

PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER

The present invention relates to a process for producing a copolymer of ethylene and an α -olefin having 4 or more carbon atoms in gas phase. In more particular, it relates to a process for producing an ethylene- α -olefin copolymer in gas phase polymerization using a fluidized bed reaction vessel having a structure of bulgy vessel upper part, of which the productivity is remarkably improved by the use of a specific catalyst system.

10 In recent years, the drastic improvement of the productivity of olefin polymers per unit amount of transition metal due to the progress of transition metal catalysts for olefin polymerization has permitted the omission of catalyst removal operation after the
15 polymerization.

Such highly active, transition metal catalysts are generally utilized in olefin polymerization methods in gas phase, which permit simpler post-polymerization operations than any other methods. In gas-phase polymer-
20 ization, fluidized bed reactors are often used to achieve a smooth progress of the polymerization. The gas-phase polymerization in fluidized bed reactors is carried out by introducing olefin gases or olefin-containing gases from the lower part of the reactor via an inlet pipe,
25 dispersing the gases uniformly through a gas distributor,

and letting the gases go up in the reactor to fluidize olefin polymer particles and catalyst particles consisting of solid particles in the fluidized bed.

Some of the fluidized bed reactors are provided with a stirring blade for improving the mixing condition of the particles in the fluidized bed. However, in the polymerization of such olefins having a large heat of polymerization as ethylene, reactors provided with no stirring blade are used in most cases. This is because in the polymerization of olefins having a large heat of polymerization, olefin gases are generally circulated at a high speed (e.g., at a gas velocity 3-5 times the minimum fluidizing velocity of olefin polymer particles under the polymerization conditions) to take advantage of heat removal by cooled olefin gases, so that satisfactorily uniform mixing of the particles in the fluidized bed can be attained without a stirring blade. At such a high gas velocity, however, the introduced solid catalyst or polymer fine particles in the growing stage are liable to leave the fluidized bed and go out of the reactor with the outgoing gas. To avoid such a problem, therefore, a bulgy upper part is provided to the reaction vessel (said part is hereinafter referred to as "enlarged part") to lower the gas velocity at this part and thereby to return the scattered solid catalyst or polymer fine particles to the fluidized bed.

Such reactors having a bulgy upper part also have problems. When the feed amount of a solid catalyst

is increased in order to improve the productivity, part of the scattered solid catalyst or polymer fine particles in the growing stage escape from the enlarged part and flow into the cyclone or the circulation line. The thus
5 leaked solid catalyst or polymer particles stick to the inner wall of the cyclone or the gas circulation line to cause poor heat removal. The reduction of the efficiency of heat removal in turn raises the temperature of the polymer particles over their melting point. As a result,
10 the polymer particles are liable to aggregate into a mass and to block the cyclone or the gas circulation line.

Furthermore, the scattered solid catalyst or polymer fine particles in the growing stage may deposit at the tapered part provided for making the enlarged part
15 (said tapered part is hereinafter referred to as "inclined part"). The deposition would cause poor heat removal which leads to undesirable increase of the polymer particle temperature. As a result, the polymer particles are liable to aggregate to form sheet-like
20 masses. The sheet-like masses thus formed may drop into the fluidized bed and clog the gas distributor to deteriorate the mixing condition. In the worst case, the solidification of the entire fluidized bed into a mass takes place. Even when the situation is not so bad, the
25 sheet-like masses may block the withdrawing pipe for polymer particles and cause inevitable stop of polymerization.

In recognition of the situation, the object of

the present invention is to improve the productivity of and remove the above-mentioned problems from a gas-phase polymerization process for producing a copolymer of ethylene and an α -olefin having 4 or more carbon atoms in a reaction vessel having an enlarged part by the use of a specific catalyst system.

The present inventors have found that the combined use of a specific amount of a compound of the formula,



with a conventional catalyst system comprising a solid catalyst component containing a magnesium halide and a titanium halide as the essential constituents and an organoaluminum compound markedly reduces the scattering of the solid catalyst or polymer fine particles in the growing stage in the course of gas-phase polymerization, while holding the polymerization activity in satisfactorily high level and keeping the quality of the resulting ethylene- α -olefin copolymer undeteriorated.

20 The present invention is based on the finding.

According to the present invention, there is provided a process for producing an ethylene- α -olefin copolymer which comprises copolymerizing ethylene and an α -olefin having 4 or more carbon atoms in gas phase in a fluidized bed reaction vessel having a structure of bulgy vessel upper part by use of a catalyst system comprising:

(A) a solid catalyst component containing a magnesium halide and a titanium halide as the essential

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constituents,

(B) an organoaluminum compound, and

(C) a silicon compound of the formula



5 wherein R' and R'' may be the same or different and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group, C₁-C₂₄ aralkyl group, etc.; X is a halogen atom; m and n are numbers satisfying the mathematical expressions:

10 $0 \leq m < 4,$
 $0 < n \leq 4, \text{ and}$
 $0 < m + n \leq 4,$

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when m is more than 1, mR's may be the same or different; and n is more than 1, nR''s may be the same or different;
15 the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falling within the range of from 0.0005 : 1 to 0.015 : 1.

Figs. 1 and 2 are a conceptional diagram showing the fluidized bed reactor having an enlarged part
20 and comprising a cylinder, a hemisphere and a tapered part, respectively, and the polymerization process, which is for facilitating the understanding of the present invention. The reactors shown in Figs. 1 and 2 refer to a typical example of the embodiment of the present inven-
25 tion, and the ethylene- α -olefin gas phase polymerization reactor used in the present invention is not limited thereto.

In Figs. 1 and 2, numeral 1 indicates a

fluidized bed reactor, 2 a catalyst system comprising a solid catalyst component (A), an organoaluminum compound (B) and a silicon compound (C), 3 a gas distributor, 4 polymer particle withdrawal, 5 a cooler, 6 an air blower, 5 7 ethylene and an α -olefin having 4 or more carbon atoms, and 8 a cyclone.

The present invention is described in more detail below.

The catalyst system used in the present invention 10 tion comprises the following three specific components (A), (B) and (C).

i) Solid catalyst component (A)

The solid catalyst component (A) in the catalyst system used in the present invention contains a 15 magnesium halide and a titanium halide as the essential constituents. The atomic ratio of titanium to magnesium ranges preferably 0.01 : 1 to 0.8 : 1, more preferably 0.02 : 1 to 0.4 : 1. The atomic ratio of chlorine to magnesium ranges preferably 1.8 : 1 to 10 : 1, more 20 preferably 2.0 : 1 to 5.0 : 1.

The solid catalyst component (A) may be prepared, for example, by the methods disclosed in JP-A-49-85483, JP-B-57-24361, JP-B-46-34090, JP-B-47-41676, JP-B-55-23561, JP-A-64-38049, JP-A-6-73118, EP-A-0 25 283 011 and EP-A-0 578 470.

Specific examples of such methods are as follows:

(1) A method comprising treating a titanium

compound (e.g., TiCl_4) with an organomagnesium compound (e.g., Grignard reagent).

(2) A method comprising reacting an organomagnesium compound (e.g., Grignard reagent) with at least one member selected from a halogenating agent and an alcohol to obtain an intermediate product and then treating the intermediate product with a titanium compound (e.g., TiCl_4).

(3) A method comprising dissolving a magnesium halide and/or an alkoxymagnesium compound in various donors (e.g., alcohol, ether) to obtain a solution and then treating the solution with a titanium compound (e.g., TiCl_4).

(4) A method comprising dissolving a magnesium halide and/or an alkoxymagnesium compound in various donors (e.g., alcohol, ether) to obtain a solution, impregnating a porous carrier with the solution to obtain a solution-impregnated carrier and treating the solution-impregnated carrier with a titanium compound (e.g., TiCl_4).

(5) A method comprising reducing an alkoxy-titanium compound with an organomagnesium compound (e.g., Grignard reagent) to obtain a reduction product and then treating the reduction product with a mixture of an ether and titanium tetrachloride.

(6) A method comprising reducing an alkoxy-titanium compound with an organomagnesium compound (e.g., Grignard reagent) in the presence of a porous carrier to

obtain a reduction product, and then treating the reduction product with a mixture of an ether and titanium tetra-chloride.

(7) A method comprising reducing an alkoxy-
5 titanium compound with an organomagnesium compound (e.g., Grignard reagent) in the presence of a porous carrier to obtain a solid product, treating the solid product with an ester to obtain an ester-treated product and then treating the ester-treated product with a mixture of an
10 ether and titanium tetrachloride.

Of the above-mentioned methods, method (7) may preferably be applied. More preferably used is a method comprising reducing an alkoxytitanium compound with an organomagnesium compound in the co-presence of an organo-
15 silicon compound having at least one Si-O bond in the molecule and an organic porous polymer carrier to obtain a solid product, treating the solid product with an ester to obtain an ester-treated product, and then treating the ester-treated product with a mixture of an ether and
20 titanium tetrachloride.

The titanium compound used in the preparation of the solid catalyst component (A) in the catalyst system used in the present invention is represented by the formula $Ti(OR^i)_aX_b$, wherein R^i is a hydrocarbon group
25 having 1-20 carbon atoms, X is a halogen atom, and a and b are numbers which satisfy the mathematical expressions, $0 \leq a \leq 4$, $0 \leq b \leq 4$ and $a+b = 3$ or 4. Specific examples of the preferably used titanium compound include titanium

trichloride, ethoxytitanium dichloride, butoxytitanium
dichloride, titanium tetrachloride, ethoxytitanium
trichloride, butoxytitanium trichloride, phenoxytitanium
trichloride, dibutoxytitanium dichloride, diphenoxy-
5 titanium dichloride, tributoxytitanium chloride, tetra-
ethoxytitanium, tetrabutoxytitanium and tetraphenoxy-
titanium.

The magnesium compounds used in the preparation
of the solid catalyst component (A) in the catalyst
10 system used in the present invention include those having
a reducing ability and those having no reducing ability.
They are appropriately selected depending upon the method
of preparation of solid catalyst component (A).

As the magnesium compounds having a reducing
15 ability due to the magnesium-carbon bond and/or
magnesium-hydrogen bond, preferably used are, for
example, diethylmagnesium, dibutylmagnesium, dihexyl-
magnesium, ethylmagnesium chloride, butylmagnesium
chloride, hexylmagnesium chloride, butylethoxymagnesium,
20 and butylmagnesium hydride. These magnesium compounds
may also be used in the form of a complex compound with
an organoaluminum compound. On the other hand, as the
magnesium compounds having no reducing ability,
preferably used are, for example, magnesium dihalides
25 (e.g., magnesium dichloride and magnesium dibromide),
alkoxymagnesium compounds (e.g., methoxymagnesium
chloride, ethoxymagnesium chloride, butoxymagnesium
chloride, phoxymagnesium chloride, diethoxymagnesium,

dibutoxymagnesium and diphenoxymagnesium), and carboxylic acid salts of magnesium (e.g., magnesium laurate and magnesium stearate). These magnesium compounds having no reducing ability may also be those which have been

- 5 prepared by a known method from magnesium compounds having a reducing ability at the time of or before the preparation of the solid catalyst component (A).

The solid catalyst component (A) may also be incorporated with a known electron donative substance.

- 10 Such an electron donative substance includes esters, ethers and alcohols. Of these, esters are preferably used. Such esters are esters of monobasic and polybasic carboxylic acids. Specifically, they are aliphatic carboxylic esters, olefinic carboxylic acid esters,
15 alicyclic carboxylic acid esters and aromatic carboxylic acid esters.

- Specific examples of the esters include methyl methacrylate, ethyl benzoate, butyl benzoate, methyl toluate, ethyl toluate, ethyl anisate, diethyl succinate,
20 dibutyl succinate, diethyl malonate, dibutyl malonate, dimethyl maleate, dibutyl maleate, diethyl itaconate, dibutyl itaconate, monoethyl phthalate, dimethyl phthalate, methyl ethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl
25 phthalate, diisobutyl phthalate, di-n-heptyl phthalate, di-n-octyl phthalate and diphenyl phthalate.

The organosilicon compound having at least one Si-O bond used in the preparation of the solid catalyst

component (A) is preferably an organosilicon compound represented by the general formula $\text{Si}(\text{OR}^3)_b\text{R}^4_{4-b}$, $\text{R}^5(\text{R}^6_2\text{SiO})_c\text{SiR}^7$ or $(\text{R}^8_2\text{SiO})_d$ (wherein R^3 is a hydrocarbon group having 1 to 20 carbon atoms, R^4 , R^5 , R^6 , R^7 and R^8 are each a hydrocarbon group having 1 to 20 carbon atoms or hydrogen atom, b is a number satisfying $0 \leq b \leq 4$, c is an integer of 1 to 1000 and d is an integer of 2 to 1000).

Specific examples of the organic porous polymer used in the preparation of the solid catalyst component (A) include polystyrene, styrene-divinylbenzene copolymer or polyvinyl chloride.

The organic porous polymer preferably has a mean particle diameter of 5 to 1,000 microns and a pore volume of 0.1 cc/g or above at a pore radius of 100 to 5,000 angstroms.

The solid catalyst component (A) may also be subjected to preliminary polymerization before use for reducing the scattering of the component in the course of gas phase polymerization and improving the properties of polymer particles formed.

The preliminary polymerization of the solid catalyst component (A) may be carried out by bringing the component into contact with an organoaluminum compound and either ethylene or an α -olefin having 4 or more carbon atoms. The organoaluminum compound used herein may be appropriately selected from the organoaluminum compounds which can be used in olefin polymerization

described later.

The preliminary polymerization of the solid catalyst component (A) is preferably conducted in the form of slurry. The solvents used for making a slurry
5 may be aliphatic hydrocarbons (e.g., butane, pentane, hexane and heptane) and aromatic hydrocarbons (e.g., toluene and xylene).

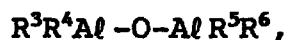
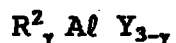
The concentration of the solid component (A) in the slurry ranges preferably 0.001-0.5 g solid/ml
10 solvent, more preferably 0.01-0.3 g solid/ml solvent. The organoaluminum compound is preferably used in such an amount that the molar ratio of Al to Ti may range from 0.1 : 1 to 100 : 1, particularly from 1 : 1 to 10 : 1.

The temperature of the preliminary polymer-
15 ization ranges preferably from -30° to +80°C, more preferably from -10° to +50°C.

The preliminary polymerization is preferably conducted under such conditions that the polymer may be formed in an amount of from 0.1 to 100 g, particularly
20 0.5 to 50 g, per gram of the solid catalyst component.

ii) Organoaluminum compound (B)

The organoaluminum compound (B) used in combination with the above-mentioned solid catalyst component (A) in the catalyst system used in the present
25 invention has at least one Al-carbon bond in the molecule. Representatives of such compounds are shown below in terms of general formulas.



wherein R^2 , R^3 , R^4 , R^5 and R^6 are each independently a hydrocarbon group having 1-8 carbon atoms, Y is halogen,
5 hydrogen or alkoxy, and γ is a number defined by the mathematical expression $2 \leq \gamma \leq 3$.

Specific examples of the organoaluminum compounds (B) include trialkylaluminums (e.g., triethylaluminum, triisobutylaluminum and trihexylaluminum),
10 dialkylaluminum hydrides (e.g., diethylaluminum hydride and diisobutylaluminum hydride), dialkylaluminum halide (e.g., diethylaluminum chloride) and alkylalumoxanes (e.g., tetraethyldialumoxane and tetrabutylaluminum oxide).
The organoaluminum compounds may be used each alone or in
15 admixture thereof.

Of these organoaluminum compounds (B), preferred are trialkylaluminums, mixtures of a trialkylaluminum and dialkylaluminum halide and alkylalumoxanes. Particularly preferred are triethylaluminum, triisobutylaluminum, a mixture of triethylaluminum and diethylaluminum chloride, and tetraethyldialumoxane.
20

The amount of the organoaluminum compound to be used is not critical. It may be selected from as wide a range of 1-1000 moles of organoaluminum compound per mole
25 of the titanium atom in the solid catalyst component (A). Particularly preferred are the range of 5-600 moles per mole of the titanium atom in the solid catalyst component (A).

iii) Silicon compound (C)

The silicon compound (C) in the catalyst system used in the present invention are represented by the formula $R'_mSi(OR^n)_nX_{4-m-n}$, wherein R' and R" may be the same or different, and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group and C₁-C₂₄ aralkyl group; X is a halogen atom; and m and n are numbers which satisfy the mathematical expressions, $0 \leq m < 4$, $0 < n \leq 4$ and $0 < n+m \leq 4$; when m is more than 1, mR's may be the same or different; and when n is more than 1, nR"s may be the same or different. Specific examples of the silicon compound (C) includes tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetraphenoxysilane, ethyltrimethoxysilane, t-butyltrimethoxysilane, cyclohexyltrimethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane, diethyldimethoxysilane, butylmethyldimethoxysilane, butylethyldimethoxysilane, t-butylmethyldimethoxysilane, hexylethyldimethoxysilane, cyclopentylmethyldimethoxysilane, cyclopentylethyl-dimethoxysilane, cyclohexylmethyldimethoxysilane, cyclohexylethyldimethoxysilane, cyclohexyl-t-butyl-dimethoxysilane, cyclohexylphenyldimethoxysilane, phenylmethyldimethoxysilane, phenyl-t-butyl-dimethoxysilane, phenylcyclopentyl-dimethoxysilane, vinylmethyldimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, t-butyltriethoxysilane, cyclohexyltriethoxysilane, phenyltriethoxysilane, dimethyldiethoxysilane, propylmethyldiethoxysilane, di-t-

butyldiethoxysilane, butylethyldiethoxysilane, t-butyl-
methyldiethoxysilane, hexylmethyldiethoxysilane,
dicyclopentyldiethoxysilane, cyclohexylmethyldiethoxy-
silane, phenylmethyldiethoxysilane, 2-norbornane-
5 trimethoxysilane, trimethylphenoxysilane and
methyltriallyloxysilane.

iv) Process for olefin polymerization

The present invention provides a process for
producing an ethylene- α -olefin copolymer which comprises
10 copolymerizing ethylene and an α -olefin having 4 or more
carbon atoms in gas phase by using a catalyst system
comprising the solid catalyst component (A), the organo-
aluminum compound (B) and the silicon compound (C)
described above. An embodiment of the copolymerization
15 process is specifically described below.

The gas phase polymerization reactor suitably
used for practicing the present invention is, for
example, a fluidized bed reaction vessel which has a
largely swollen vessel upper part, namely an enlarged
20 part, as shown in Fig. 1. The vessel preferably has
vertically connected two cylinders having different
diameters with a tapered part placed therebetween,
wherein the diameter of the upper cylinder is larger than
that of the lower cylinder. The fluidized bed reaction
25 vessel may be the vessel comprising a cylinder, a
hemisphere of which diameter is larger than that of the
cylinder, and a tapered part placed therebetween for
connecting the cylinder and the hemisphere as shown in

Fig. 2.

A vessel having a stirring blade provided therein may also be used without any problem.

Each of the components of the catalyst system
5 may be fed to the reaction vessel under anhydrous conditions by using an inert gas (e.g., nitrogen and argon) or hydrogen, ethylene, etc. They may also be fed after being diluted with a solvent.

The solid catalyst component (A), the organo-
10 aluminum compound (B) and the silicon compound (C) may be fed each individually; or alternatively, they may be fed after preliminarily mixing any optional combination of components (A), (B) and (C) (e.g., (A)+(B), (A)+(C), (B)+(C) or (A)+(B)+(C)).

15 The molar ratio of the silicon compound (C) to the organoaluminum compound (B) used in the polymerization ranges from 0.0005 : 1 to 0.015 : 1, preferably 0.001 : 1 to 0.010 : 1, more preferably 0.003 : 1 to 0.005 : 1, and most preferably 0.003 : 1 to 0.010 : 1.
20 When the ratio is lower than 0.0005 : 1, the effect of the present invention is poorly exhibited. When it is higher than 0.015 : 1, the activity of the resulting catalyst system is unsatisfactory.

The copolymerization is preferably carried out
25 under such conditions that the monomers may not liquefy in the polymerization vessel. Such conditions are within the temperature range not higher than the melting point of the copolymer formed, preferably from 20° to 100°C,

more preferably from 40° to 90°C; and within the pressure range of from 1 to 40 kg/cm². In the copolymerization, hydrogen is preferably added as the molecular weight controller in order to adjust the melt flowability of the
5 final product. Further, an inert gas may be present in the gas mixture during copolymerization, but too high a proportion of inert gas causes undesirable reduction of productivity.

The α -olefins which can be used in the present
10 invention have 4 or more carbon atoms, preferably 4-6 carbon atoms. Specific examples thereof include butene-1, pentene-1, hexene-1, 3-methylpentene-1, 4-methylpentene-1 and octene-1. In the copolymerization, a mixture of two or more kinds of olefins may be brought
15 into contact with the catalyst system to obtain a copolymer. The ethylene- α -olefin copolymer obtained preferably has a density of 0.900-0.960 g/cc.

The process of the present invention is described in more detail below with reference to
20 Examples, but the invention is not limited by the Examples.

The polymer properties shown in Examples were determined in the following manner:

The density was determined according to JIS
25 K-6760.

The melt index was determined according to JIS K-6760 at 190°C.

Example 1

(a) Synthesis of organomagnesium compound

An autoclave of 100-ℓ inner volume equipped with a stirrer, reflux condenser, dropping funnel and
5 thermometer was flushed with argon, and then 3.2 kg of magnesium turnings for Grignard reagent was placed therein.

Then, 12 kg of butyl chloride and 50 ℓ of dibutyl ether were placed in the dropping funnel, and
10 about 3 ℓ of the resulting mixture was added by drops to the magnesium in the autoclave to initiate the reaction. After the initiation of reaction, the remaining mixture was continuously added to the magnesium by drops at 50°C over a period of 4 hours. After completion of the
15 dropwise addition, the reaction was allowed to continue at 60°C for further 1 hour. Thereafter, the thus obtained reaction liquid was cooled to room temperature, and the solid formed was filtered off.

The resulting solid-free solution containing
20 butylmagnesium chloride in dibutylether was sampled. The sample was hydrolyzed with 1N sulfuric acid. The hydrolyzed sample was back-titrated with 1N sodium hydroxide using phenolphthalein as the indicator to find that the concentration of the butylmagnesium chloride was
25 2.0 mole/ℓ.

(b) Synthesis of solid product

An autoclave of 100-ℓ inner volume equipped with a stirrer and dropping funnel was flushed with

argon. A styrene-divinylbenzene copolymer having an average particle diameter of 50 μm and a pore volume within the pore radius range of 100-5,000 $\text{\AA}$ (said pore volume being hereinafter referred to as dVp) of 1.05 cc/g
5 as determined with a porosimeter was dried under vacuum at 80°C for 30 minutes. 7.5 Kilograms of the thus dried styrene-divinylbenzene copolymer, 40 l of heptane, 670 g (1.97 moles) of tetrabutoxytitanium and 7.1 kg (34.0 moles) of tetraethoxysilane were placed in the autoclave
10 and stirred at 30°C for 45 minutes.

Subsequently, 18 l of the organomagnesium compound synthesized in section (a) above was added by drops from the dropping funnel to the autoclave over a period of 45 minutes while keeping the temperature in the
15 autoclave at 5°C. After completion of the dropwise addition, the reaction mixture was stirred at 5°C for 45 minutes and further at 30°C for 45 minutes. Thereafter, the reaction product was washed twice with 30 l of hexane, and then dried under reduced pressure to obtain
20 12.3 kg of a brown solid product.

(c) Synthesis of solid catalyst component

An autoclave of 50-l inner volume was flushed with argon. Then, 5.8 kg of the solid product synthesized by the reductive reaction in section (b)
25 above, 20 l of toluene and 1.6 l (6.0 moles) of diisobutyl phthalate were placed therein. The resulting mixture was allowed to react at 95°C for 1 hour.

After the reaction, the solid formed was

separated from the liquid and washed twice with 20 l of toluene.

After completion of the washing, 20 l of toluene, 240 ml (1.4 moles) of butyl ether and 3.44 l (31.2 moles) of titanium tetrachloride were added to a flask and the resulting mixture was allowed to react at 95°C for 3 hours. After completion of the reaction, the solid formed was separated from the liquid at 95°C and washed twice with 20 l of toluene at the same temperature.

The thus washed solid was further washed twice with 20 l of hexane and then dried under reduced pressure to obtain 5.08 kg of a brown solid catalyst component. The solid catalyst component contained 0.54% by weight of titanium atom, 7.1% by weight of magnesium atom and 1.5% by weight of phthalic ester. The average particle diameter of the solid catalyst component was 50 μ m.

(d) Preliminary polymerization of solid catalyst component

An autoclave of 100-l inner volume equipped with a stirrer was flushed with argon. Then, 1.5 kg of the solid catalyst component obtained in section (c) above, 100 l of butane and 1.1 moles of triethylaluminum were added to the autoclave. Then, ethylene was continuously fed to the resulting mixture at a rate of 2.3 g/g-solid catalyst·hour to carry out reaction for 9 hours. After the reaction, the butane was flash-vaporized to obtain 30.5 kg of a prepolymerized solid

catalyst component. The prepolymerized solid catalyst component contained 270 ppm of titanium atom.

(e) Polymerization of olefin

In a continuous fluidized reactor for gas phase
5 polymerization (upper part diameter : 90 cm, lower part
diameter : 50 cm, vessel length : 4 m) was charged as a
dispersant 60 kg of thoroughly dried ethylene- α -olefin
copolymer particles having an average particle diameter
of about 1000 μ m. The atmosphere in the reactor was
10 replaced with nitrogen. After gas circulation had been
started, ethylene, 1-butene as the α -olefin, and hydrogen
as the molecular weight controller were charged into the
reactor such that the proportion of ethylene, 1-butene
and hydrogen relative to the entire gas might be 68.6,
15 22.8 and 8.6% by mole, respectively, to raise the
internal pressure up to 20 kg/cm². Thereafter, the gas
velocity in the reaction vessel was set at 35 cm/sec to
keep the charged ethylene- α -olefin copolymer particles in
a thoroughly fluidized state. While maintaining the
20 fluidized state of the particles, triethylaluminum (B)
diluted with hexane and cyclohexylethyldimethoxysilane
(C) diluted with hexane were simultaneously charged into
the vessel at a rate of 0.1 mole/hour and 0.1 mmole/hour,
respectively (i.e., the molar ratio of (C) to (B) =
25 0.001 : 1).

After 2 hours, the prepolymerized solid
catalyst component (A) obtained in section (d) above was
charged into the vessel by use of nitrogen gas to

initiate the polymerization. Thereafter, while maintaining the total pressure in the vessel constant by continuously feeding ethylene, 1-butene and hydrogen so as to keep their concentrations in the polymerization system unchanged, the polymerization was carried out at 85°C for 24 hours. The polymer particles formed were intermittantly withdrawn from the vessel, separated from the gas, treated with an alcohol in order to deactivate the catalyst system contained therein and dried to obtain ethylene-1-butene copolymer particles. In this polymerization, the amount of the charged prepolymerized solid catalyst component was 52.6 g/hour and the production rate was 20.0 kg/hour. Accordingly, the yield (kg) of ethylene-1-butene copolymer per gram of titanium atom in the solid catalyst component was 1646 (kg-polymer/g-Ti). Hereinafter, the yield was abbreviated as "activity". The copolymer had a melt flow rate (MFR) of 1.00 g/10 min and a density of 0.9205 g/cc. The weight of the particles collected at the cyclone during the polymerization was 13.1 g/hour on the average. During the polymerization, no blockage was taken place in the cyclone nor in the gas circulation line, and no formation of sheet-like mass was observed, either.

Examples 2-4

The same procedure as in Example 1 was repeated except that the feeding rate of cyclohexylethyldimethoxysilane (C) was varied while keeping the feeding rate of

triethylaluminum (B) unchanged (i.e., the molar ratio of (C) to (B) was varied) and that the concentration ratio of ethylene to 1-butene was varied, to produce copolymers of approximately the same density as in Example 1 at a
5 production rate of 20.0 kg/hour. Table 1 shows the results. In any of these runs, no blockage occurred in the cyclone nor in the gas circulation line and no formation of sheet-like mass was observed, during the polymerization.

10 The results of these Examples in which cyclohexylethyldimethoxysilane was used as the silicon compound (C) reveal:

 that the weight of the particles collected in the cyclone, i.e., the amount of the scattered particles,
15 is desirably reduced with the increase of the molar ratio of (C) to (B),

 that, to the contrary, the "activity" is undesirably reduced with the increase of the molar ratio of (C) to (B), and

20 that it is practically disadvantageous to carry out the polymerization in a molar ratio of (C) to (B) higher than 0.015 : 1.

Examples 5 and 6

 The same procedure as in Example 1 was repeated
25 except that, as shown in Table 1, cyclohexylethyl-
dimethoxysilane used in Example 1 as the silicon compound was replaced by tetraethoxysilane (C), that the feeding

rate of tetraethoxysilane was varied while keeping the feeding rate of triethylaluminum (B) unchanged (i.e., the molar ratio of (C) to (B) was varied) and that the concentration ratio of ethylene to 1-butene in gas phase was varied, to produce copolymers of approximately the same density at a production rate of 20.0 kg/hour.

The results of these Examples reveal that also when tetraethoxysilane is used as the silicon compound (C), the weight of the particles collected in the cyclone is reduced with the increase of the molar ratio of (C) to (B). In both of Examples 5 and 6, no blockage occurred in the cyclone nor in the gas circulation line, and no formation of sheet-like mass was observed, during the polymerization.

15 Comparative Example 1

The same procedure as in Example 1 was repeated except that, as shown in Table 1, the silicon compound (C) was omitted, and that the concentration ratio of ethylene to 1-butene in gas phase was varied, to produce a copolymer of approximately the same density at a production rate of 20.0 kg/hour.

The absence of the silicon compound (C) undesirably increased the weight of the particles collected in the cyclone, and gave small sheet-like masses in an amount of 6.0 g/hour on the average during the polymerization.

Comparative Example 2.

The same procedure as in Example 1 was repeated except that, as shown in Table 1, methyl methacrylate was used in place of the silicon compound (C) in a molar
5 ratio of methyl methacrylate to triethylaluminum of 0.010 : 1 and that the concentration ratio of ethylene to 1-butene in the gas phase was varied, to obtain a copolymer of approximately the same density at a production rate of 20.0 kg/hour.

10 The replacement of the silicon compound (C) by methyl methacrylate greatly increased the weight of the particles collected in the cyclone, and gave small sheet-like masses in an amount of 13.0 g/hour on the average during the polymerization.

Table 1

	Silicon compound (C)	Molar ratio of (C) to (B)	Ethylene concentration (mol%)	1-Butene concentration (mol%)	MFR (g/10 min)	Density (g/cc)	Activity* (kg-copolymer /g-Ti)	Cyclone-collected particle weight (g/hr)
Example 1	Cyclohexylethyl-dimethoxysilane	0.001:1	68.1	22.9	1.00	0.9205	1646	13.1
" 2		0.003:1	67.2	23.6	1.09	0.9209	1596	8.0
" 3		0.005:1	65.2	24.9	1.05	0.9207	1324	4.1
" 4		0.010:1	62.8	26.5	1.04	0.9203	1180	2.5
" 5	Tetraethoxy-silane	0.003:1	67.6	23.4	1.02	0.9204	1593	9.5
" 6		0.010:1	63.5	25.3	0.96	0.9208	930	3.8
Comp. Example 1	-	-	68.6	22.8	1.02	0.9208	1690	16.8
" 2	Methyl methacrylate (MMA)	0.010:1	72.1	19.2	0.98	0.9205	1415	25.3

Notes: Organoaluminum compound (B) : triethylaluminum

*; Yield (kg) of ethylene- α -olefin copolymer per gram of titanium atom in solid catalyst component (A)

The use of a solid catalyst in an increased feed amount to improve the productivity to ethylene- α -olefin copolymers in a fluidized bed reactor having an enlarged part would cause undesirable formation of masses
5 in the cyclone, gas circulator line or inclined portion of the enlarged part of the reactor by the scattering of the solid catalyst used or polymer fine particles in the growing stage.

The process of the present invention enables
10 the manufacture of ethylene- α -olefin copolymers with high productivity by greatly reducing the amount of scattered solid catalyst or polymer fine particles in the growing stage and suppressing the formation of masses.



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WHAT IS CLAIMED IS:

1. A process for producing an ethylene- α -olefin copolymer which comprises copolymerizing ethylene and an α -olefin having 4 or more carbon atoms in gas phase in a fluidized bed reaction vessel having a structure of bulgy vessel upper part by use of a catalyst system comprising:

(A) a solid catalyst component containing a magnesium halide and a titanium halide as the essential constituents,

(B) an organoaluminum compound, and

(C) a silicon compound of the formula,



wherein R' and R'' may be the same or different and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group, C₁-C₂₄ aralkyl group, etc.; X is a halogen atom; m and n are numbers satisfying the mathematical expressions:

$$0 \leq m < 4,$$

$$0 < n \leq 4, \text{ and}$$

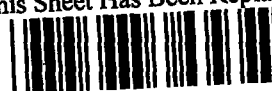
$$0 < m+n \leq 4;$$

when m is more than 1, mR's may be the same or different; and when n is more than 1, nR''s may be the same or different;

the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falling within the range of from 0.0005 : 1 to 0.015 : 1.

2. The process according to Claim 1, wherein the solid catalyst component (A) is obtained by impregnating

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an organic porous polymer carrier with a catalyst component comprising titanium, magnesium and chlorine.

3. The process according to Claim 1, wherein the solid catalyst component (A) is a trivalent titanium compound-containing solid catalyst component which is obtained by reducing a titanium compound of the formula,



wherein R^1 is a hydrocarbon group having 1-20 carbon atoms; X is a halogen atom; and m and n are numbers satisfying the mathematical expressions:

$$0 \leq a \leq 4,$$

$$0 \leq b \leq 4, \text{ and}$$

$$a + b = 3 \text{ or } 4;$$

with an organomagnesium compound in the presence of an organosilicon compound having at least one Si-O bond in the molecule and an organic porous polymer to obtain a solid product, treating the solid product with an ester to obtain an ester-treated solid product, and then treating the ester-treated solid product with a mixture of an ether and titanium tetrachloride.

4. The process according to Claim 1, wherein the solid catalyst component (A) is an organic porous polymer carrying thereon a catalyst component comprising titanium, magnesium and chlorine.

5. The process according to Claim 1, wherein the fluidized bed reaction vessel has vertically connected two cylinders having different diameters with a tapered part placed therebetween, the diameter of the upper





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cylinder being larger than that of the lower cylinder, or the fluidized bed reaction vessel comprises a cylinder, a hemisphere of which diameter is larger than that of the cylinder, and a tapered part placed therebetween for connecting the cylinder and the hemisphere.

6. The process according to Claim 1, wherein the α -olefin having 4 or more carbon atoms is an α -olefin selected from the group consisting of butene-1, pentene-1, hexene-1, 3-methylpentene-1, 4-methylpentene-1 and octene-1.

7. The process according to Claim 1, wherein the silicon compound (C) is a silicon compound selected from the group consisting of cyclohexylethyldimethoxysilane and tetraethoxysilane.

8. The process according to Claim 1, wherein the molar ratio of the silicon compound (C) to the organo-aluminum compound (B) falls within the range of from 0.001 : 1 to 0.010 : 1.

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FIG. 1

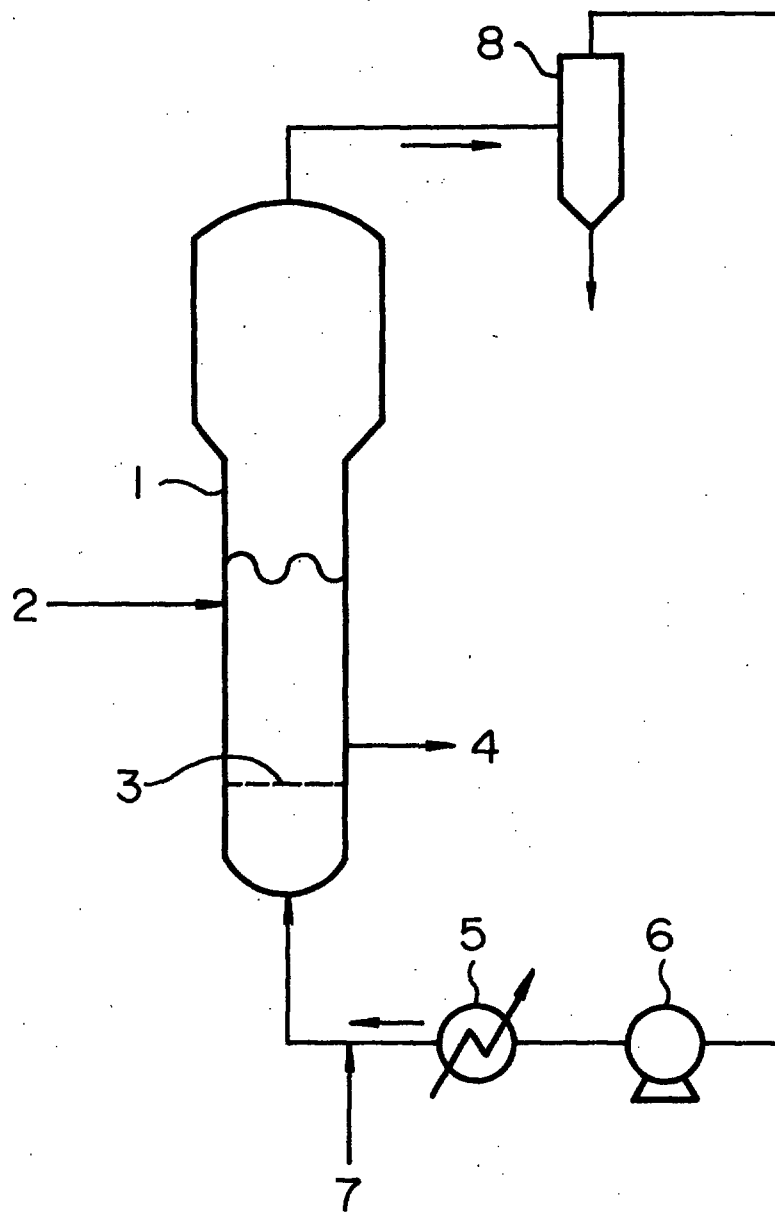
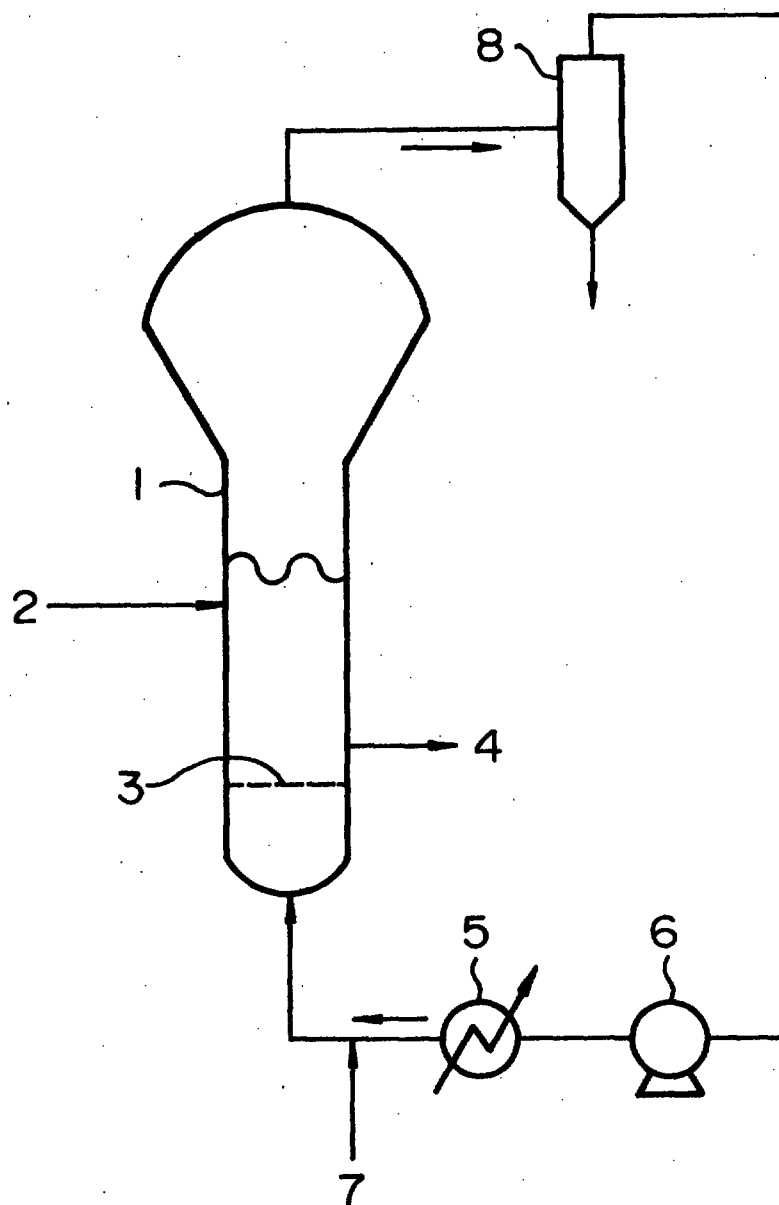


FIG. 2



ABSTRACTS OF THE DISCLOSURE

PROCESS FOR PRODUCING ETHYLENE- α -OLEFIN COPOLYMER

The use of a catalyst system containing:

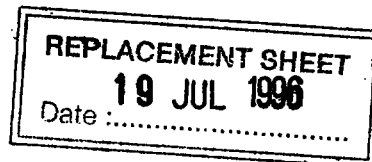
- (A) a solid catalyst component containing a magnesium halide and a titanium halide,
- (B) an organoaluminum compound, and
- (C) a silicon compound of the formula,



enables highly productive manufacture of ethylene- α -olefin copolymers in gas phase in a fluidized bed reaction vessel having a structure of bulgy vessel upper part through remarkable reduction of scattering of solid catalyst or polymer particles in the course of the polymerization.

(Figure 1)

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constituents,

- (B) an organoaluminum compound, and
- (C) a silicon compound of the formula



wherein R' and R'' may be the same or different and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group, C₁-C₂₄ aralkyl group, etc; X is a halogen atom; m and n are numbers satisfying the mathematical expressions:

$$0 \leq m < 4,$$

$$0 < n \leq 4, \text{ and}$$

$$0 < m + n \leq 4,$$

when m is more than 1, mR's may be the same or different; and n is more than 1, nR''s may be the same or different;

the molar ratio of the silicon compound (c) to the organoaluminum compound (B) falling within the range of from 0.0005:1 inclusive to 0.010:1 exclusive.

Figs. 1 and 2 are a conceptional diagram showing the fluidized bed reactor having an enlarged part and comprising a cylinder, a hemisphere and a tapered part, respectively, and the polymerization process, which is for facilitating the understanding of the present invention. The reactors shown in Figs. 1 and 2 refer to a typical example of the embodiment of the present invention, and the ethylene- α -olefin gas phase polymerization reactor used in the present invention is not limited thereto.

In Figs. 1 and 2, numeral 1 indicates a

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~~Substitute sheet~~ 19 July 1996

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Date: 19 JUL 1996



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WHAT IS CLAIMED IS:

1. A process for producing an ethylene- α -olefin copolymer which comprises copolymerizing ethylene and an α -olefin having 4 or more carbon atoms in gas phase in a fluidized bed reaction vessel having a structure of bulgy vessel upper part by use of a catalyst system comprising:

- (A) a solid catalyst component containing a magnesium halide and a titanium halide as the essential constituents,
- (B) an organoaluminum compound, and
- (C) a silicon compound of the formula,



wherein R' and R'' may be the same or different and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group, C₁-C₂₄ aralkyl group, etc; X is a halogen atom; m and n are numbers satisfying the mathematical expressions:

$$0 \leq m < 4,$$

$$0 < n \leq 4, \text{ and}$$

$$0 < m+n \leq 4;$$

when m is more than 1, mR's may be the same or different; and
when n is more than 1, nR''s may be the same or different;

the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falling within the range of from 0.0005:1 inclusive to 0.101:1 exclusive.

2. The process according to claim 1, wherein the solid catalyst component (A) is obtained by impregnating an organic porous

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polymer carrier with a catalyst component comprising titanium, magnesium and chlorine.

3. The process according to claim 1, wherein the solid catalyst component (A) is a trivalent titanium compound-containing solid catalyst component which is obtained by reducing a titanium compound of the formula,



wherein R^1 is a hydrocarbon group having 1-20 carbon atoms; X is a halogen atom; and m and n are numbers satisfying the mathematical expressions:

$$0 \leq a \leq 4,$$

$$0 \leq b \leq 4, \text{ and}$$

$$a + b = 3 \text{ or } 4;$$

with an organomagnesium compound in the presence of an organosilicon compound having at least one Si-O bond in the molecule and an organic porous polymer to obtain a solid product, treating the solid product with an ester to obtain an ester-treated solid product, and then treating the ester-treated solid product with a mixture of an ether and titanium tetrachloride.

4. The process according to claim 1, wherein the solid catalyst component (A) is an organic porous polymer carrying thereon a catalyst component comprising titanium, magnesium and chlorine.
5. The process according to claim 1, wherein the fluidized bed reaction vessel has vertically connected two cylinders having different diameters with a tapered part placed therebetween, the



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diameter of the upper cylinder being larger than that of the lower cylinder, or the fluidized bed reaction vessel comprises a cylinder, a hemisphere of which diameter is larger than that of the cylinder, and a tapered part placed therebetween for connecting the cylinder and the hemisphere.

6. The process according to claim 1, wherein the α -olefin having 4 or more carbon atoms is an α -olefin selected from the group consisting of butene-1, pentene-1, hexene, 3-methylpentene-1, 4-methylpentene-1 and octene-1.
7. The process according to claim 1, wherein the silicon compound (C) is a silicon compound selected from the group consisting of cyclohexylethyldimethoxysilane and tetraethoxysilane.
8. The process according to claim 1, wherein the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falls within the range of from 0.001:1 inclusive to 0.010:1 exclusive.
9. The process according to claim 1, wherein the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falls within the range of from 0.003:1 inclusive to 0.005:1 inclusive.



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WHAT IS CLAIMED IS:

1. A process for producing an ethylene- α -olefin copolymer which comprises copolymerizing ethylene and an α -olefin having 4 or more carbon atoms in gas phase in a fluidized bed reaction vessel having a structure of bulgy vessel upper part by use of a catalyst system comprising:

- (A) a solid catalyst component containing a magnesium halide and a titanium halide as the essential constituents,
- (B) an organoaluminum compound, and
- (C) a silicon compound of the formula,



wherein R' and R" may be the same or different and each denote a hydrocarbon group such as a C₁-C₂₄ alkyl group, C₁-C₂₄ aryl group, C₁-C₂₄ aralkyl group, etc; X is a halogen atom; m and n are numbers satisfying the mathematical expressions:

$$0 \leq m < 4,$$

$$0 < n \leq 4, \text{ and}$$

$$0 < m+n \leq 4;$$

when m is more than 1, mR's may be the same or different; and

when n is more than 1, nR"s may be the same or different;

the molar ratio of the silicon compound (C) to the organoaluminum compound (B) falling within the range of from 0.0005:1 inclusive to ^{0.010}~~0.10~~:1 exclusive.

2. The process according to claim 1, wherein the solid catalyst component (A) is obtained by impregnating an organic porous