are used.

The temperature of the reduction is -50°C to
25 70°C , preferably -30°C to 50°C , and particularly preferably -25°C to 35°C . If the temperature of reduction is too high, catalytic activity is deteriorated.

The production of a solid product by the

1 reduction of titanium compound with an organomagnesium
compound may be carried out in the presence of a porous
material made of inorganic oxide, organic polymer or the
like in order to impregnate the solid product into the
5 porous material.

As said porous material, those having a pore
volume of 0.3 ml/g or above at a pore radius of 200 to
2,000 angstroms (Å) and having a mean particle diameter
of 5 to 300 μm are preferable.

10 As said porous inorganic oxide, SiO_2 , Al_2O_3 ,
 MgO , TiO_2 , ZrO_2 , SiO_2 , Al_2O_2 , $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and
 $\text{MgO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ can be referred to.

As said porous organic polymer, polystyrene
type, polyacrylic ester type, polymethacrylic ester type,
15 polyacrylonitrile type, polyvinyl chloride type and
polyolefin type polymers can be referred to, of which
typical examples include polystyrene, styrene-divinyl-
benzene copolymer, styrene-N,N'-alkylenedimethacrylamide
copolymer, styrene-ethylene glycol dimethyl methacrylate
20 copolymer, methyl polyacrylate, ethyl polyacrylate, methyl
acrylate-divinylbenzene copolymer, ethyl acrylate-divinyl-
benzene copolymer, polymethyl methacrylate, methyl
methacrylate-divinylbenzene copolymer, polyethylene glycol
dimethyl methacrylate, polyacrylonitrile, acrylonitrile-
25 divinylbenzene copolymer, polyvinyl chloride, polyvinyl-
pyrrolidine, polyvinylpyridine, ethylvinylbenzene-divinyl-
benzene copolymer, polyethylene, ethylene-methyl acrylate
copolymer. and polypropylene. Among these porous

1 materials, SiO_2 , Al_2O_3 and polystyrene type polymers
are preferable.

Although the time of addition is not critical,
it is usually about 30 minutes to about 6 hours. After
5 completion of the reduction, a post reaction may be
carried out at a temperature of 20°C to 120°C for 0.5 to 6
hours.

As expressed in terms of atomic ratio of silicon
atom to titanium atom (Si/Ti), the organic silicon
10 compound is used in an amount of 1 to 50, preferably 3 to
30 and particularly preferably 5 to 25.

As expressed in terms of atomic ratio of the sum
of titanium and silicon atoms to magnesium atom
(Ti+Si/Mg), the organomagnesium compound is used in an
15 amount of 0.1 to 10, preferably 0.2 to 5.0, and
particularly preferably 0.5 to 2.0.

The solid product obtained by the reduction is
separated from liquid matter and several times washed with
an inert hydrocarbon solvent such as hexane and heptane.
20

The solid product thus obtained contains
trivalent titanium, magnesium and hydrocarbyloxy group,
and generally exhibits an amorphous character or a very
weak crystalline character. From the viewpoint of
25 catalytic performances, amorphous structure is more
preferable.

The solid product obtained by the above-
mentioned procedure is then treated with an ester compound.

1. The ester compound is used in an amount of 0.1 to 50 moles, preferably 0.3 to 20 moles and particularly preferably 0.5 to 10 moles, per one mole of the titanium atom in the solid product.

5 Per one mole of magnesium atom in the solid product, the ester compound is used in an amount of 0.01 to 1.0 mole, preferably 0.03 to 0.5 mole, and most preferably 0.05 to 0.4 mole. If the amount of the ester compound is excessively large, disintegration of solid
10 product particle takes place.

The treatment of the solid product with an ester compound may be carried out by any known methods capable of contacting both the materials such as slurry method, mechanical pulverization using ball mill, and the like.
15 However, mechanical pulverization is undesirable from the viewpoint of industry because it generates a large quantity of fine powder in the solid catalyst component and broadens its particle size distribution. Preferably, both the materials are contacted together in the presence
20 of a diluent.

As the diluent, aliphatic hydrocarbons such as pentane, hexane, heptane and octane, aromatic hydrocarbons such as benzene, toluene and xylene,

alicyclic hydrocarbons such as cyclohexane and
25 cyclopentane, and halogenated hydrocarbons such as 1,2-dichloroethane, and monochlorobenzene can be used. Among them, aromatic hydrocarbons and halogenated hydrocarbons are particularly preferable.

1 The diluent is used in an amount of 0.1 to 1,000
ml and preferably 1 to 100 ml, per 1 g of solid product.
The temperature of the treatment is -50°C to 150°C, and
preferably 0°C to 120°C. The time period of the treatment
5 is 10 minutes or longer, and preferably 20 minutes to 3
hours. After completion of the treatment, the mixture is
allowed to stand to separate the solid matter from the
liquid matter, and the solid matter is several times
washed with an inert hydrocarbon solvent to obtain an
10 ester-treated solid.

Next, the ester-treated solid is further treated
with a mixture of an ether compound and titanium tetra-
chloride. This treatment is preferably carried out in a
state of slurry. The solvents which can be used for
15 formation of the slurry include aliphatic hydrocarbons
such as pentane, hexane, heptane, octane and decane;

aromatic hydrocarbons such as toluene and xylene;

alicyclic hydrocarbons such as cyclohexane,
methylcyclohexane and decaline; and halogenated
20 hydrocarbons such as dichloroethane, trichloroethane,
trichloroethylene, monochlorobenzene, dichlorobenzene and
trichlorobenzene. Among them, halogenated
hydrocarbons and aromatic hydrocarbons are preferable.

Concentration of the slurry is 0.05 to 0.7 g
25 solid/ml solvent, and preferably 0.1 to 0.5 g solid/ml
solvent. Temperature of the reaction is 30°C to 150°C,
preferably 45°C to 120°C, and particularly preferably 60°C
to 100°C. Though the reaction time is not critical, it is

1 usually 30 minutes to 6 hours.

As the method for feeding the ester-treated solid, the ether compound and titanium tetrachloride, a method which comprises adding an ether compound and
5 titanium tetrachloride to an ester-treated solid and an inverse method which comprises adding an ester-treated solid to a solution containing an ether compound and titanium tetrachloride are both adoptable.

In the method of adding an ether compound and
10 titanium tetrachloride to an ester-treated solid, a method of adding an ether compound and thereafter adding titanium tetrachloride and a method of simultaneously adding an ether compound and titanium tetrachloride are preferable. Particularly preferably, a preliminarily prepared mixture
15 of ether compound and titanium tetrachloride is added to an ester-treated solid.

The reaction of the ester-treated solid with the ether compound and titanium tetrachloride may be carried out repeatedly twice or more. From the viewpoint of
20 catalytic activity and stereospecificity, it is preferable to repeat the reaction using a mixture of an ether compound and titanium tetrachloride at least twice.

The ether compound is used in an amount of 0.1 to 100 moles, preferably 0.5 to 50 moles and particularly
25 preferably 1 to 20 moles, per one mole of titanium atom in the solid product.

The titanium tetrachloride is added in an amount of 1 to 1,000 moles, preferably 3 to 500 moles and

1 particularly preferably 10 to 300 moles, per one mole of
the titanium atom in the solid product.

The treatment of the ester-treated solid with a
mixture of ether compound and titanium tetrachloride may
5 be carried out in the presence of an ester compound. The
ester compound for this purpose is used in an amount of 30
moles or less, preferably 15 moles or less and particular-
ly preferably 5 moles or less, per one mole of the
titanium atom in the solid product.

10 The trivalent titanium compound-containing solid
catalyst precursor obtained by the above-mentioned
procedure is subjected to a solid-liquid separation, and
then the solid matter is several times washed with an
inert hydrocarbon solvent such as hexane and heptane
15 and thereafter put to treatment with an olefin.

From the viewpoint of catalytic activity and
stereospecificity, it is preferable to wash the solid
matter having been separated from liquid matter at least
once with a large quantity of halogenated hydrocarbon
20 solvent such as monochlorobenzene or aromatic
hydrocarbon solvent such as toluene at a
temperature of 50°C to 120°C, then additionally wash it
with an aliphatic hydrocarbon solvent such as hexane
several times and thereafter put it to treatment
25 using an olefin.

Next, the solid catalyst precursor thus obtained
is treated with a small quantity of olefin in the presence
of an organoaluminum compound. This treatment is

1 preferably carried out in the state of a slurry. As the solvent used for forming the slurry, inert hydrocarbon solvents such as propane, butane, pentane, hexane, heptane and octane can be referred to.

5 The amount of the organoaluminum compound may be selected from wide range such as 0.5 to 700 moles per one mole of titanium atom in the solid catalyst precursor. However, 0.8 to 500 mole is preferable, and 1 to 200 moles is particularly preferable.

10 The amount of the olefin used for the treatment is 0.05 to 1,000 g, preferably 0.1 to 500 g and particularly preferably 0.2 to 200 g, per one gram of the solid catalyst precursor.

 Concentration of the slurry at the time of
15 treatment is preferably 1 to 500 g solid/liter solvent and particularly preferably 3 to 300 g solid/liter solvent. Temperature of the treatment is preferably -20°C to 100°C and particularly preferably 0°C to 80°C. Partial pressure of the olefin in gas phase at the time of the treatment is
20 0.01 to 20 kg/cm² and preferably 0.1 to 10 kg/cm².
Though the time of the treatment is not critical, it is usually 2 minutes to 15 hours.

 As the method for feeding the solid catalyst precursor, organoaluminum compound and olefin, a method
25 which comprises contacting a solid catalyst precursor with an organoaluminum compound and thereafter feeding an olefin and a method which comprises contacting a solid catalyst precursor with an olefin and thereafter feeding

1 an organoaluminum compound are both usable. As the method
for feeding the olefin, a method which comprises gradually
feeding an olefin while maintaining a predetermined
pressure in the treating tank and a method which comprises
5 wholly feeding the predetermined quantity of olefin at the
beginning are both usable.

In treating a solid catalyst precursor with a
small quantity of olefin in the presence of an organo-
aluminum compound, an electron donor may be added to the
10 system if desired. The amount of the electron donor is
0.01 to 400 moles, preferably 0.02 to 200 moles and
particularly preferably 0.03 to 100 moles, per one mole of
titanium atom in the solid catalyst precursor; and 0.005
to 5 moles, preferably 0.01 to 3 moles and particularly
15 preferably 0.015 to 1.0 mole per one mole of
organoaluminum compound.

The method for feeding the electron donor is not
critical, and it may be fed separately from the
organoaluminum compound or may be fed after a previous
20 contact with the organoaluminum compound. It is also
possible to previously react an electron donor with an
organoaluminum compound chemically and feed the reaction
product for the sake of treatment using an olefin.

The trivalent titanium compound-containing solid
25 catalyst component obtained by the above-mentioned
procedure is subjected to a solid-liquid separation and
thereafter either dried directly or washed several times
with an inert hydrocarbon solvent such as butane, pentane,

1 hexane or heptane and then dried. Subsequently,
it is used for polymerization.

The method of drying is not limited particularly, so far as it is carried out in an atmosphere of
5 inert gas such as argon. As a method for introducing heat at the time of drying, the methods of hot gas heat input, conduction heat input, radiation heat input and high frequency wave heat input are also usable. As the drying type of powder, material standing type,
10 material conveying type, material agitating type and hot gas conveying type are also usable. Concretely speaking, the drying can be effected by the use of vacuum box type drier, freeze drying apparatus, box type drier, ordinary pressure drum drier, vacuum drum drier, vertical drier,
15 cylindrical drier, band drier, ventilation rotary drier, ventilation agitation drier, fluidized bed drier, cylindrical agitation drier, multi-stage disc drier, grooved agitation drier, spray drier or gas stream drier.

Further, the drying can also be carried out by
20 the use of combination of these driers. Among these drying methods, a drying method using a drier in which ventilation and agitation are combined exhibits a particularly remarkable effect of this invention.

The solid catalyst component of this invention
25 is combined with an organoaluminum compound and an electron donor and put to use in polymerization of olefin. The organoaluminum compound and the electron donor used for this purpose can be selected from those

1 mentioned above in the paragraph of olefin-treatment of
solid catalyst precursor.

(j) Method for Polymerization of Olefin

The method for feeding the catalyst components
5 into polymerization reactor is not critical, so far as
they are fed in a water-free state in an inert gas such as
nitrogen, argon or the like.

The solid catalyst component, organoaluminum
compound and electron donor may be fed separately, or any
10 two of them may be previously contacted together and then
fed. It is also possible to feed an organoaluminum
compound and an electron donor after previously reacting
them chemically.

The polymerization can be carried out at a
15 temperature of -30°C to 300°C preferably -20°C to 240°C ,
particularly preferably 0°C to 120°C . Though pressure of
the polymerization is not critical, a pressure ranging
from about 3 atmospheres to about 2,000 atmospheres is
preferable from the viewpoint of industrial practicability
20 and economicity. As the process of polymerization,
continuous process and batch process are both adoptable.
Slurry polymerization or solution polymerization using an
inert hydrocarbon solvent such as propane, butane,
pentane, hexane, heptane or octane, liquid polymerization
25 using no solvent, and gas phase polymerization are also
adoptable. As the organoaluminum compound and electron
donor, the same compounds as used in the previous steps

1 can be used.

The α -olefins which can be polymerized with the polymerization catalyst component of this invention are those having 3 or more carbon atoms. Concrete
5 examples of the α -olefin include propylene, butene-1, pentene-1, hexene-1, 3-methylbutene-1, 3-methylpentene-1, 4-methylpentene-1, octene-1, decene-1 and dodecene-1,

although this invention is by no means limited by them. The polymerization according to this invention can
10 be practised in any modes of homopolymerization and copolymerization. In case of copolymerization, two or more species of olefins selected from the group consisting of ethylene and α -olefins are mixed together and contacted with the catalyst, whereby a copolymer can be
15 obtained. A heteroblock copolymerization in which the polymerization is carried out in two or more steps can also be effected easily. For regulating molecular weight of the polymer, a chain transfer agent such as hydrogen and the like can also be added.

20 Next, this invention will be illustrated in more detail by way of the following examples and comparative examples. This invention is by no means limited by the examples.

Example 1

25 (a) Synthesis of Organomagnesium Compound

After replacing inner atmosphere of a one liter flask equipped with a stirrer, a reflux condenser, a

1 dropping funnel and a thermometer with argon gas, 32.0 g
of sliced metallic magnesium for Grignard reagent was
introduced into the flask. After charging 120 g of butyl
chloride and 500 ml of dibutyl ether into the dropping
5 funnel, about 30 ml of the mixture was dropwise added onto
the magnesium in the flask to start a reaction. After
start of the reaction, the dropping was continued at 50°C
for 4 hours. After completion of dropping, the reaction
was continued for an additional one hour at 60°C. Then,
10 the reaction mixture was cooled to room temperature and
the liquid matter was separated from solid.

The butylmagnesium chloride dissolved in the
dibutyl ether was hydrolyzed with 1N sulfuric acid, and
the remaining sulfuric acid was back titrated with 1N
15 aqueous solution of sodium hydroxide to determine the
concentration of butylmagnesium chloride, using
phenolphthalein as an indicator. As the result, its
concentration was 2.1 moles/liter.

(b) Synthesis of Solid Product

20 After replacing inner atmosphere of a 500 ml
flask equipped with a stirrer, a dropping funnel and a
thermometer with argon gas, 240 ml of hexane, 6.70 g (19.7
mmoles) of tetrabutoxytitanium and 61.4 g (295 mmoles) of
tetraethoxysilane were charged and made into a uniform
25 solution. Then, 150 ml of the organomagnesium compound
synthesized in (a) was slowly dropped from the dropping
funnel over a period of 5.75 hours, while keeping the

1 inner temperature of the flask at 5°C. After completion
of dropping, the content of the flask was stirred at 20°C
for an additional one hour, and then the solid matter was
separated from liquid and twice washed with each 217 ml
5 portion of toluene. Then, a part of the solid was sampled
out and dried, and its composition was analyzed to reveal
that the solid product contained 2.0% by weight of
titanium atom, 34.1% by weight of ethoxy group and 3.1% by
weight of butoxy group.

10 Wide angle X ray diffraction chart, using Cu-Ka
ray, of the solid product exhibited no clear diffraction
peak at all, demonstrating its amorphous structure.

(c) Synthesis of Ester-Treated Solid

After completing the washing step of (b),
15 toluene was added into the flask to prepare 250 ml of
slurry. Then, 27.0 ml (101 mmoles) of diisobutyl
phthalate was added and reacted at 95°C for 30 minutes.

After the reaction, the solid matter was
separated from liquid and once washed with 217 ml of
20 toluene.

(d) Syhthesis of Solid catalyst Precursor

After completing the washing step of (c),
toluene was added into the flask to prepare 107 ml of a
slurry. Further, 1.2 ml (4.5 mmoles) of diisobutyl
25 phthalate, 2.3 ml (14 mmoles) of butyl ether and 90 ml

1 (820 mmoles) of titanium tetrachloride were added and
reacted at 95°C for 3 hours. After the reaction, the
solid matter was separated from liquid at 95°C and once
washed with 217 ml of toluene at that temperature. Then,
5 the above-mentioned treatment using diisobutyl phthalate,
butyl ether and titanium tetrachloride was repeated once
more under the same conditions as above, and the solid
matter was washed first three times with each 217 ml
portion of toluene at 95°C and thereafter three times with
10 each 194 ml portion of hexane at room temperature to
obtain a solid catalyst precursor. Then, 194 ml portion
of hexane was introduced to obtain a slurry containing a
solid catalyst precursor. One milliliter of the slurry
thus obtained contained 0.18 g of solid catalyst
15 precursor. The solid catalyst precursor contained 2.2% by
weight of titanium atom, 19.1% by weight of magnesium atom
and 12.2% by weight of phthalic ester.

(e) Synthesis of Solid Catalyst Component

After replacing inner atmosphere of a 300 ml
20 flask equipped with a stirrer and a thermometer, with
argon gas, 34 ml of the slurry containing a solid catalyst
precursor which had been obtained in (d), 156 ml of
hexane, 9.0 mmoles of triethylaluminum and 1.35 mmoles of
phenyltrimethoxysilane were charged, and then inner
25 atmosphere of the flask was replaced with propylene gas.
Further, 8 g of propylene gas was fed into the flask over
a period of 33 minutes at room temperature, after which

1 inner atmosphere of the flask was again replaced with
argon gas, and stirring was continued for one hour.

After completion of the reaction, the solid
matter was separated from liquid and dried under a stream
5 of argon gas with stirring at 75°C for 2 hours to obtain
12.5 g of a solid catalyst component. It contained 0.34%
by weight of hydrocarbon solvent and 49% by weight of
solid catalyst precursor.

(f) Polymerization of Propylene

10 After replacing inner atmosphere of a stainless
steel autoclave equipped with a magnetic stirrer and a
thermometer having a capacity of 130 ml with argon gas,
0.57 mmole of triethylaluminum, 0.057 mmole of phenyl-
triethoxysilane, 10.1 mg the solid catalyst component
15 obtained in (e) and 80 ml of liquefied propylene were
charged into the autoclave.

While stirring the content of the autoclave, it
was kept at 60°C for one hour. After discharging the
excessive propylene, the formed polypropylene was
20 air-dried for 24 hours. Thus, 16.36 g of polypropylene
was obtained.

This means that yield (g) of polypropylene per
one gram of solid catalyst component (hereinafter referred
to as "PP/cat") was 1,620.

25 When the polypropylene powder thus obtained was
extracted with boiling heptane for 6 hours, the percentage
of residue [hereinafter referred to as "IX" (% by weight)]

1 was 98.5 (% by weight). Bulk density [hereinafter referred to as "BD" (g/ml)] of the polypropylene powder was 0.47 (g/ml).

(g) Measurement of Particle Size Distribution of
5 Polypropylene Powder

The polypropylene powder obtained in (f) was fractionated by means of JIS Standard Sieve having a mesh size of 88 to 1,400 μ m. The polymers remaining on
10 sieves were weighed, and their proportions to total polymer weight were determined and cumulated from the side of smaller particle diameter. The results of the sieving were shown in Table 1 and Fig. 1 as cumulative fractions (% by weight). Bulk densities (BD) are also shown in Table 1.

15 Comparative Example 1

(a) Drying of Solid Catalyst Precursor

After replacing a 200 ml flask equipped with a stirrer with argon gas, 27 ml of the slurry containing a solid catalyst precursor, obtained in Example 1(d), was
20 added into the flask and the solid catalyst precursor was separated from liquid by evacuating the liquid through glass filter which was connected with tube and inserted into the slurry. Then, the residual catalyst precursor was dried with stirring under a stream of argon gas at
25 75°C for 2 hours to obtain 4.8 g of a solid catalyst precursor. It contained 0.59% by weight of hydrocarbon

1 solvent.

(b) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst precursor
5 obtained in (a) of this example was used as solid catalyst component. The results were as follows: PP/cat = 3,570, IY = 97.7% by weight, BD = 0.44 g/ml.

Particle size distribution of the polypropylene powder thus obtained was determined in the same manner as
10 in Example 1(g). The results are shown in Table 1 and Fig. 1.

Since no treatment using small quantity of olefin was carried out in this example, the cumulative fraction of polymer having smaller particle diameter
15 having remained on the sieves up to a sieve dimension of 125 μ m was 2.67% by weight, indicating that the proportion of fine powdery polymer was much greater than in Example 1. Further, the polymer had a low bulk density.

Example 2

20 (a) Synthesis of Solid Catalyst Component

A solid catalyst component was synthesized in the same manner as in Example 1(e), except that the quantity of propylene gas fed into the flask was 5 g. The solid catalyst component thus obtained contained 0.42% by
25 weight of hydrocarbon solvent and 61% by weight of solid catalyst precursor.

1 (b) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst component obtained in (a) of this example was used.

5 The results were as follows: PP/cat = 1,980, IY = 97.1% by weight, BD = 0.46 g/ml.

Particle size distribution of the polypropylene powder thus obtained was determined in the same manner as in Example 1(g). The results are shown in Table 1.

10 Example 3

(a) Preparation of Organoaluminum Component

After replacing inner atmosphere of a 100 ml flask equipped with a stirrer and a thermometer, with argon gas, 41.7 ml of heptane, 5.74 g (50 mmoles) of
15 triethylaluminum and 1.49 g (7.5 moles) of phenyltri-methoxysilane were charged and reacted at 60°C for 6 hours with stirring.

(b) Synthesis of Solid Catalyst Component

A solid catalyst component was synthesized in
20 the same manner as in Example 2(a), except that the triethylaluminum and phenyltrimethoxysilane used in Example 2(a) were replaced with the reaction product of (a) of this example. The solid catalyst component thus obtained contained 0.35% by weight of hydrocarbon solvent
25 and 57% by weight of solid catalyst precursor.

1 (c) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst component obtained in (b) of this example was used, and the
5 triethylaluminum and phenyltrimethoxysilane used in Example 1(f) were replaced with the reaction product obtained in (a) of this example. The results were as follows: PP/cat = 2,750, IY = 99.1% by weight, BD = 0.46 g/ml. Further, particle size distribution of the
10 polypropylene powder obtained herein was determined in the same manner as in Example 1(g) to obtain the results shown in Table 1.

Example 4

(a) Synthesis of Solid Catalyst Component

15 After replacing inner atmosphere of a 300 ml flask equipped with a stirrer and a thermometer with argon gas, 36 ml of the slurry containing a solid catalyst precursor, obtained in Example 1(d), was charged together with 161 ml of hexane and 9.2 mmoles of triethylaluminum.
20 Then, ethylene gas was introduced into the mixture at ordinary pressure at a rate of 300 ml/minute, over a period of 15 minutes. After completion of the reaction, the solid matter was separated from liquid and dried with stirring at 75°C for 2 hours under a stream of argon gas
25 to obtain 10.0 g of a solid catalyst component. The solid catalyst component contained 0.56% by weight of hydrocarbon solvent and 60% by weight of solid catalyst

1 precursor.

(b) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst component
5 obtained in (a) of this example was used. The results were as follows: PP/cat = 1,900, IV = 92.3% by weight, BD = 0.46 g/ml.

Further, particle size distribution of the polypropylene powder obtained herein was determined in the
10 same manner as in Example 1(g) to obtain the results shown in Table 1.

Example 5

(a) Synthesis of Solid Catalyst Component

A solid catalyst component was synthesized in
15 the same manner as in Example 2(a), except that the phenyltrimethoxysilane used in Example 2(a) was replaced with cyclohexylethyldimethoxysilane. The solid catalyst component thus obtained contained 0.47% by weight of hydrocarbon solvent and 62% by weight of solid catalyst
20 precursor.

(b) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst component obtained in (a) of this example was used and the
25 phenyltriethoxysilane was replaced with cyclohexylethyl-

1 dimethoxysilane. The results were as follows: PP/cat =
2,250, IY = 99.0% by weight, BD = 0.46 g/ml. Further,
particle size distribution of the polypropylene powder
obtained herein was determined in the same manner as in
5 Example 1(g) to obtain the results shown in Table 1.

Example 6

(a) Synthesis of Solid Catalyst Component

A solid catalyst component was synthesized in
the same manner as in Example 2(a), except that the
10 phenyltrimethoxysilane used in Example 2(a) was replaced
with t-butylmethyldimethoxysilane. The solid catalyst
component thus obtained contained 0.39% by weight of
hydrocarbon solvent and 57% by weight of solid catalyst
precursor.

15 (b) Polymerization of Propylene

Propylene was polymerized in the same manner as
in Example 1(f), except that the solid catalyst component
obtained in (a) of this example was used, and the phenyl-
triethoxysilane was replaced with t-butylmethyldimethoxy-
20 silane. The results were as follows: PP/cat = 2,070, IY =
99.5% by weight, BD = 0.46 g/ml. Further, particle size
distribution of the polypropylene powder obtained herein
was determined in the same manner as in Example 1(g) to
obtain the results shown in Table 1.

1 Example 7

(a) Synthesis of Solid Catalyst Component

A solid catalyst component was synthesized in the same manner as in Example 2(a), except that the 1.35
5 mmoles of phenyltrimethoxysilane used in Example 2(a) was replaced with 2.70 mmoles of 2,2,6,6-tetramethyl-piperidine. The solid catalyst component thus obtained contained 0.37% by weight of hydrocarbon solvent and 60% by weight of solid catalyst precursor.

10 (b) Polymerization of Propylene

Propylene was polymerized in the same manner as in Example 1(f), except that the solid catalyst component obtained in (a) of this example was used, and the 0.057
mmole of phenyltriethoxysilane used in Example 1(f) was
15 replaced with 0.114 mmole of 2,2,6,6-tetramethyl-piperidine. The results were as follows: PP/cat = 3,790, IY = 93.7% by weight, BD = 0.46 g/ml. Further, particle size distribution of the polypropylene powder obtained herein was determined in the same manner as in Example
20 1(g) to obtain the results shown in Table 1.

As has been mentioned above, the use of the solid catalyst component of this invention brings about the following effects:

(1) Since the solid catalyst component of this
25 invention has a very high catalytic activity per one titanium atom, coloration of polymer can be prevented and the contents of halogen and titanium atoms closely related

1 to corrosiveness of polymers can be minimized, even if no
particular procedure for removing catalyst residue is
provided. This makes the apparatus for removing catalyst
residue unnecessary and makes it possible to reduce the
5 production cost of α -olefin polymer.

(2) The use of the solid catalyst component of this
invention makes it possible to produce a very highly
stereospecific α -olefin polymer. Since only a very
small quantity of amorphous polymer is formed as
10 by-product, an α -olefin polymer excellent in mechanical
properties can be produced without removing amorphous
polymer.

(3) Since polymer having a low stereospecificity and
soluble in polymerization medium is formed only in a very
15 small quantity, there occur no troubles in process such as
deposition of polymer onto reactor, pipings, flash hopper,
etc. Further, since soluble polymer is formed only in a
small quantity, the starting monomer can be utilized
effectively.

20 (4) By the use of the solid catalyst component of
this invention, α -olefin polymers having a very high
bulk density can be produced. This makes it possible to
reduce the size of production apparatuses such as reactor
and thereby to enhance productivity greatly.

25 (5) Since the solid catalyst component of this
invention is excellent in crush resistance, formation of
fine powder from it is much prevented and it retains an
excellent particle size distribution. This means that

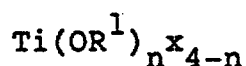
- 1 formation of fine powder α -olefin polymer can also be prevented, because the resulting α -olefin polymer resembles the solid catalyst component in shape. Accordingly, the troubles caused by fine powders such as
- 5 clogging in pipings, mass formation in reactor, etc. can be prevented from occurring.

Table 1

Dimension of sieve (µm)	Cumulative fraction (% by wt.)							
	Example 1	Comparative Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
1400	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1000	100.0	100.0	99.7	99.7	99.7	99.8	100.0	96.3
850	99.8	100.0	99.2	99.2	99.6	99.6	100.0	94.8
710	99.6	100.0	98.4	98.7	99.3	99.5	100.0	92.9
590	99.4	100.0	97.5	95.3	99.2	99.3	100.0	90.9
500	96.0	99.2	90.4	92.8	98.3	98.0	99.3	80.3
420	93.3	95.3	84.3	88.7	97.6	96.1	98.3	58.0
350	83.0	75.8	67.9	70.9	84.7	82.5	87.2	24.5
287	26.5	19.3	19.3	30.5	17.7	24.3	19.2	1.49
177	0.90	5.53	0.62	1.45	1.70	1.07	1.62	0.09
125	0.30	2.67	0.18	0.26	0.36	0.44	0.72	0.00
88	0.00	0.59	0.00	0.00	0.00	0.09	0.18	0.00
Pan	0.00	0.30	0.00	0.00	0.00	0.00	0.09	0.00
Bulk density (BD)	0.47	0.44	0.46	0.46	0.46	0.46	0.46	0.46

CLAIMS

1. A solid-catalyst component for use in the polymerization of α -olefins obtained by reducing a titanium compound represented by the following general formula:



wherein R^1 represents a hydrocarbon group having 1 to 20 carbon atoms, X represents a halogen atom and n represents a number satisfying $0 < n \leq 4$, with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond to produce a solid product,

treating the solid product with an ester compound,

treating the ester-treated solid product with a mixture of an ether compound and titanium tetrachloride or with a mixture of an ether compound, titanium tetrachloride and an ester compound to obtain a trivalent titanium compound-containing solid catalyst precursor, and

treating the solid catalyst precursor with a small quantity of an olefin in the presence of an organoaluminum compound to obtain a solid catalyst component for use in the polymerization of α -olefins.

2. A solid catalyst component according to Claim 1, wherein R^1 in the general formula $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$ is an alkyl group having 2 to 18 carbon atoms or an aryl group having



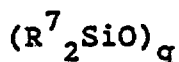
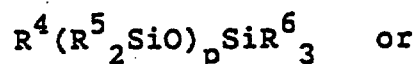
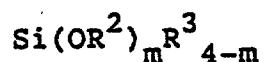
6 to 18 carbon atoms.

3. A solid catalyst component according to Claim 1, wherein R^1 in the general formula $Ti(OR^1)_nX_{4-n}$ is a straight chain alkyl group having 2 to 18 carbon atoms.

4. A solid catalyst component according to Claim 1, wherein the halogen atom is chlorine, bromine or iodine.

5. A solid catalyst component according to Claim 1, wherein n in the general formula $Ti(OR^1)_nX_{4-n}$ is $2 \leq n \leq 4$.

6. A solid catalyst component according to any one of Claims 1 to 5 wherein the organic silicon compound is one represented by the following general formulas



where R^2 represents a hydrocarbon group having 1 to 20 carbon atoms, R^3 , R^4 , R^5 , R^6 and R^7 each represents a hydrocarbon group having 1 to 20 carbon atoms or a hydrogen atom, m represents a number satisfying $0 < m \leq 4$, p represents an integer of 1 to 1,000, and q represents an integer of 2 to 1,000.

7. A solid catalyst component according to Claim 6, wherein the organic silicon compound is an alkoxy silane compound represented by the general formula $Si(OR^2)_mR^3_{4-m}$



where m satisfies $1 \leq m \leq 4$.

8. A solid catalyst component according to Claim 7, wherein the organic silicon compound is a tetraalkoxysilane compound where $m = 4$.

9. A solid catalyst component according to any one of Claims 1 to 8 wherein the organomagnesium compound is a Grignard compound represented by general formula R^8MgX , wherein R^8 represents a hydrocarbon group having 1 to 20 carbon atoms and X represents a halogen, or a dialkyl- or diaryl-magnesium compound represented by general formula $R^9R^{10}Mg$, wherein R^9 and R^{10} each represents a hydrocarbon group having 1 to 20 carbon atoms.

10. A solid catalyst component according to Claim 9, wherein the Grignard compound is methylmagnesium chloride, ethylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium iodide, propylmagnesium chloride, propylmagnesium bromide, butylmagnesium chloride, butylmagnesium bromide, sec-butylmagnesium chloride, sec-butylmagnesium bromide, tert-butylmagnesium chloride, tert-butylmagnesium bromide, amylmagnesium chloride, isoamylmagnesium chloride, phenylmagnesium chloride or phenylmagnesium bromide.

11. A solid catalyst component according to Claim 9, wherein the dialkyl- or diaryl-magnesium compound is diethylmagnesium, dipropylmagnesium, diisopropylmagnesium, dibutylmagnesium, di-sec-butylmagnesium, di-tert-butylmagnesium, butyl-sec-butylmagnesium, diamylmagnesium or diphenylmagnesium.



12. A solid catalyst component according to any one of Claims 1 to 11 wherein the ester compound is aliphatic carboxylic ester, olefinic carboxylic ester, alicyclic carboxylic ester or aromatic carboxylic ester.

13. A solid catalyst component according to Claim 12, wherein the ester compound is methacrylic ester, maleic ester or phthalic ester.

14. A solid catalyst component according to any one of Claims 1 to 13 wherein the ether compound is diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diamyl ether, diisoamyl ether, dineopentyl ether, dihexyl ether, dioctyl ether, methyl butyl ether, methyl isoamyl ether or ethyl isobutyl ether.

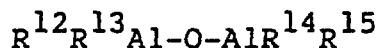
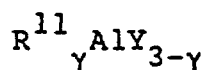
15. A solid catalyst component according to Claim 14, wherein the ether compound is dibutyl ether or diisoamyl ether.

16. A solid catalyst component according to any one of Claims 1 to 15, wherein the olefin is one having 2 to 20 carbon atoms.

17. A solid catalyst component according to Claim 16, wherein the olefin is ethylene, propylene, butene-1, pentene-1, hexene-1, 3-methylbutene-1, 3-methylpentene-1, 4-methylpentene-1, octene-1, decene-1 or dodecene-1.

18. A solid catalyst component according to any one of Claims 1 to 17 wherein the organoaluminum compound is that represented by the following general formulas:





wherein R^{11} , R^{12} , R^{13} , R^{14} and R^{15} each represents a hydrocarbon group having 1 to 20 carbon atoms, Y represents halogen, hydrogen or an alkoxy group, and γ represents a number satisfying $2 \leq \gamma \leq 3$.

19. A solid catalyst component according to Claim 18, wherein the organoaluminum compound is trialkylaluminum, a mixture of trialkylaluminum and dialkylaluminum halide or alkylalumoxane.

20. A solid catalyst component according to Claim 19 wherein the organoaluminum compound is triethylaluminum, triisobutylaluminum, a mixture of triethylaluminum and diethylaluminum chloride, or tetraethyldialumoxane.

21. A solid catalyst component according to any one of Claims 1 to 20 wherein treatment of the solid catalyst component with a small quantity of olefin in the presence of organoaluminum compound is carried out in the presence of an electron donor.

22. A solid catalyst component according to Claim 21, wherein the electron donor is one selected from the group consisting of organic silicon compounds having $Si-OR^{16}$ bond wherein R^{16} represents a hydrocarbon group having 1 to 20 carbon atoms or a Si-N-C bond, aromatic carboxylic ester compounds and sterically



hindered amines.

23. A solid catalyst component according to Claim 22, wherein the electron donor is an alkoxysilane compound represented by the general formula $R^{17}_tSi(OR^{16})_{4-t}$ or 2,6-substituted piperidine wherein R^{16} and R^{17} each represents a hydrocarbon group having 1 to 20 carbon atoms and t represents a number satisfying $0 \leq t \leq 3$.

24. A solid catalyst component according to Claim 23, wherein the 2,6-substituted piperidine is 2,2,6,6-tetramethylpiperidine.

25. A solid catalyst component according to any one of Claims 1 to 24 wherein the production of solid product by the reduction of a titanium compound with an organomagnesium compound is carried out in the presence of a porous material made of inorganic oxide or organic polymer.

26. A solid catalyst component according to any one of Claims 1 to 25 wherein in the reduction, the organic silicon compound is used in an amount of 1 to 50 in terms of atomic ratio of silicon atom to titanium atom (Si/Ti), and the organomagnesium compound is used in an amount of 0.1 to 10 in terms of atomic ratio of the sum of titanium and silicon atoms to magnesium atom (Ti+Si/Mg).

27. A solid catalyst component according to any one of Claims 1 to 26 wherein the reduction is carried out in a solvent at -50 to 70°C for 30 minutes to 6 hours.

28. A solid catalyst component according to any one of Claims 1 to 27 wherein in the ester-treatment, the ester compound is used in an amount of 0.1 to 50 moles per one mole of the



titanium atom in the solid product and in an amount of 0.01 to 1.0 mole per one mole of magnesium atom in the solid product.

29. A solid catalyst component according to ^{any one of} Claims 1 to 28 wherein the ester-treatment is carried out in a diluent at -50 to 150°C for 10 minutes or longer.

30. A solid catalyst component according to any one of Claims ^{1 to 29} wherein in the treatment of the ester-treated product, the ether compound is used in an amount of 0.1 to 100 moles and the titanium tetrachloride is used in an amount of 1 to 1,000 moles, and the ester compound is used if necessary in an amount of 30 moles or less per one mole of the titanium atom in the solid product, respectively.

31. A solid catalyst component according to ^{any one of} Claims 1 to 30 wherein the treatment of the ester-treated product is carried out in a slurry state in solvent at 30 to 150°C for 30 minutes to 6 hours.

32. A solid catalyst component according to ^{any one of} Claims 1 to 31 wherein in the olefin-treatment, the organoaluminum compound is used in an amount of 0.5 to 700 moles per one mole of titanium atom in the solid catalyst precursor, and the olefin is used in an amount of 0.05 to 1,000 g per one gram of the solid catalyst precursor.

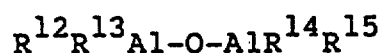
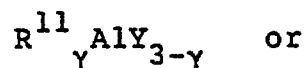
33. A solid catalyst component according to ^{any one of} Claims 1 to 32 wherein the olefin-treatment is carried out in a slurry state at -20 to 100°C for 2 minutes to 15 hours with olefin-partial pressure of 0.01 to 20 kg/cm².

34. A process for polymerization of α -olefins



which comprises:

polymerizing α -olefins in the presence of a solid catalyst component according to any one of Claims 1 to 33, an organoaluminum compound represented by the general formula



wherein R^{11} , R^{12} , R^{13} , R^{14} and R^{15} each represents a hydrocarbon group having 1 to 20 carbon atoms, Y represents halogen, hydrogen or an alkoxy group, and γ represents a number satisfying $2 \leq \gamma \leq 3$, and an electron donor.

35. A process according to Claim 34, wherein the α -olefin is ethylene, propylene, butene-1, pentene-1, hexene-1, 3-methylbutene-1, 3-methylpentene-1, 4-methylpentene-1, octene-1, decene-1 or dodecene-1.

36. A process according to any one of Claims 34 and 35, wherein the organoaluminum compound is triethylaluminum, triisobutylaluminum, a mixture of triethylaluminum and diethylaluminum chloride, or tetraethyldialumoxane.

37. A process according to any one of Claims 34 to 36, wherein the electron donor is alkoxy silane compound represented by the general formula $R^{17}_tSi(OR^{16})_{4-t}$ and 2,6-substituted piperidine wherein R^{16} and R^{17} each represents a hydrocarbon group having 1 to 20 carbon atoms and t represents a



number satisfying $0 \leq t \leq 3$.

38. A process according to any one of Claims 34 to 37, wherein the polymerization is carried out at -30 to 300°C under a pressure of 3-2000 atmospheres.



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FIG. 1

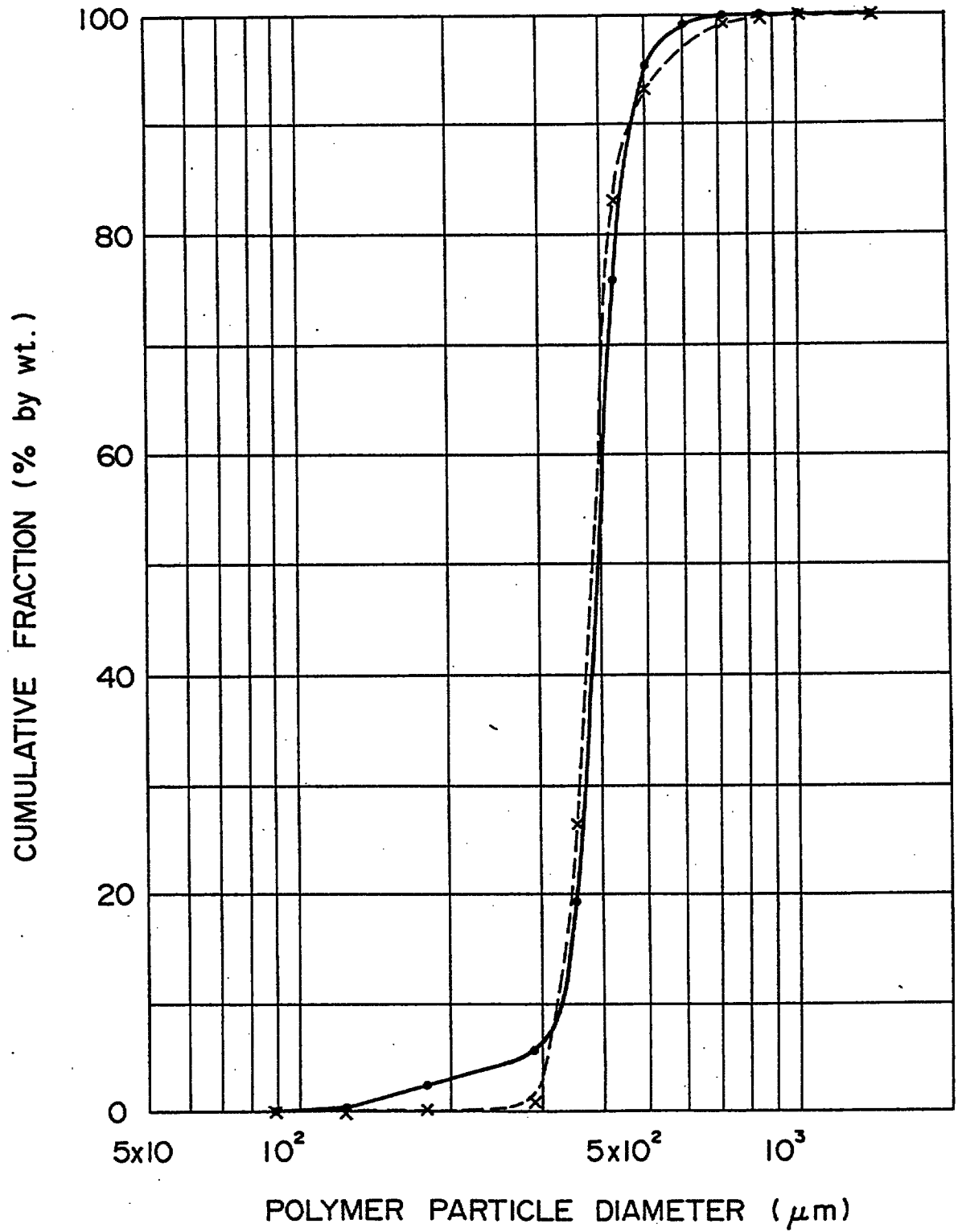
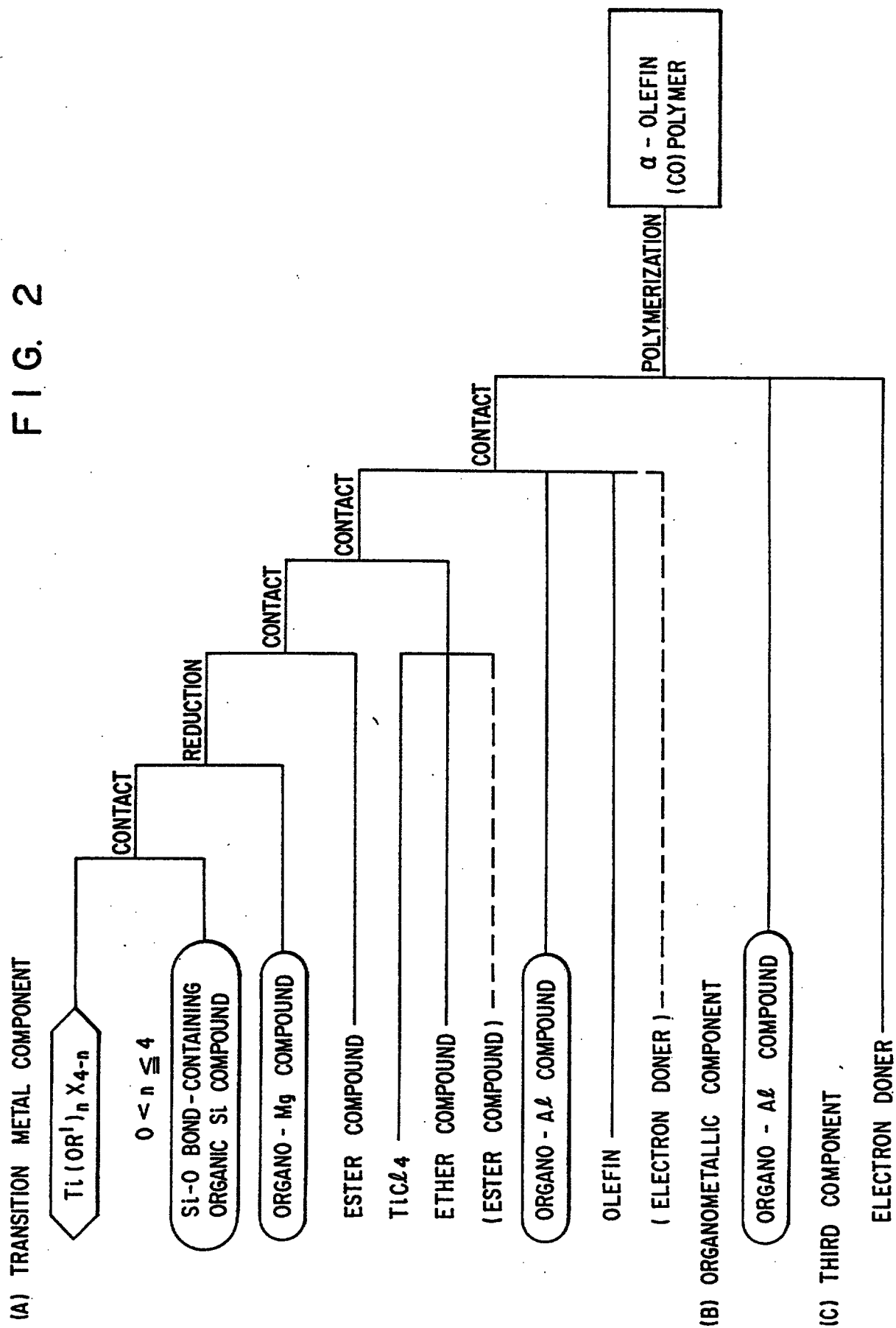


FIG. 2



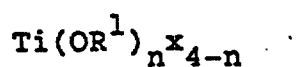
ABSTRACT

(Figures 1 & 2)

SOLID CATALYST COMPONENT

FOR USE IN POLYMERIZATION OF α -OLEFINS

A solid-catalyst component for use in the polymerization of α -olefins obtained by reducing a titanium compound represented by the following general formula:



wherein R^1 represents a hydrocarbon group having 1 to 20 carbon atoms, X represents a halogen atom and n represents a number satisfying $0 < n \leq 4$, with an organomagnesium compound in the presence of an organic silicon compound having Si-O bond to produce a solid product,

treating the solid product with an ester compound,

treating the ester-treated solid product with a mixture of an ether compound and titanium tetrachloride or with a mixture of an ether compound, titanium tetrachloride and an ester compound to obtain a trivalent titanium compound-containing solid catalyst precursor, and

treating the solid catalyst precursor with a small quantity of an olefin in the presence of an organoaluminum compound to obtain a solid catalyst component for use in the polymerization of α -olefins.

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