

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
11 July 2002 (11.07.2002)

PCT

(10) International Publication Number  
WO 02/053604 A1

- (51) International Patent Classification<sup>7</sup>: C08F 4/64
- (21) International Application Number: PCT/KR01/02284
- (22) International Filing Date:  
28 December 2001 (28.12.2001)
- (25) Filing Language: Korean
- (26) Publication Language: English
- (30) Priority Data:  
2000/85531 29 December 2000 (29.12.2000) KR
- (71) Applicant (for all designated States except US): SAM-SUNG GENERAL CHEMICALS CO., LTD. [KR/KR]; San 222-2, Dokgod-Ri, Daesan-Up, Seosan 356-711 (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): KIM, Il, Seop [KR/KR]; 108-903, Hanmaul Apartment, Songgang-Dong, Yusong-Gu, Taejeon 305-503 (KR). SHIN, Moon, Young [KR/KR]; 101-204, Saejong Apartment, Junmin-Dong, Yusong-Gu, Taejeon 305-390 (KR). RO, Ki, Su [KR/KR]; 110-903, Saejong Apartment, Junmin-Dong, Yusong-Gu, Taejeon 305-390 (KR).
- (74) Agents: KIM, Hak, Je et al.; Kwangwhamoon P.O.Box 1828, Seoul 110-618 (KR).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report  
— entirely in electronic form (except for this front page) and available upon request from the International Bureau
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/053604 A1

(54) Title: METHOD FOR PREPARING CATALYST FOR OLEFIN POLYMERIZATION

(57) Abstract: Disclosed is a preparation method of titanium catalyst for olefin polymerization, the method comprising (1) preparing magnesium compound solution by resolving non-deoxidative magnesium halide and IIIA group atom compound in a solvent mixture of cyclic ether, at least one alcohol, phosphorus compound and organosilane with or without hydrocarbon solvent; (2) reacting said magnesium compound solution with titanium compound, silicon compound, tin compound or mixture thereof to produce a support; and (3) reacting said support with titanium compound and electron donor to produce solid complex titanium catalyst, wherein the particle size and particle size distribution of said catalyst are regulated by controlling solubility of the reactants in said steps (2) and/or (3).

**METHOD FOR PREPARING CATALYST FOR OLEFIN POLYMERIZATION****Technical Field**

The present invention relates to a preparation method  
5 of catalyst for  $\alpha$ -olefin polymerization, more  
particularly, a preparation method of titanium solid  
catalyst which is supported by a magnesium-containing  
supporter and the particle size of which can be easily  
controlled.

10

**Background Art**

Until now, many catalysts for olefin polymerization  
and polymerization processes wherein they are used have  
been reported. However, in order to improve physical  
properties of produced polymer or to produce polymer having  
15 special physical properties, development of novel catalysts  
is urgent.

Magnesium-containing catalysts for olefin  
polymerization are suitable to gaseous phase polymerization  
method and have high catalyst activity and provide polymers  
20 of excellent stereoregularity. In catalysts for gaseous  
phase polymerization method, catalyst activity and  
stereoregularity are important in order to reduce cost.  
Besides, shape, size, size distribution of catalyst  
particle, etc. are important. To satisfy catalyst activity  
25 and stereoregularity in  $\alpha$ -olefin polymerization, many  
researches have been conducted. Thanks to these researches,  
elimination process of catalyst residue and atactic  
composition is not required in most of the present,  
commercial preparation processes of polyolefin,

particularly, polypropylene.

However, nowadays, polypropylene having more improved physical properties, particularly stereoregularity is needed. To obtain these polypropylenes, novel catalyst is  
5 needed.

In viewpoint of mean size of catalyst particle, for example, in order to produce impact resistant copolymer, which is comprised of a high content ratio of ethylene of which mean particle size is about 1000 $\mu\text{m}$  and propylene, a  
10 catalyst is required to have the mean particle size of about 30 $\mu\text{m}$  to about 55 $\mu\text{m}$ .

In viewpoint of size distribution of catalyst particle, too small particle is problematic in catalyst transfer and too large particle is problematic in forming  
15 lumps of polymer during polymerization. Thus, catalyst having narrow distribution of particle size is required.

Furthermore, catalyst must have excellent resistance against abrasion generated in polymerization process and sufficiently high bulk density.

Thus, polymerization catalyst of which preparation process is simple and of which particle size can be easily controlled is urgently required.  
20

Many catalysts which are based on magnesium-containing titanium for olefin polymerization and many preparation  
25 methods thereof have been reported. Especially, many preparation methods where magnesium solution is used in order to obtain catalyst for olefin polymerization, of which particle size can be easily controlled have been reported. In the presence of hydrocarbon solvent, magnesium  
30 compound is reacted with electron donors such as alcohols,

amines, cyclic ethers, carboxy oxides, etc. to provide magnesium solution.

Alcohol is used as an electron donor in U.S. Pat. Nos.4,330,649, 5,106,807 and Japanese Laid-Open Publication  
5 No. SHO 58-83006. Preparation methods of magnesium solution are reported in U.S. Pat. Nos.4,315,874, 4,399,054 and 4,071,674.

Tetrahydrofuran which is a cyclic ether has been diversely used as magnesium chloride compound(for example,  
10 U.S. Pat. No.4,482,687), as an additive of cocatalyst(U.S. Pat. No.4,158,642), and as a solvent(U.S. Pat. No.4,477,639), etc.

U.S. Pat. Nos.4,347,158, 4,422,957, 4,425,257, 4,618,661 and 4,680,381 disclose preparation methods of  
15 catalysts, comprising: (1) adding Lewis acids such as aluminum chloride to a supporter, that is, magnesium chloride to provide a mixture and (2) grinding the mixture.

In the aforementioned inventions, high catalyst activity was achieved. However, uniformity in shape and  
20 size, narrowness of size distribution, etc. of catalyst particle and excellent stereoregularity were not achieved.

As described in the above, novel catalyst for olefin polymerization, which can be simply prepared and has high polymerization activity, large mean particle size and  
25 narrow particle size distribution, the size of which can be regulated, and thus, can be used to provide highly stereoregular polymer is urgently required.

#### Disclosure of the Invention

A feature of the present invention is to provide

simpler preparation methods of novel catalysts for olefin polymerization, wherein catalysts have more improved activity, narrow distribution of particle sizes by controlling solubility of the reactants in preparation processes of catalysts and polymers prepared using the catalysts have more improved stereoregularity.

In accordance with the feature of the present invention, there is provided a preparation method of titanium catalyst for olefin polymerization, comprising (1) preparing magnesium compound solution by dissolving magnesium halide having no reducing ability and IIIA group element compound in a solvent mixture of cyclic ether, at least one alcohol, phosphorus compound and organosilane with or without hydrocarbon solvent; (2) reacting said magnesium compound solution with titanium compound, silicon compound, tin compound or mixture thereof to produce a supporter; and (3) reacting said supporter with titanium compound and electron donor to produce solid complex titanium catalyst, wherein the particle size and particle size distribution of said catalyst are regulated by controlling solubility of the reactants in said steps (2) and/or (3).

Examples of the magnesium halide compounds having no reducing ability are halogenated magnesium, alkylmagnesium halide, alkoxymagnesium halide, aryloxymagnesium halide and the like. These magnesium halide compounds may be effectively used as mixtures of two or more or in complex with other metals.

Examples of IIIA group element compounds, which are used in combination of magnesium halide compounds in the preparation of magnesium compound solution, are boron

halide such as boron fluoride, boron chloride and boron bromide; aluminum halide such as aluminum fluoride, aluminum bromide, aluminum chloride and aluminum iodide. A preferred IIIA group element compounds is aluminum halide, above all aluminum chloride. The preferred molar ratio of IIIA group element compound to magnesium compound is 0.25 or less. If the ratio exceeds 0.25, the resultant catalyst is of variable size and reduced activity.

Examples of the hydrocarbon solvents which can be used in the preparation of magnesium compound solution include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane and kerosene; alicyclic hydrocarbons such as cyclopentane, methyl cyclopentane, cyclohexane, methylcyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene; and halogenated hydrocarbons such as trichloroethylene, carbon tetrachloride and chlorobenzene.

To make magnesium halide compound from magnesium solution, as described in the above, a solvent mixture of cyclic ether, at least one alcohol, phosphorus compound and organosilane is used in the presence or absence of hydrocarbon solvent.

Examples of cyclic ethers which can be used in the preparation of magnesium solution according to the present invention include C<sub>2-15</sub> cyclic ethers such as tetrahydrofuran, 2-methyl tetrahydrofuran and tetrahydropyran. Preferred example of cyclic ether is tetrahydrofuran. If cyclic ether having carbon atom higher than 15 is used, it is difficult to prepare magnesium solution.

Examples of alcohols which can be used in the preparation of magnesium solution according to the present invention include C<sub>1-20</sub> alcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecylalcohol, benzylalcohol, phenylethylalcohol, isopropylbenzylalcohol, and cumylalcohol. Preferred examples of alcohols are C<sub>1-12</sub> alcohols. If alcohols having carbon atom higher than 20 is used, it is difficult to prepare magnesium solution.

Mean size and size distribution of catalyst particle which is prepared differ depending upon the ratio of alcohol to cyclic ether, etc. However, to obtain spherical catalyst having particle size of about 50 $\mu$ m, the total sum of alcohol and cyclic ether must be about 0.5 moles to about 20 moles, preferably about 1.0 mole to about 20 moles, more preferably about 2.0 moles to about 10 moles per 1 mole of magnesium compound in preparation of said magnesium solution.

If the total sum of alcohol and cyclic ether is less than 0.5 mole per 1 mole of magnesium compound in the said step, it is difficult to prepare magnesium solution. If the total sum of alcohol and cyclic ether is more than 20 moles per mole of magnesium compound in the said step, size of catalyst particle is reduced.

Furthermore, alcohol must be used in an amount of 0.05 mole to 0.95 mole per 1 mole of cyclic ether. If alcohol is less than 0.05 mole per 1 mole of cyclic ether, it is difficult to prepare spherical catalyst. If alcohol is more than 0.95 mole per 1 mole of cyclic ether, the catalyst activity of the resultant catalyst is reduced.

At this moment, as said alcohols, mixed alcohols of C<sub>1-3</sub> alcohol having relatively low molecular weight and C<sub>4-20</sub> alcohol having relatively high molecular weight is preferable.

5 Alcohol having relatively low molecular weight must be used in an amount of 1 mole% to 40 mole%, preferably 1 mole% to 25 mole% based on the total alcohols.

If alcohol having relatively low molecular weight is used in an amount less than 1 mole%, the catalyst activity  
10 of the resultant catalyst is reduced. If alcohol having relatively low molecular weight is used in an amount more than 25 mole%, it is difficult to prepare spherical catalyst.

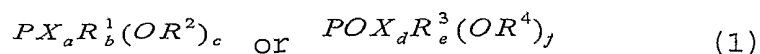
The preferred example of alcohol having relatively low  
15 molecular weight is methanol or ethanol, and the preferred example of alcohol having relatively high molecular weight is butanol, isoamyl alcohol or 2-ethylhexanol.

At least one alcohol employed in the present  
invention, partly or totally, can be used in order to  
20 dissolve magnesium compound. Alternatively, firstly, magnesium solution is prepared by dissolving magnesium compound. Secondly, at least one alcohol employed in the present invention, partly or totally, is added thereto.

However, in (2) supporter preparation step, when  
25 magnesium solution reacts with transition metal compound to provide solid particles, the total amount of the aforementioned at least one alcohol must be kept constant.

Phosphorus compounds used to prepare the magnesium solution are represented by the following Formula(1):





wherein X is a halogen atom;

each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently C<sub>1-20</sub> alkyl, alkenyl or aryl;

5 each of a, b and c is independently an integer of 0-3, provided that a+b+c=3; and

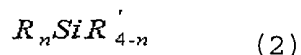
each of d, e and f is independently an integer of 0-3, provided that d+e+f=3.

Examples of phosphorus compounds which can be used in the preparation of magnesium solution according to the present invention include trichlorophosphine, tribromophosphine, diethylchlorophosphite, diphenylchlorophosphite, diethylbromophosphite, diphenylbromophosphite, methylchlorophosphite, phenylchlorophosphite, trimethylphosphite, triethylphosphite, trinormalbutylphosphite, trioctylphosphite, tridecylphosphite, triphenylphosphite, phosphorus oxychloride, triethylphosphate, trinormalbutylphosphate, triphenylphosphate and the like.

20 Any other phosphorus compound to satisfy the above Formula (1) is also available. A phosphorus compound may be used in an amount of 0.01 mole to 0.25 mole, preferably 0.05 mole to 0.2 mole per 1 mole of magnesium compound. If the used amount is less than 0.01 mole per 1 mole of magnesium compound, polymerization activity of catalyst is reduced. 25 If the used amount is more than 0.25 mole per 1 mole of magnesium compound, it is difficult to prepare spherical catalyst.

Organosilanes used to prepare magnesium solution are

represented by the following Formula(2):



wherein R is a hydrogen atom, C<sub>1-10</sub> alkyl, alkoxy, haloalkyl or aryl, or C<sub>1-8</sub> halosilylalkyl group;

5 R' is halo, C<sub>1-10</sub> alkoxy, haloalkoxy or aryloxy, or C<sub>1-8</sub> halosilylalkoxy; and

n is an integer of 0-4.

Examples of Organosilanes to satisfy the above Formula (2) include trimethylchlorosilane, trimethylethoxysilane, 10 dimethylchlorosilane, tetraethoxysilane, tetrabutoxysilane, etc.

An organosilane is used as a size-controlling agent in the present invention. It can prevent the production of too tiny particle and too small particle.

15 The organosilane is used in an amount of 0.01 mole to 0.25 mole, preferably 0.05 mole to 0.2 mole per 1 mole of magnesium compound. If organosilane is less than 0.01 mole per 1 mole of magnesium compound, the organosilane cannot make its role as a size-controlling agent. If organosilane 20 is more than 0.25 mole per 1 mole of magnesium compound, it is difficult to prepare catalyst particle having the size desired in the present invention.

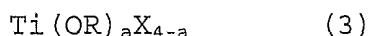
In order to prepare magnesium solution, it is preferable that magnesium compound is reacted with a 25 solvent mixture of cyclic ether, alcohol, phosphorus compound and organosilane in hydrocarbon medium.

Reaction temperature differs depending upon the species and the amount of cyclic ether, alcohol, phosphorus compound and organosilane. However, reaction can be carried

out well at temperature of at least about  $-25^{\circ}\text{C}$  to about  $200^{\circ}\text{C}$ , preferably about  $-10^{\circ}\text{C}$  to about  $200^{\circ}\text{C}$ , more preferably about  $0^{\circ}\text{C}$  to about  $150^{\circ}\text{C}$  for about 1 hr to about 20 hrs, preferably about 5 hrs to about 10 hrs.

5           The magnesium compound solution prepared in aforementioned manner is reacted with transition metal compound, specifically titanium compound, silicon compound, tin compound or mixture thereof to provide a supporter.

          An titanium compound which is used in the  
10       aforementioned supporter preparation step is in the liquid state and is represented by the following Formula(3):



wherein R is a  $\text{C}_{1-10}$  alkyl group;

X is a halogen atom; and

15       a is an integer of 0-4.

          Using this titanium compound renders the size of catalyst particle constant and large, distribution of particle size narrow.

          The examples of titanium compounds to satisfy the  
20       above Formula (3) include tetrahalogenated titanium such as  $\text{TiCl}_4$ ,  $\text{TiBr}_4$  and  $\text{TiI}_4$ ; trihalogenatedalkoxy titanium such as  $\text{Ti}(\text{OCH}_3)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$  and  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Br}_3$ ; dihalogenatedalkoxy titanium such as  $\text{Ti}(\text{O}(\text{i-C}_4\text{H}_9))_2\text{Cl}_2$  and tetraalkoxy titanium such as  $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Br}_2$ ;  $\text{Ti}(\text{OCH}_3)_4$ ,  
25        $\text{Ti}(\text{OC}_2\text{H}_5)_4$  and  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ . These compounds can be used singly or in combination. Preferably titanium compounds containing halogen atoms, more preferably  $\text{TiCl}_4$  is used.

          The examples of said silicon compound include silicon tetrahalide, silicon alkylhalide and the like. The examples  
30       of said tin compounds include tin tetrahalide, tin

alkylhalide, tin hydrohalide and the like.

Titanium compound, silicon compound, tin compound, or mixture thereof, employed in order to precipitate magnesium compound solution is used in an amount of about 0.1 to  
5 about 200 moles, preferably about 0.1 to about 100 moles, more preferably about 0.2 to about 80 moles per 1 mole of magnesium compound.

When magnesium compound solution is reacted with titanium compound, silicon compound, tin compound or  
10 mixture thereof, shape, size and size distribution of the precipitated solid particle (supporter) highly depend on reaction condition.

By reacting magnesium compound solution with titanium compound, silicon compound, tin compound or mixture thereof  
15 at a sufficiently low temperature, the immediate production of solid product is prevented. Subsequently, by heating the reaction product slowly, solid composition is produced.

The Solubilities of reactants can be regulated by controlling reaction temperature and pressure.

20 Temperature of contact reaction is preferably between about  $-70^{\circ}\text{C}$  and about  $70^{\circ}\text{C}$ , more preferably between about  $-50^{\circ}\text{C}$  and about  $50^{\circ}\text{C}$ . After the contact reaction, the reaction temperature is slowly elevated to a temperature between about  $50^{\circ}\text{C}$  and about  $150^{\circ}\text{C}$ , preferably between  
25 about  $60^{\circ}\text{C}$  and about  $80^{\circ}\text{C}$ . Then, the reaction is completely carried out for the time between about 30 minutes and 5 hrs.

Reactor pressure is fixed to a value between about 0 bar and about 2 bar (gauge pressure), preferably between  
30 about 0.01 and about 0.5 bar (gauge pressure). By fixing

reactor pressure to such a low value, evaporated amount of alcohols which dissolve magnesium halide is controlled. In the result, supporter and catalyst are provided with large size and narrow distribution of size. Additionally, the amount of organosilane used as a size-controlling agent is reduced.

The supporter produced in the aforementioned manner is reacted with titanium compound in the presence of an appropriate electron donor to provide catalyst according to the present invention.

Conventionally, this reaction is comprised of two steps: (1) reacting magnesium supporter with titanium compound, optionally together with an electron donor, and subsequently separating solid composition; and (2) reacting said solid composition with titanium compound and an electron donor once more, separating solid composition, and subsequently drying solid composition.

Alternatively, magnesium supporter is reacted with titanium compound in the presence or absence of hydrocarbon solvent or halogenated hydrocarbon solvent for appropriate hours. And then, an electron donor is introduced thereto and the reaction is carried out.

It is desirable to conduct reaction at a temperature of about 90°C to about 120°C and at a gauge pressure of about 0 bar to about 2 bar.

The examples of said titanium compounds include titanium halide, C<sub>1-20</sub> halogenatedalkoxy titanium, or mixture thereof. Preferably, titanium halide or C<sub>1-8</sub> halogenatedalkoxy titanium, more preferably, titanium tetrahalide is used.

According to the present invention, titanium catalyst for olefin polymerization having mean particle size of 30  $\mu\text{m}$  - 120  $\mu\text{m}$  is prepared.

Catalyst prepared according to the present invention, directly or prepolymerized, can be effectively used in polymerizing propylene. Especially, this catalyst is useful in copolymerizing olefins such as ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene and 1-hexene and copolymerizing monomers having polyunsaturated compounds such as conjugated or unconjugated dienes.

#### Best Mode for Carrying Out the Invention

Now, the preferred embodiments of the present invention will be described in detail by the following Examples without limiting the scope of the invention in any way.

#### EXAMPLE 1 : preparation of solid complex titanium catalyst

Solid complex titanium catalyst was prepared through the following 3 steps:

<1 step> preparation of magnesium compound solution

A mixture of 6Kg of  $\text{MgCl}_2$ , 1364 Kg of  $\text{AlCl}_3$  and 180.32Kg (208 L) of toluene was introduced into a 500 L reactor with a mechanical stirrer under nitrogen atmosphere and then was stirred at a velocity of 70 rpm.

10.66Kg (12 L) of tetrahydrofuran, 9.4Kg (11.6 L) of butanol, 180g (240ml) of ethanol, 560g (600ml) of silicon tetraethoxide(  $\text{Si}(\text{OEt})_4$  ) and 1.18Kg (1.2 L) of tributyl

phosphate were introduced thereto. The temperature was raised to 105°C and the reaction was carried out for 7 hours. Homogeneous solution obtained after reaction was cooled to a room temperature.

5

<2 step> preparation of solid supporter

Said magnesium solution was transferred to a 500 L reactor maintained at a temperature of 13°C. The irritator was maintained at a velocity of 82 rpm. 4.8Kg(3.24 L) of SiCl<sub>4</sub> was introduced thereto for 30 minutes.

Then, 4.22Kg(2.44 L) of TiCl<sub>4</sub> was introduced thereto. The temperature was gradually raised to 60°C over 1 hour to provide solid supporter. All the processes to produce solid supporter were conducted in a closed reactor of which inner pressure is 1.5 bar.

After the reaction was carried out at a temperature of 60°C for 1 hour, supporter was transferred into a 300L reactor in 1 minute by using nitrogen pressure in order to prepare catalyst.

20

<3 step> preparation of catalyst

After said solid supporter was precipitated, the liquid portion was eliminated. Then, the remained was washed 2 times with 52Kg(60 L) of toluene to provide a suspension. Then, the suspension was precipitated. Then, the liquid portion was eliminated from the suspension.

31.9Kg(36.8 L) of toluene and 60Kg(34.8 L) of TiCl<sub>4</sub> were introduced into a reactor maintained at a temperature of 15°C and equipped with irritator of 60 rpm.

Then, the reactor temperature was raised to 110°C and

30

the solution was stirred at this temperature for 1 hour and followed by precipitation of solid supporter. The liquid portion was eliminated out from the suspension.

5 52Kg(60 L) of toluene and 34.52Kg(20 L) of  $TiCl_4$  were fed into the reactor. Then, 1.447Kg(1.392 L) of diisobutylphthalate was fed thereto at a temperature of 88°C.

10 The temperature of reactor was raised to 120°C and then the suspension was stirred at this temperature for 1 hour. The liquid portion was eliminated out from the suspension. 31.9Kg(36.8 L) of toluene was fed into the reactor. Then, the reactor is cooled to a temperature of 90°C, was stirred for 30 minutes.

15 After the completion of irritation, the liquid portion was eliminated out from the solution. 60Kg(34.8 L) of  $TiCl_4$  was introduced to the reactor, followed by the irritation at a temperature of 88°C for 30 minutes.

20 All the processes to produce catalyst except introduction and elimination of reactant were conducted in a closed reactor of which inner pressure was 1.5 bar.

The catalyst prepared in this manner was washed 7 times with 40 L of purified hexane until no free titanium compound was detected in the wash liquid. The solid was then dried under nitrogen atmosphere to afford a catalyst.

25 Particle size distributions of supporters and those of catalysts were measured by using laser particle analyzer (Mastersizer X, Malvern Instruments).

30 The compositions of supporters and those of catalysts were analyzed by using ICP (inductively coupled plasma). Surface areas were analyzed by using BET.



Catalyst yield (%) is defined as the ratio of the weight of final product to the weight of  $\text{MgCl}_2$  introduced initially. The results are shown in Table 1.

5           EXAMPLE 2

Example 1 was repeated except that inner pressure of reactor was changed to 0.01bar.

The results are shown in Table 1.

10           EXAMPLE 3

Example 1 was repeated except that inner pressure of reactor was changed to 0 bar by setting the vent line of reactor open.

The results are shown in Table 1.

15

EXAMPLE 4

Example 1 was repeated except that a size-controlling agent , that is,  $\text{Si}(\text{OEt})_4$  was introduced at an amount of 300g(600ml). The results are shown in Table 1.

20

EXAMPLE 5

Example 1 was repeated except that inner pressure of reactor was changed to 0.20 bar and a size-controlling agent , that is,  $\text{Si}(\text{OEt})_4$  was introduced at an amount of 300g(600ml).

25

The results are shown in Table 1.

EXAMPLE 6

Example 1 was repeated except that inner pressure of reactor was changed to 0.01 bar and a size-controlling

30

agent , that is,  $\text{Si}(\text{OEt})_4$  was introduced at an amount of 300g(600ml).

The results are shown in Table 1.

5

#### EXAMPLE 7

Example 1 was repeated except that inner pressure of reactor was changed to 0 bar by setting the vent line of reactor open and a size-controlling agent , that is,  $\text{Si}(\text{OEt})_4$  was introduced at an amount of 300g(600ml).

10

The results are shown in Table 1.

Table 1

(properties of catalysts prepared)

Example	Silicon tetraethoxide (g)	Pressure (atm)	Catalyst yield (%)	Particle size ( $\mu\text{m}$ )	Ti (wt%)	Mg (wt%)	Al (ppm)	Si (ppm)	Surface area ( $\text{m}^2/\text{g}$ )
1	560	1.50	30	50	3.1	18.8	250	230	241
2	560	0.01	100	60	3.1	18.2	380	261	261
3	560	0	100	90	3.6	17.2	400	482	266
4	300	1.50	30	30	2.8	19.2	250	100	275
5	300	0.20	80	40	2.9	19.9	265	85	222
6	300	0.01	90	50	3.4	18.0	380	112	254
7	300	0	100	60	3.2	20.0	330	140	240

15

#### EXAMPLE 8

By using the catalyst prepared according to Example 1 of the present invention, prepolymerization was conducted, followed by polymerization.

20

#### prepolymerization

300ml of hexane and 6mmol of  $\text{AlEt}_3$  were transferred to

4g of catalyst in glass bottle. This catalyst slurry was fed into a 1L glass reactor and kept at a temperature of 15°C and a pressure of 0.5 bar or less.

While propylene being introduced at a velocity of 100cc/minutes, said catalyst slurry was stirred at a velocity of 200rpm for 100 minutes to provide prepolymer.

The degree of prepolymerization of prepolymer made in this manner was 3g propylene (PP)/g catalyst (Cat.).

10           polymerization

A 2L reactor for high pressure was dried in oven and assembled hot. A glass vial containing 27mg of catalyst prepared in said prepolymerization step was put into said reactor.

15           By repeating purging with nitrogen and evacuating to vacuum 3 times, the reactor was filled with nitrogen gas.

1000ml of n-hexane was fed into the reactor, and then, triethyl aluminum(Al/Ti molar ratio=450) and cyclohexyl methyl dimethoxy silane(Si/Al molar ratio=0.1), that is, an exterior electron donor was put thereto.

20           With propylene pressure set to 20psi, said glass vial was broken by a stirrer, and the mixture was stirred at a velocity of 630rpm at a room temperature for 5 minutes to provide polymer.

25           100ml of hydrogen was added thereto and the mixture was heated to 70°C and pressurized to 100psi with propylene.

After the mixture was stirred for 1 hour, the mixture was cooled, followed by addition of excess ethanol solution thereto.

30

polymer produced was collected, and then, dried in a vacuum oven at 50°C for at least 6 hours, yielding white powdery polypropylene.

5 Activity, bulk density, melt index (MI), decane solubility and so on of polymer produced were measured by using NMR, GPC and DSC.

The results are shown in Table 2.

10 EXAMPLE 9

Example 8 was repeated except that the catalyst of example 2 was used.

The results are shown in Table 2.

15 EXAMPLE 10

Example 8 was repeated except that the catalyst of example 3 was used.

The results are shown in Table 2.

20 EXAMPLE 11

Example 8 was repeated except that the catalyst of example 4 was used.

The results are shown in Table 2.

25 EXAMPLE 12

Example 8 was repeated except that the catalyst of example 5 was used.

The results are shown in Table 2.

30 EXAMPLE 13



### Industrial Applicability

As apparent from the above examples, a polymer obtained by employing the solid catalyst produced according to the present invention has more improved stereoregularity. The solid catalyst produced according to the present invention has narrow distribution of particle size. In the preparation method according to the present invention, particle size can be so easily regulated that is advantageous to  $\alpha$ -olefin copolymerization. By using the preparation method according to the present invention, catalyst having improved activity can be produced in high yield.

### Claims

1. A preparation method of titanium catalyst for olefin polymerization, comprising

5 (1) preparing magnesium compound solution by dissolving magnesium halide having no reducing ability and IIIA group element compound in a solvent mixture of cyclic ether, at least one alcohol, phosphorus compound and organosilane with or without hydrocarbon solvent;

10 (2) reacting said magnesium compound solution with titanium compound, silicon compound, tin compound or a mixture thereof to produce a supporter; and

(3) reacting said supporter with titanium compound and an electron donor to produce solid complex titanium catalyst,

15 wherein the particle size of said catalyst is regulated by controlling solubilities of the reactants in said steps (2) and/or (3).

2. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein said solubilities of the reactants in said steps (2) and/or (3) are controlled by controlling inner pressure of a reactor.

25 3. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (2), contact reaction is conducted at a temperature of  $-70^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ , and then, the reaction is conducted at a temperature of  $50^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and at a gauge pressure of 0 bar to 2 bar, in said step (3), the reaction is conducted

at a temperature of 90°C to 120°C and at a gauge pressure of 0 bar to 2 bar, and thereby, to provide titanium catalyst having mean particle size of 30 $\mu$ m-120 $\mu$ m for olefin polymerization.

5

4. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (1), said IIIA group element compound is aluminum halide which is used in an amount of 0.25 mole or less per 10 1 mole of magnesium halide compound.

5. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (1), said cyclic ether is selected from the group 15 consisting of tetrahydrofuran, 2-methyl tetrahydrofuran, and tetrahydropyran and said at least one alcohol is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecylalcohol, benzylalcohol, 20 phenylethylalcohol, isopropylbenzylalcohol, and cumylalcohol.

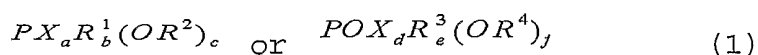
6. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said 25 step (1), total sum of said alcohol and said cyclic ether is about 0.5 mole to about 20 moles per 1 mole of said magnesium compound and said alcohol is used in an amount of 0.05 mole to 0.95 mole per 1 mole of cyclic ether.

30 7. The preparation method of catalyst for  $\alpha$ -olefin



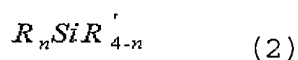
polymerization according to the claim 1, wherein, in said  
 step (1), said alcohol is a mixture of 1 to 40 mole% of C<sub>1-3</sub>  
 alcohol having relatively low molecular weight and 99 to 60  
 mole% of C<sub>4-20</sub> alcohol having relatively high molecular  
 5 weight

8. The preparation method of catalyst for  $\alpha$ -olefin  
 polymerization according to the claim 1, wherein, in said  
 step (1), said phosphorus compound is represented by the  
 10 following Formula(1):



wherein X is a halogen atom;  
 each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently C<sub>1-20</sub> alkyl,  
 alkenyl or aryl;  
 15 each of a, b and c is independently an integer of 0 to 3,  
 provided that a+b+c=3; and  
 each of d, e and f is independently an integer of 0 to 3,  
 provided that d+e+f=3.

20 9. The preparation method of catalyst for  $\alpha$ -olefin  
 polymerization according to the claim 1, wherein, in said  
 (1) step, said organosilane is represented by the following  
 Formula(2):



25 wherein R is a hydrogen atom, C<sub>1-10</sub> alkyl, alkoxy, haloalkyl  
 or aryl, or C<sub>1-8</sub> halosilylalkyl group;  
 R' is halo, C<sub>1-10</sub> alkoxy, haloalkoxy or aryloxy, or C<sub>1-8</sub>  
 halosilylalkoxy; and  
 n is an integer of 0 to 4.

10. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (1), each of said phosphorus compound and said organosilane is independently used in an amount of 0.01 mole to 0.25 mole per 1 mole of magnesium halide compound.

11. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (1), said magnesium compound is reacted with said mixture of cyclic ether, alcohol, phosphorus compound and organosilane at a temperature of  $-25^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  for 1 hour to 20 hours.

12. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (2), said titanium compound is at least one selected from the group consisting of tetrahalogenated titanium, dihalogenated alkoxytitanium and tetraalkoxytitanium, said silicon compound is at least one selected from the group consisting of silicon tetrahalide and silicon alkylhalide, and said tin compound is at least one selected from the group consisting of tin tetrahalide, tin alkylhalide and tin hydrohalide.

13. The preparation method of catalyst for  $\alpha$ -olefin polymerization according to the claim 1, wherein, in said step (2), said titanium compound, silicon compound, tin compound, or mixture thereof is used in an amount of 0.1 mole to 200 moles per 1 mole of magnesium compound.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR01/02284

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
<p style="text-align: center;"><b>IPC7 C08F 4/64</b></p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC07 C08F, B01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean patents and applications for inventions		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9117190 A (QUANTUM CHEMICAL CORPORATION) 14 November 1991 See the whole document	1-13
A	JP 07-238114 A (MITSUI CHEMICALS. INC.) 12 September 1995 See the whole document	1-13
A	US 3,953,414 A (MONTECATINI S.P.A.) 27 April 1976 See the whole document	1-13
A	US 5,221,651 A (HIMONT INCORPORATED) 22 June 1993 See the whole document	1-13
-----		
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search <p style="text-align: center;">18 APRIL 2002 (18.04.2002)</p>	Date of mailing of the international search report <p style="text-align: center;">19 APRIL 2002 (19.04.2002)</p>	
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 920 Dunsan-dong, Seo-gu, Daejeon Metropolitan City 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer <p style="text-align: center;">SOHN, Chang Ho</p> Telephone No. 82-42-481-5538	



**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/KR01/02284

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9117190 A	14-11-1991	EP 480017 A1	18-09-1996
		US 5126302 A	30-06-1992
		KR 92-7001266 A	11-08-1992
JP 07-238114 A	12-09-1995	US 5962615 A	05-10-1999
		EP 670337 A1	06-09-1995
		KR 153870 B1	01-12-1998
US 3,953,414 A	27-04-1976	JP 49-65999 A2	26-06-1974
		GB 1434543 A	05-05-1976
US 5,221,651 A	22-06-1993	NONE	