Title: METHOD FOR PREPARING A TITANIUM CATALYST COMPONENT. TITANIUM CATALYST COMPONENT, METHOD FOR PREPARING A TITANIUM CATALYST AND TITANIUM CATALYST

Abstract: The present invention relates to a method for preparing a titanium catalyst component, comprising the steps: a) reacting a magnesium dihalide, an electron donor solvent and a titanium halide, b) reacting an alkyl borate ester with the reaction mixture obtained in step a), c) adding inorganic oxide particles to the reaction mixture obtained in step b), d) spray drying the suspension obtained in step c), a titanium catalyst component obtainable by said method, a method for preparing a titanium catalyst and a titanium catalyst obtainable by said method.
Method for preparing a titanium catalyst component, titanium catalyst component, method for preparing a titanium catalyst and titanium catalyst.

Technical field

The present invention relates to a method for preparing a titanium catalyst component, a titanium catalyst component, a method for preparing a titanium catalyst and a titanium catalyst.

The titanium catalyst on the basis of the titanium catalyst component according to the present invention is used for ethylene polymerization and copolymerization, in particular ethylene gas-phase polymerization using a fluidized bed in a condensation state or a super-condensation state, and can provide high catalytic activity to produce a polymer with a low amount of hexane-extractable components, a narrow particle size distribution and an improved particle morphology.

Background of the invention

For use in the Unipol gas-phase fluidized bed process, which is the most typical gas-phase polymerization process of ethylene, the catalyst is usually prepared by providing silica gel having a large particle size with active components (Ti and Mg). Because the shape of the catalyst completely depends on the particle
shape of the silica gel carrier, catalyst performance also depends on the particle size and the microporous structure of silica gel used to prepare the catalyst.

For example, according to the catalyst for gas-phase polymerization by a fluidized bed process disclosed in US 4,302,565, the average particle size of the silica gel used is generally 40 µm to 80 µm. An LLDPE film-type resin made by this catalyst can provide excellent processing and mechanical properties. In the commercial gas-phase fluidized bed device, ethylene polymerization activity of this catalyst is generally about 3500 g PE/g cat.

However, the activity will significantly lower due to a reduction of the residence time of the catalyst, in case it is used for the condensation technology of the gas-phase fluidized bed, which consequently increases the ash content of the obtained ethylene polymer, which affects its performance. Thus, improving the catalytic activity of this kind of catalyst is one of the critical factors for enhancing the quality of an ethylene polymer produced by such a catalyst. In addition, the form and particle size distribution of polymer particles are the major factors of affecting the stable operation of a gas-phase fluidized bed device. Thus, excellent polymer particle morphology, particle size distribution and a lower content of fine powders is the target for this kind of catalyst.

With respect to the catalyst carrier disclosed in US 4,302,565, it is difficult to control a uniform distribution of the active components on the catalyst carrier, because the active components of the catalyst are loaded on the catalyst carrier
by the impregnation method, which results in difficulties in reproducing the preparation procedure of the catalyst. Thus, catalyst activity, particle morphology and particle size distribution of the obtained polymer are not satisfactory.

On the basis of the above active components of the catalyst, fumed SiC$_2$ is used as the filler and mixed with a mixture obtained by reacting a titanium compound, a magnesium compound and electron donor compound according to US 4,376,062 and CN 1,493,599 A. The catalyst can be obtained by a spray drying method. For applying the catalyst in a gas-phase fluidized bed polymerization process of ethylene, the particle size and morphology of the obtained catalyst can be easily controlled, while the catalyst efficiency is also improved to some extent. However, the catalytic activity of the catalyst and the shape of the polymerization product are still unsatisfactory. Moreover, when this catalyst is applied in the copolymerization of ethylene and higher-level $\alpha$-olefins (such as 1-hexene), the content of hexane extracts is still high in the obtained polymer, which will reduce final product performance of a PE (Polyethylene) (co)polymer resin.

The purpose of the present invention is to overcome the above disadvantages of the technical methods in the art and to provide a catalyst for ethylene polymerization and copolymerization, in particular ethylene gas-phase polymerization using a fluidized bed in a condensation state or a super-condensation state, with high catalytic activity, which enables to reduce the hexane extracts in the obtained ethylene (co)polymer and to significantly improve the particle morphology and particle size distribution of the obtained PE (co)polymer.
In order to achieve the above purpose, the present invention provides according to one aspect a method for preparing a titanium catalyst component, comprising the steps of:

a) reacting a magnesium dihalide, an electron donor solvent and a titanium halide,

b) reacting an alkyl borate ester with the reaction mixture obtained in step a),

c) adding inorganic oxide particles to the reaction mixture obtained in step b),

d) spray drying the suspension obtained in step c).

According to a preferred embodiment of the method for preparing a titanium catalyst component, the magnesium dihalide is selected from the group consisting of MgCl₂, MgBr₂ and MgI₂.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the electron donor solvent is selected from the group consisting of C₁-C₄ alcohols, C₂-C₆ fatty ethers and C₃-C₄ cyclic ethers.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the electron donor solvent is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, butanol, isobutanol, ethylethers, hexylethers, tetrahydrofuran and mixtures thereof, wherein tetrahydrofuran is most preferred.
According to a further preferred embodiment of the method for preparing a titanium catalyst component, the titanium halide is selected from the group consisting of TiCl$_3$, TiCl$_4$, TiBr$_3$ and TiBr$_4$.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the alkyl borate ester has the general formula

$$B(OR)_nX_{3-n}$$

wherein

- $R$ is a C$_1$-C$_\text{o}$ alkyl group,
- $X$ is halogen, and
- $1 \leq n \leq 3$.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the alkyl borate ester is selected from the group consisting of trimethylborate, triethylborate, tripropylborate, tributylborate, dichloromethoxyborane, chlorodiethoxyborane and dichloroethoxyborane.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the inorganic oxide particles are selected from the group consisting of particles of SiC$_{\geq2}$, Al$_2$O$_3$ and mixtures thereof.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the inorganic oxide particles are added in an amount in step c) such that the obtained
suspension contains 10 wt.% to 60 wt.%, preferably 20 wt.% to 40 wt.% of the inorganic oxide particles.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the inorganic oxide particles have a particle size of 0.01 \( \mu \text{m} \) to 10 \( \mu \text{m} \), preferably of 0.01 \( \mu \text{m} \) to 1 \( \mu \text{m} \).

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the inorganic oxide particles are \( \text{SiO}_2 \) particles having a particle size of 0.01 \( \mu \text{m} \) to 1 \( \mu \text{m} \).

Before using the inorganic carrier in the method for preparing a titanium catalyst component according to the present invention, it is preferred to subject the inorganic carrier to a baking dehydration treatment or to activate the inorganic carrier by an alkylation with usual alkylating agents like butyllithium, methyllithium etc.

The spray drying in the method for preparing a titanium catalyst component according to the present invention can be carried out by a conventional method using suitable conditions well known to the skilled person.

According to a further preferred embodiment of the method for preparing a titanium catalyst component, the magnesium dihalide, the titanium halide and the alkyl borate ester are provided in amounts such that 1 < \( \text{Mg/Ti} < 20 \) (mol/mol) and 0 < \( \text{OR/Ti} < 5 \) (mol/mol), preferably \( \text{OR/Ti} = 0.1 \) to 1.0 (mol/mol), and wherein
the electron donor solvent is provided in an amount of 3 to 500 mol, preferably 10 to 100 mol, based on one mol of Ti.

According to a further aspect, the present invention provides a titanium catalyst component, obtainable by the method for preparing a titanium catalyst component according to the present invention.

According to a preferred embodiment of the titanium catalyst component, the average particle diameter of the titanium catalyst component is 5 µm to 45 µm.

In case the present titanium catalyst component is used as a basis for a corresponding titanium catalyst, it can provide high catalytic activity to produce a polymer with a high bulk density, narrow particle size distribution and very fine particles in case the titanium catalyst is used for ethylene polymerization and copolymerization, in particular for ethylene gas-phase polymerization using a fluidized bed in a condensation state or a super-condensation state.

In order to be used for ethylene polymerization and copolymerization the titanium catalyst component according to the present invention must be activated, which means that it must be treated with sufficient activator compound to transform the Ti atom in the titanium catalyst component to an active state, such that a titanium catalyst is obtained.

Therefore, according to a further aspect the present invention provides a method for preparing a titanium catalyst, comprising the steps of:
reacting a titanium catalyst component according to the 
present invention with an organic aluminum compound having 
the general formula

$$A1R'^nX_{3-n}$$

wherein

- $R^1$ is hydrogen or a C$_1$-C$_{20}$ alkyl group,
- $X$ is F, Cl, Br or I, and
- $1 < n \leq 3$

in a hydrocarbon solvent.

According to a preferred embodiment of the method for preparing 
a titanium catalyst, the organic aluminum compound is selected 
from the group consisting of AlEt$_3$, AlEt$_2$Cl, Al(isobutyl)$_3$, 
Al(n-C$_6$H$_{13}$)$_3$, Al(n-C$_8$H$_{17}$)$_3$ and mixtures thereof.

According to a further preferred embodiment of the method for 
preparing a titanium catalyst, the hydrocarbon solvent is 
selected from the group consisting of isopentane, hexane, 
heptane, toluene, xylene, naphtha, mineral oil and mixtures 
thereof.

In another aspect the present invention provides a titanium 
catalyst, obtainable by the method for preparing a titanium 
catalyst according to the present invention.

According to a preferred embodiment of the titanium catalyst, 
the molar ratio of Al in the organic aluminum compound and Ti 
in the titanium catalyst compound is in a range of 10 to 1000. 
Before the actual polymerization, a pre-polymerization can be
carried out with said titanium catalyst component and ethylene or an \( \alpha \)-olefin. This pre-polymerization can be conducted at a low temperature in the presence of a hydrocarbon solvent (such as hexane), the above titanium catalyst component, said organic aluminum compound (such as triethyl aluminum) and ethylene or an \( \alpha \)-olefin at an appropriate pressure.

In another aspect the present invention provides the use of a catalyst according to the present invention for ethylene polymerization and copolymerization.

The catalyst according to the present invention can be used for homopolymerization of ethylene or copolymerization of ethylene with other \( \alpha \)-olefins, like for example propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene. A gas-phase method, a slurry method and a solution may be used in the polymerization process, wherein a condensate or super-condensate operation technology of the gas-phase fluidized bed process is preferred.

To ensure a high polymerization rate, the polymerization using a titanium catalyst according to the present invention should be conducted at a suitable temperature. Generally, the polymerization temperature is 20 °C to 200 °C, preferably 60 °C to 95 °C. During the polymerization process, the pressure of the monomer is preferably 1 atm to 100 atm, more preferably 2 atm to 50 atm.

The following Examples are given to illustrate the present invention and are not intended to limit its scope.
Example 1

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0 g TiCl₃ - 1/3 AlCl₃, 4.61 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)₃ is added in a molar ratio of Trialkoxy group =1:0.2 and reacted at 65 °C for 2 h. After that the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.12 %, 6.08 % and 30.9 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt₂Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(CeH₃)₃ is added. AlEt₂Cl and Al(CeH₃)₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(C₆H₁₃)₃ is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl
aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80 °C. The results of the polymerization are shown in Table 1.

3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 300 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, C₂H₄ = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 160 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.73 MPa. The polymerization results are shown in Table 2.

Example 2

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0g TiCl₃ · 1/3 AlCl₃, 4.6 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)₃ is added
in a molar ratio of Tiialkoxy group =1:0.4 and reacted at 65 °C for 2 h. After that the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.24 %, 6.25 % and 29 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt₂Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(C₆H₃)₃ is added. AlEt₂Cl and Al(C₆H₃)₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(C₆H₃)₃ is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80°C. The results of the polymerization are shown in Table 1.
3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, C₂H₄ = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.

Example 3

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0 g TiCl₃ * 1/3 AlCl₃, 4.6 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)₃ is added in a molar ratio of Ti:alkoxy group =1:0.6 and reacted at 65 °C for 2 h. After that the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet
temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.49 %, 6.12 % and 30 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt<sub>2</sub>Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(C<sub>6</sub>H<sub>i</sub>3) is added. AlEt<sub>2</sub>Cl and Al(CeH<sub>i</sub>)<sub>3</sub> are added such that the molar ratio of THF:AlEt<sub>2</sub>Cl:Al(C<sub>6</sub>H<sub>i</sub>3) is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N<sub>2</sub> and H<sub>2</sub> is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H<sub>2</sub> is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80°C. The results of the polymerization are shown in Table 1.

3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H<sub>2</sub>, ethylene, 1-butene and N<sub>2</sub> in a ratio of H<sub>2</sub> = 11.0 %, C<sub>2</sub>H<sub>4</sub> = 56.8 %, 1-butene = 22.2 % and N<sub>2</sub> = 10.0 % as well as 15 mmol
triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.

Example 4

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N2, is charged with 2.0 g TiCl3 · 1/3 AlCl3, 4.6 g MgCl2 and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)3 is added in a molar ratio of Ti:alkoxy group =1:1 and reacted at 65 °C for 2 h. After that the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N2, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.26 %, 5.99 % and 31.8 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt2Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(CeH13)3 is added.
AlEt₂Cl and Al(C₆H₁₃)₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(C₆H₁₃)₃ is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 L reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 L hexane, 1 mmol triethyl aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80 °C. The results of the polymerization are shown in Table 1.

3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, C₂H₄ = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.
Example 5

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0 g TiCl₃, 1/3 AlCl₃, 4.6 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)₃ is added in a molar ratio of Ti:alkoxy group = 1:1.5 and reacted at 65 °C for 2 h. After that, the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.33 %, 6.01 % and 30.9 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt₂Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(CeH₁₃)₃ is added. AlEt₂Cl and Al(CeH₁₃)₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(CeH₁₃)₃ is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl
aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80°C. The results of the polymerization are shown in Table 1.

3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, C₂H₄ = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.

Comparative Example 1

1. Preparation of a titanium catalyst

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0g TiCl₃ · 1/3 AlCl₃, 4.6 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. After that the
obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.41 %, 6.19 % and 33 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt₂Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(C₆H₁₃)₃ is added. AlEt₂Cl and Al(C₆H₁₃)₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(C₆H₁₃)₃ is 1:0.5:0.2.

2. *Slurry polymerization of ethylene*

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80°C. The results of the polymerization are shown in Table 1.
3. **Gas-phase copolymerization of ethylene and 1-butene**

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, C₂H₄ = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.

15 **Comparative Example 2**

1. **Preparation of a titanium catalyst**

A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 2.0g TiCl₃ • 1/3 AlCl₃, 4.6 g MgCl₂ and 115 ml tetrahydrofuran. The contents of the flask are heated to 65 °C under agitation and reacted for 2 h at 65 °C. B(OEt)₃ is added in a molar ratio of Tiralkoxy group =1:0.3 and reacted at 65 °C for 2 h. After that the obtained reaction mixture is cooled to 30 °C. A 250 ml three-neck flask, wherein the air has been replaced by N₂, is charged with 6.9 g silica gel (TS-610, particle size = 0.02 µm to 0.1 µm, supplied by Cabot Corporation, MA, USA), the above cooled reaction mixture is added to the flask and the temperature is maintained at 30 °C for 2 h under agitation. The stirred mixture is then spray dried with a spray dryer under the following conditions: inlet temperature = 160 °C, outlet
temperature = 80 °C. The solid titanium catalyst component obtained after spray drying had a content of Ti, Mg and THF of 2.28 %, 6.39 % and 33 %, respectively. Mineral oil is added to the titanium catalyst component, such that a mineral oil solution with a solid content of 30 % is obtained. AlEt₂Cl is added to the mineral oil solution and reacted with the titanium catalyst component for 20 min, whereupon Al(\(C_6H_{13}\))₃ is added. AlEt₂Cl and Al(\(C_6H_{13}\))₃ are added such that the molar ratio of THF:AlEt₂Cl:Al(\(C_6H_{13}\))₃ is 1:0.5:0.2.

2. Slurry polymerization of ethylene

A 2 l reaction vessel is heated to 80 °C and the air in the vessel is replaced by dry N₂ and H₂ is blown into the vessel. The vessel is then simultaneously charged with 1 l hexane, 1 mmol triethyl aluminum, and 50 mg of the above prepared titanium catalyst. The contents of the vessel are heated to 75 °C and H₂ is fed into the vessel such that the pressure in the vessel reaches 0.18 MPa. Then ethylene is fed into the vessel such that the total pressure in the vessel reaches 1.03 MPa (gauge pressure) and a polymerization is carried out for 2 h at 80°C. The results of the polymerization are shown in Table 1.

3. Gas-phase copolymerization of ethylene and 1-butene

The gas-phase copolymerization of ethylene and 1-butene is carried out in an ethylene gas-phase polymerization apparatus with a gas-phase fluidized bed having a diameter of 150 mm. The apparatus is charged with 350 g PE base material and then H₂, ethylene, 1-butene and N₂ in a ratio of H₂ = 11.0 %, \(C_2H_4\) = 56.8 %, 1-butene = 22.2 % and N₂ = 10.0 % as well as 15 mmol
triethylaluminum are fed into the apparatus, the apparatus is heated to 85 °C and 150 mg of the above prepared titanium catalyst are added to start the polymerization. The polymerization time is 4 h and the total pressure of the circulating gas having the above-indicated composition is 1.7 MPa. The polymerization results are shown in table 2.

Table 1  Results of the ethylene/1-butene slurry polymerization

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<tr>
<th>Catalyst</th>
<th>Catalytic activity (g PE/g cat)</th>
<th>Bulk density (g/cm³)</th>
<th>Melt index (g/10 min)</th>
<th>Ti/OEt</th>
<th>Particle size distribution</th>
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<td>&lt;150 µm</td>
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<td>3.7</td>
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</table>

Ex.: Example
Comp.-Ex.: Comparative example
Table 2 Results of the ethylene/1-butene gas-phase fluidized bed polymerization

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalytic activity (g PE/g cat)</th>
<th>Bulk density (g/cm³)</th>
<th>Hexane extracts (%)</th>
<th>Density (g/ml)</th>
<th>Particle size distribution</th>
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<td>&lt;150 µm</td>
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</table>

Ex.: Example
Comp.-Ex.: Comparative example

The experimental results show that the titanium catalyst according to the present invention prepared from the titanium catalyst component according to the present invention can provide a polyethylene having a high bulk density, a very narrow particle size distribution and a low amount of fine particles, which is particularly suitable for ethylene gas-phase polymerization using a fluidized bed, preferably in a condensation state or a super-condensation state.
Claims

1. A method for preparing a titanium catalyst component, comprising the steps of:
   a) reacting a magnesium dihalide, an electron donor solvent and a titanium halide,
   b) reacting an alkyl borate ester with the reaction mixture obtained in step a),
   c) adding inorganic oxide particles to the reaction mixture obtained in step b),
   d) spray drying the suspension obtained in step c).

2. The method according to claim 1, wherein the magnesium dihalide is selected from the group consisting of MgCl₂, MgBr₂ and MgI₂.

3. The method according to claim 1 or 2, wherein the electron donor solvent is selected from the group consisting of C₁-C₄ alcohols, C₂-C₆ fatty ethers and C₃-C₄ cyclic ethers.

4. The method according to claim 3, wherein the electron donor solvent is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, butanol, isobutanol, ethylethers, hexylethers, tetrahydrofuran and mixtures thereof.
5. The method according to claim 4, wherein the electron donor solvent is tetrahydrofuran.

6. The method according to any one of claims 1 to 5, wherein the titanium halide is selected from the group consisting of TiCl₃, TiCl₄, TiBr₃ and TiBr₄.

7. The method according to any one of claims 1 to 6, wherein the alkyl borate ester has the general formula

$$\text{B(OR)}_n\text{X}_{3-n}$$

wherein

- R is a C₁-C₁₀ alkyl group,
- X is halogen, and
- $1 \leq n \leq 3$.

8. The method according to claim 7, wherein the alkyl borate ester is selected from the group consisting of trimethylborate, triethylborate, tripropylborate, tributylborate, dichloromethoxyborane, chlorodiethoxyborane and dichloroethoxyborane.

9. The method according to any one of claims 1 to 8, wherein the inorganic oxide particles are selected from the group consisting of particles of SiO₂, Al₂O₃ and mixtures thereof.

10. The method according to claim 9, wherein in step c) the inorganic oxide particles are added in an amount such that the obtained suspension contains 10 wt.% to 60 wt.% of the inorganic oxide particles.
11. The method according to claim 9 or 10, wherein the inorganic oxide particles have a particle size of 0.01 µm to 10 µm.

12. The method according to claim 11, wherein the inorganic oxide particles are SiO₂ particles having a particle size of 0.01 µm to 1 µm.

13. The method according to any one of claims 1 to 12, wherein the magnesium dihalide, the titanium halide and the alkyl borate ester are provided in amounts such that 1 < Mg/Ti < 20 (mol/mol) and 0 < OR/Ti < 5 (mol/mol), and wherein the electron donor solvent is provided in an amount of 3 to 500 mol based on one mol of Ti.

14. A titanium catalyst component, obtainable by the method of any one of claims 1 to 13.

15. The titanium catalyst component according to claim 14, wherein the average particle diameter of the titanium catalyst component is 5 µm to 45 µm.

16. A method for preparing a titanium catalyst, comprising:

reacting a titanium catalyst component according to claim 14 or 15 with an organic aluminum compound having the general formula

\[ \text{AlR'}_nX_{3-n} \]

wherein
\( R' \) is hydrogen or a \( \text{C}_1-\text{C}_2 \) alkyl group,

\( X \) is \( F, Cl, Br \) or \( I \), and

\( 1 < n \leq 3 \)

in a hydrocarbon solvent.

17. The method according to claim 16, wherein the organic aluminum compound is selected from the group consisting of \( \text{AlEt}_3, \text{AlEt}_2\text{Cl}, \text{Al (isobutyl)}_3, \text{AMn-C}_6\text{H}_{13}_3, \text{Al (n-C}_8\text{H}_{17})_3 \) and mixtures thereof.

18. The method according to claim 16 or 17, wherein the hydrocarbon solvent is selected from the group consisting of isopentane, hexane, heptane, toluene, xylene, naphtha, mineral oil and mixtures thereof.

19. A titanium catalyst, obtainable by the method of any one of claims 16 to 18.

20. The catalyst according to claim 19, wherein the molar ratio of \( \text{Al} \) in the organic aluminum compound and \( \text{Ti} \) in the titanium catalyst compound is in a range of 10 to 1000.

21. Use of a catalyst according to claim 19 or 20 for ethylene polymerization and copolymerization.
A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F10/00 C08F4/657

According to International Patent Classification (IPC) and/or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CO8F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C  
[X] See patent family annex

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'E' earlier document but published on or after the international filing date

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'P' document published prior to the international filing date but later than the priority date claimed

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'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

'B' document member of the same patent family

Date of the actual completion of the International search: 11 September 2009

Date of mailing of the international search report: 01/10/2009

Name and mailing address of the ISA:
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NL-2280 HV Rijswijk
Tel (+31-70) 340-2040
Fax (+31-70) 340-3016

Authorized officer: Parry, Julian
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