

A catalyst for ethylene polymerization, a process for preparing the same and use thereof

Technical Field

The present invention relates to a catalyst for olefins polymerization, in particular for ethylene polymerization, to a process for preparing the same and to use thereof.

Technical background

It is well known that catalysts comprising magnesium, titanium, halogen and electron donor as essential ingredients have been broadly used in homopolymerization of ethylene or copolymerization of ethylene with other alpha-olefins. When this type of catalysts is used in gas phase fluidized-bed process of polymerization, aforementioned catalyst ingredients are usually supported on a carrier such as silica and the like in order to ensure that particle morphology and particle size distribution of the catalysts are suitable for the operation in fluidized state. For instance, those catalysts suitable for gas phase fluidized-bed process of polymerization as disclosed in US4,302,565, US4,379,759 and CN 1064870A are prepared by impregnating a mother component, which is prepared from a titanium compound, a magnesium compound and an electron donor compound, on a carrier such as silica and the like, and then treating the impregnated mother component with an activator. The silica carrier used in US4,302,565 and US4,379,759 has generally an average particle size of from 50 to 150 microns.

In the above patents, since the catalytic active component is loaded on the carrier by impregnating process and the like, it is difficult to control the catalytic active component distributing homogeneously on said catalyst

carrier and reproducibility of the catalyst preparation is poor so that catalyst activity as well as particle morphology and particle size distribution of obtained polymer powders are not satisfactory. In order to overcome above problems, on the basis of the above catalytic active components, US4,376,062 prepares a catalyst by mixing fumed silica as filler with a mother component prepared from a titanium compound, a magnesium and an electron donor and then spray drying. The particle size and morphology of this catalyst are easy to be controlled, and catalyst activity is also improved to some extent. However, the catalyst is still not satisfactory in activity, and when the catalyst is used in copolymerization of ethylene and another alpha-olefin, the obtained polymer has a higher content of hexane extractable which will lower the product quality of the final polyethylene resin.

Summary of the invention

One object of the invention is to provide an improved catalyst for ethylene polymerization.

Another object of the invention is to provide a process for the preparation of a catalyst for ethylene polymerization.

Still another object of the invention is to provide use of a catalyst for ethylene polymerization in homopolymerization of ethylene or copolymerization of ethylene and other alpha-olefin(s).

Detailed description of the invention

In the first aspect, the invention provides an improved catalyst for ethylene polymerization. When this catalyst, together with an organoaluminium cocatalyst, is used in copolymerization of ethylene and a higher alpha-olefin, obtained polyethylene has reduced hexane extractable, catalyst activity is markedly enhanced, and particle morphology and particle size distribution of the polymer are also improved. The objective is achieved

through adding a treating agent having at least one alkoxy, i.e. an alkyl silicate of formula $\text{Si}(\text{OR})_n\text{X}_{4-n}$, in which X is a halogen atom and R is an alkyl having from 1 to 10 carbon atoms, during the preparation of the mother liquid of catalyst active component and controlling molar ratio of alkoxy group to titanium less than 1.

Thus, the invention provides a catalyst for ethylene polymerization, which comprises a reaction product of:

(i) titanium-containing active component, comprising at least one magnesium dihalide, at least one titanium halide, at least one electron donor compound and at least one alkyl silicate of formula $\text{Si}(\text{OR})_n\text{X}_{4-n}$ in which X is a halogen atom and R is an alkyl having from 1 to 10 carbon atoms supported on superfine inorganic oxide support, wherein molar ratio of OR group to Ti meets an inequation of $0 < \text{OR}/\text{Ti} < 1$, and said electron donor compound is selected from the group consisting of ethers, esters and ketones; and

(ii) activator component: an organoaluminium compound of formula $\text{AlR}'_n\text{X}_{3-n}$, in which R' represents hydrogen or a hydrocarbonyl having from 1 to 20 carbon atoms, X represents a halogen, and n is a value meeting $1 < n \leq 3$.

The term “polymerization” as used herein intends to include homopolymerization and copolymerization. The term “polymer” as used herein intends to include homopolymer, copolymer and terpolymer.

The catalyst according to the present invention can be prepared through a process comprising the steps of:

(1) Preparing a mother liquid: reacting a magnesium dihalide, a titanium halide, and an alkyl silicate in an electron donor compound to form a mother liquid.

The electron donor compound can be selected from the group consisting of ethers, esters and ketones, such as lower alkyl esters of C_1 - C_4 saturated aliphatic carboxylic acids, lower alkyl esters of C_7 - C_8 aromatic carboxylic acids, C_2 - C_6 aliphatic ethers, C_3 - C_4 cyclic ethers, C_3 - C_6 saturated aliphatic

ketones, and mixture thereof. The term “lower alkyl” as used herein intends to mean a linear or branched alkyl having from 1 to 6 carbon atoms. Examples of the electron donor compound include, but are not limited to, methyl formate, ethyl acetate, butyl acetate, diethyl ether, dihexyl ether, tetrahydrofuran, acetone, and isobutyl methyl ketone, with tetrahydrofuran being preferred. These electron donor compounds can be used alone or in combination.

The titanium halide is titanium chloride or titanium bromide, preferably TiCl_3 or TiCl_4 .

Examples of the magnesium dihalide include magnesium dichloride, magnesium dibromide, and magnesium diiodide, with magnesium dichloride being preferred.

The alkyl silicate has a formula of $\text{Si}(\text{OR})_n\text{X}_{4-n}$, in which X is a halogen atom and R is an alkyl having from 1 to 10 carbon atoms. Examples include, but are not limited to, tetraethyl orthosilicate, tetrabutyl orthosilicate, triethoxy chlorosilane, diethoxy dichlorosilane, dimethoxy dichlorosilane, and the like.

In the preparation of the mother liquid, the ratio of individual components is preferably controlled in such a manner that molar ratio of Mg to Ti is larger than 1 and less than 20, molar ratio of OR group to Ti is larger than 0 and less than 1, preferably in a range of from 0.1 to 0.8. The electron donor compound(s) is generally added in an amount of from about 3 to 500 moles, preferably from 10 to 300 moles, with respect to one mole of Titanium.

(2) Mixing support: mixing the mother liquid obtained in step (1) with superfine inorganic oxide support to form a slurry.

The inorganic oxide support useful in the present invention is generally silica and/or alumina having typically an average particle size of from 0.01 to 5 microns, preferably from 0.05 to 2 microns. Most preferably, silica support

having an average particle size of from 0.1 to 1 micron is used. When used, such a support should be dried, namely, having no absorbed water. The support should be mixed with the mother liquid in an adequate amount to form a slurry suitable for spray drying. That is, the content of the support in the slurry should be in a range of from 10 to 60 percent by weight, preferably from 20 to 40 percent by weight, based on the weight of the total slurry.

(3) Molding by spray process: drying the slurry obtained in step (2) through spray drying process to form solid catalyst component having an average particle size of from 5 to 50 microns.

Spray drying can be performed by techniques well known in the art. In general, spray drying is carried out by passing the slurry together with an inert drying gas through a spray dryer to obtain solid catalyst component having an average particle size of from 5 to 50 microns, with inlet temperature of the spray dryer being controlled at from 80 to 300 °C, and outlet temperature of the spray dryer being controlled at from 50 to 200 °C.

(4) Pre-reduction.

In order to render the titanium-containing solid catalyst component obtained by spray drying suitable for the production of ethylene polymer, it is generally desired that the solid catalyst component is pre-reductively treated with an organoaluminium compound so as to make the catalyst component standing in a state of effectively polymerizing ethylene. For this purpose, in general, the solid catalyst component obtained in step (3) is reacted with an organoaluminium activator component in a hydrocarbon solvent to form a catalyst.

Said activator component is organoaluminium compound of formula AlR'_nX_{3-n} , in which R' represents hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, X represents a halogen, and n is a value meeting $1 < n \leq 3$. Specifically, the activator component can be one or more selected from the group consisting of $AlEt_3$, $Al(iso-Bu)_3$, $Al(n-C_6H_{13})_3$, $Al(n-C_8H_{17})_3$ and

AlEt_2Cl .

Examples of said hydrocarbon solvent include, but are not limited to, isopentane, hexane, heptane, toluene, xylene, naphtha, and mineral oil.

The catalyst subjected to reduction can be added to polymerization reactor after further drying, alternatively, it is possible to add this slurry containing the catalyst component and the activator directly to the reactor. Additional activator is used to completely activate the catalyst in the reactor. Said additional activator is organoaluminium compound of formula $\text{AlR}'_n\text{X}_{3-n}$, in which R' represents hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, X represents a halogen, and n is a value meeting $1 < n \leq 3$, can be same as or different from the activator used in the pre-reduction, and can be one or more selected from the group consisting of AlEt_3 , $\text{Al}(\text{iso-Bu})_3$, $\text{Al}(\text{n-C}_6\text{H}_{13})_3$, $\text{Al}(\text{n-C}_8\text{H}_{17})_3$ and AlEt_2Cl .

The catalysts of the invention can be used in homopolymerization of ethylene and copolymerization of ethylene and other alpha-olefins such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and 4-methyl-1-pentene.

The catalysts of the invention can be used in various known ethylene polymerization processes, either continuous polymerization or batch polymerization. For instance, the catalysts of the invention are suitable for gas phase process, slurry process or solution process of ethylene polymerization, especially for gas phase fluidized-bed process of ethylene polymerization, in particular for condensed-mode technique of gas phase fluidized-bed process.

When used in copolymerization of ethylene and a higher alpha-olefin, the catalysts of the present invention exhibit higher catalytic activity, the obtained polyethylene has reduced hexane extractable, and particle morphology and particle size distribution of the polymer are also remarkably improved. At the mean time, since the catalysts of the present invention have a less average particle size, it is possible to dilute the catalysts with an inert diluent such as mineral oil and the like and achieve homogeneous feed of the catalyst slurry

through pump feeding manner. By this way, the feeding is homogeneous and the operation is stable.

Embodiments of the Invention

The following examples further describe the invention, but do not make limitation to the invention in any way.

Testing methods:

1. Melt index: measured according to ASTM D1238-99.
2. Density: measured according to ASTM D1505.
3. Hexane extractables: W_1 grams of polyethylene powders which have been dried at 70°C under vacuum for 2 hours are added to 200ml of hexane, and the mixture is heated at 68°C for 4 hours, followed by filtrating. The powders obtained by filtrating are dried at 70°C under vacuum for 2 hours and then weighed as W_2 grams. The content of hexane extractable in the polymer is calculated as $(W_1 - W_2)/W_1 \times 100\%$.

Example 1

1. Preparation of the Catalyst

To a 250ml three-necked reactor purged with N_2 , 1.3g of $TiCl_3 \cdot 1/3 AlCl_3$, 3.0g of $MgCl_2$ and 75ml of tetrahydrofuran (THF) were added successively. The mixture was heated with stirring to 65°C and held at that temperature for 2 hours. 0.054g of $Si(OEt)_4$ was added, and the mixture was allowed to react at constant temperature of 65°C for further 2 hours, and then cooled to 30°C.

To a 250ml three-necked reactor purged with N_2 , 4.5g of silica (TS-610 available from Cabot Corporation, having particle diameters of from 0.02 to 0.1 micron) was added, followed by the addition of above cooled mother liquid while the temperature was maintained at 30°C. After stirring for 2 hours, the stirred slurry was spray dried in a spray dryer operated at

conditions of inlet temperature: 150°C, and outlet temperature: 70°C. A solid catalyst component having a Ti content of 2.34% by weight, a magnesium content of 6.1% by weight and a THF content of 33% by weight was obtained. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by weight, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar ratio of THF to $\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.2.

2. Slurry Polymerization of Ethylene

To a 2L stainless steel autoclave, which had been evacuated and replaced with hydrogen for several times, were added 1L of hexane, 1ml of 1mmol/ml solution of AlEt_3 in hexane and 0.05g of above catalyst (calculated on the weight of solid catalyst component) in N_2 atmosphere with stirring. The reactor was heated to 75°C, made up appropriate amount of hydrogen to an pressure of 0.28MPa, then introduced ethylene gas to make ethylene fractional pressure being 0.75MPa. The polymerization reaction was continued for 2 hours at constant temperature of 85°C and ethylene was made up during the polymerization to maintain the fractional pressure of ethylene unchanged. Then the temperature of the autoclave was reduced, the pressure was relieved and the product was discharged. The polymerization results were listed in Table 1.

3. Gas Phase Polymerization

The gas phase polymerization reaction was carried out in a fluidized bed reactor having a diameter of 150 mm and a height of 3000 mm, which had been purged with nitrogen in advance. First, 350 g of dried base of particulate polyethylene was charged into the fluidized bed reactor, and circulating gas comprising hydrogen, ethylene, 1-butene and nitrogen was then passed

through the reactor, followed by the addition of 15 ml of 1mmol/ml solution of AlEt_3 in hexane. After the reactor was heated to 85 °C, 0.45 g of the above catalyst slurry was charged to initiate the polymerization. The polymerization was performed for 4 hour at a total pressure of the circulating gas of 1.7MPa, with the composition of the circulating gas being 9% nitrogen, 60% ethylene, 21% 1-butene, 10% H_2 . The polymerization results were shown in Table 2.

Example 2

1. Preparation of the catalyst:

A solid catalyst component having a Ti content of 2.35% by weight, a magnesium content of 6.3% by weight and a THF content of 28% by weight was prepared according to same procedure as that discribed in Example 1, except that 0.1359g of $\text{Si}(\text{OEt})_4$ was added such that the molar ratio of Ti to alkoxy group was 1:0.4. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by wieght, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar retio of THF to $\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.3.

2.Slurry Polymerization of Ethylene

The procedure was same as that described in Example 1, and the polymerization results were listed in Table 1.

3. Gas Phase Polymerization

The procedure was same as that described in Example 1, and the polymerization results were listed in Table 2.

Example 3

1. Preparation of the catalyst:

A solid catalyst component having a Ti content of 2.16% by weight, a magnesium content of 6.0% by weight and a THF content of 27% by weight was prepared according to same procedure as that discribed in Example 1, except that 0.2038g of $\text{Si}(\text{OEt})_4$ was added such that the molar ratio of Ti to alkoxy group was 1:0.6. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by wieght, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar retio of THF to $\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.3.

2. Slurry Polymerization of Ethylene

The procedure was same as that described in Example 1, and the polymerization results were listed in Table 1.

3. Gas Phase Polymerization

The procedure was same as that described in Example 1, and the polymerization results were listed in Table 2.

Comparative Example 1

1. Preparation of the catalyst:

A solid catalyst component having a Ti content of 2.4% by weight, a magnesium content of 6.0% by weight and a THF content of 27% by weight was prepared according to same procedure as that discribed in Example 1, except that no $\text{Si}(\text{OEt})_4$ was added. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by wieght, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar retio of THF to

$\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.3.

2. Polymerization of Ethylene

Ethylene polymerization was carried out according to the same procedures as that described in Example 1, and the polymerization results were listed in Table 1 and Table 2.

Comparative Example 2

1. Preparation of the catalyst:

A solid catalyst component having a Ti content of 2.4% by weight, a magnesium content of 6.6% by weight and a THF content of 24% by weight was prepared according to same procedure as that discribed in Example 1, except that 0.3397g of $\text{Si}(\text{OEt})_4$ was added such that the molar ratio of Ti to alkoxy group was 1:1. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by wieght, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar retio of THF to $\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.3.

2. Polymerization of Ethylene

Ethylene polymerization was carried out according to the same procedures as that described in Example 1, and the polymerization results were listed in Table 1 and Table 2.

Comparative Example 3

1. Preparation of the catalyst:

A solid catalyst component having a Ti content of 2.4% by weight, a magnesium content of 7.2% by weight and a THF content of 22% by weight was prepared according to same procedure as that discribed in Example 1,

except that 0.6794g of $\text{Si}(\text{OEt})_4$ was added such that the molar ratio of Ti to alkoxy group was 1:2. The solid catalyst component was added to a mineral oil to form a slurry in mineral oil having a solid content of 30% by weight, then $\text{Al}(\text{Et})_2\text{Cl}$ was added and the mixture was allowed to react for 20 minutes, then $\text{Al}(\text{C}_6\text{H}_{13})_3$ was added and the mixture was allowed to react for 2 hours to form a catalyst slurry. The amounts of $\text{Al}(\text{Et})_2\text{Cl}$ and $\text{Al}(\text{C}_6\text{H}_{13})_3$ were so determined based on the content of THF that molar ratio of THF to $\text{Al}(\text{Et})_2\text{Cl}$ to $\text{Al}(\text{C}_6\text{H}_{13})_3$ was 1 to 0.5 to 0.3.

2. Polymerization of Ethylene

Ethylene polymerization was carried out according to the same procedures as that described in Example 1, and the polymerization results were listed in Table 1 and Table 2.

Table 1. Results of Slurry Polymerization of Ethylene

Catalyst	Activity kgPE/gTi	MI g/10min	OEt/Ti
Example 1	507	0.81	0.16
Example 2	502	0.85	0.4
Example 3	617	0.84	0.6
Comparative Example 1	440	0.75	0
Comparative Example 2	460	0.425	1
Comparative Example 3	200	0.31	2

Table 2. Results of Gas Phase Polymerization of Ethylene

Catalyst	Activity kgPE/gTi	MI g/10min	%Hexane Extractable	Density of Polymer g/ml
Example 1	660	2.1	9.34	0.9202
Example 2	596	2.3	9.76	0.9211
Example 3	521	2.2	9.43	0.9216
Comparative Example 1	436	2.0	14.53	0.9206

What is claimed is:

1. A catalyst for ethylene polymerization, comprising a reaction product of:

(i) titanium-containing active component, comprising at least one magnesium dihalide, at least one titanium halide, at least one electron donor compound and at least one alkyl silicate of formula $\text{Si}(\text{OR})_n\text{X}_{4-n}$ in which X is a halogen atom and R is an alkyl having from 1 to 10 carbon atoms supported on superfine inorganic oxide support, wherein molar ratio of OR group to Ti meets an inequation of $0 < \text{OR}/\text{Ti} < 1$, and said electron donor compound is selected from the group consisting of ethers, esters and ketones; and

(ii) activator component: an organoaluminium compound of formula $\text{AlR}'_n\text{X}_{3-n}$, in which R' represents hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, X represents a halogen, and n is a value meeting $1 < n \leq 3$.

2. The catalyst for ethylene polymerization of claim 1, wherein the superfine inorganic oxide support is silica having an average particle size of less than 5 microns.

3. The catalyst for ethylene polymerization of claim 1, wherein the superfine inorganic oxide support is silica having an average particle size of from 0.1 to 1 micron.

4. The catalyst for ethylene polymerization of claim 1, wherein the titanium halide is TiCl_3 or TiCl_4 .

5. The catalyst for ethylene polymerization of claim 1, wherein the electron donor compound is one or more selected from the group consisting of lower alkyl esters of C_1 - C_4 saturated aliphatic carboxylic acids, lower alkyl esters of C_7 - C_8 aromatic carboxylic acids, C_2 - C_6 aliphatic ethers, C_3 - C_4 cyclic ethers, C_3 - C_6 saturated aliphatic ketones.

6. The catalyst for ethylene polymerization of claim 1, wherein the electron donor compound is one or more selected from the group consisting of methyl formate, ethyl acetate, butyl acetate, diethyl ether, dihexyl ether, tetrahydrofuran, acetone, and isobutyl methyl ketone.
7. The catalyst for ethylene polymerization of claim 1, wherein the electron donor compound is tetrahydrofuran.
8. The catalyst for ethylene polymerization of claim 1, wherein the magnesium dihalide is magnesium dichloride, magnesium dibromide, or magnesium diiodide.
9. The catalyst for ethylene polymerization of claim 1, wherein the activator component is one or more selected from the group consisting of AlEt_3 , $\text{Al}(\text{iso-Bu})_3$, $\text{Al}(\text{n-C}_6\text{H}_{13})_3$, $\text{Al}(\text{n-C}_8\text{H}_{17})_3$ and AlEt_2Cl .
10. A process for the preparation of a catalyst according to any one of claims 1-9, comprising the steps of:
 - (i) reacting a magnesium dihalide, a titanium halide and an alkyl silicate of formula $\text{Si}(\text{OR})_n\text{X}_{4-n}$, in which X is a halogen atom and R is an alkyl having from 1 to 10 carbon atoms, in an electron donor compound to form a mother liquid;
 - (ii) mixing the mother liquid obtained in step (i) with superfine inorganic oxide support to form a mixture;
 - (iii) drying the mixture obtained in step (ii) through spray drying process to form a solid catalyst component;
 - (iv) pre-reducing the solid catalyst component obtained in step (iii) with an activator component in mineral oil to form a catalyst.

11. Use of a catalyst according to any one of claims 1-9 in ethylene polymerization.

12. Use of a catalyst according to any one of claims 1-9 in gas phase fluidized bed process of ethylene polymerization.