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(54) **Title**: A CATALYST FOR THE PRODUCTION OF LINEAR LOW DENSITY POLYETHYLENE

(57) **Abstract**: The invention is directed to a catalyst for the production of linear low density polyethylene. The catalyst is obtained by an one pot process comprising the steps (1) reacting a support with a compound having the formula $RMgX$ or MgR^1R^2, wherein R, R^1 and R^2 are selected from the group consisting of alkyl, cycloalkyl, aryl or alkaryl, and X is selected from the group consisting of halogen, OR^3 or $OC(O)R^4$ wherein R^3 and R^4 are alkyl groups containing 2-50 carbon atoms (2) reacting the magnesium treated support with a compound which is able to react with unreacted magnesium units and (3) reacting the product obtained in step (2) with a compound containing a group IV transition metal component wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

A CATALYST FOR THE PRODUCTION OF LINEAR LOW DENSITY POLYETHYLENE

The present invention relates to a catalyst for the production of linear low density polyethylene. The invention is also directed to a process for the production of linear low density polyethylene in the presence catalyst according to the invention.

The production of polyethylene in the presence of a catalyst system is very well known in the art. Dall'Occo et al. disclose in "Transition Metals and Organometallics as Catalysts for Olefin Polymerization" (Springer, 1988, at page 209) that the main requirements of industrial catalysts for the polymerisation of ethylene are high productivity, proper kinetic, no reactor fouling , control of morphology , average particle size and bulk density of the polymer particles.

The bulk density of the polyethylene powder particles is important because the obtained powder has to be stored and to be transported. A higher bulk density may decrease clogging at its transportation and it is possible to increase a storable amount per unit volume. By increasing the bulk density, the weight of the polyethylene per unit volume present in a polymerization vessel will be increased and the concentration of the polyethylene powder in the polymerization vessel can be enhanced.

Polyethylenes and their polymerization processes are disclosed at pages 27-67 of Handbook of Polyethylene by Peacock (ISBN 0-8247-9546-6). Polyethylenes such as for example linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) are substantially linear polymers with numbers of short branches. The production of LLDPE or HDPE can be initiated by the use of transition metal based catalysts for example Ziegler catalysts and Philips catalysts. The polymerization process can take place in for example a solution phase reactor, a, slurry phase reactor or a gas phase reactor. In solution phase reactions octene is often applied as the co monomer while in slurry phase or gas phase reactions in general butene and hexene are copolymerized with ethylene.

LLDPE possesses properties that distinguish it from other ethylene polymers. Ethylene copolymers are used in for example blown and cast films, injection molding, rotational molding, blow molding, pipe, tubing, and wire and cable applications. LLDPE can be used to make thinner films with improved environmental stress cracking resistance. LLDPE has good resistance to chemicals and to ultraviolet radiation and good electrical properties. A huge amount of publications is directed to the use of Ziegler-Natta type polymerisation catalysts. In general Ziegler Natta catalysts have as a disadvantage that in the case that the activity of the catalyst is relatively high the bulk density of the resulting polymer is relatively low. It is highly desirable to obtain a Ziegler-Natta catalyst which can be manufactured easily with the same or better productivity and at the same time produces higher bulk density LLDPE.

It is the object of the present invention to provide a catalyst with a high catalyst activity which results in LLDPE displaying a high powder bulk density. This catalyst has also to result in other desired properties of the obtained polymer and the polymerisation process such as for example a lower density and reduced resin stickiness, reduced chunk formation and reduced reactor fouling in the fluid bed gas-phase process, especially at high production rates.

The catalyst according to the invention is obtained by an one pot process comprising the steps:

(1) reacting a support with a compound having the formula RMgX or MgR^1R^2, wherein R, R1 and R^2 are selected from the group consisting of alkyl, cycloalkyl, aryl or alkaryl, and X is selected from the group consisting of halogen, OR^3 or $OC(O)R^4$ wherein R^3 and R^4 are an alkyl group containing 2-50 carbon atoms

(2) reacting the magnesium treated support with a compound which is able to react with unreacted R-Mg moieties and

(3) reacting the product obtained in step (2) with a compound containing a group IV (of Mendeleev's Periodic System of Chemical Elements) transition metal component wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

Generally, the alkyl, cycloalkyl, aryl and/or alkaryl group in step (1) comprises 1-50 carbon atoms.

The process according to the present invention wherein all process steps are performed in one vessel results in catalyst particles with a controlled and consistent particle size, shape and size distribution. The catalyst also has a good hydrogen response.

The Ziegler-Natta catalysts obtained with the process according to the invention result in LLDPE having the desired bulk density, good co monomer incorporation and high polymer productivity.

LLDPE obtained with the catalyst according to the invention has a density ranging between 900 kg/m^3 and 929 kg/m^3; a melting point ranging between 95^{0}C and 135 ^{0}C and a bulk density ranging between 290 kg/m^3 and 500 kg/m^3

More preferably the titanium loading of the catalyst ranges between 1.2 % by weight and 3.0 % by weight relative to the total weight of the catalyst.

According to a preferred embodiment of the invention the catalyst is obtained by an one pot process comprising the following steps:

(1) reacting a support with a compound having the formula RMgX or MgR^1R^2, wherein R, R^1 and R^2 are selected from the group consisting of alkyl, cycloalkyl, aryl or alkaryl, and X is selected from the group consisting of halogen, OR^3 or $OC(O)R^4$ wherein R^3 and R^4 are alkyl groups containing 2-50 carbon atoms

(2) reacting the magnesium treated support with a compound which is able to react with unreacted R-Mg moieties

(3) reacting the product obtained in step (2) with a compound containing a group IV transition metal component and

(4) adding a donor, a co catalyst and/or a promoter

wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

Examples of suitable support material include inorganic oxides, magnesium chloride, clays and zeolites, polystyrene, polyethylene, polypropylene, graphite and/or layered silicates. Suitable inorganic oxide

materials include for example oxides of silica, alumina, magnesia, titanium and/or zirconium.

According to a preferred embodiment of the invention the support includes silica and/or alumina.

According to a further preferred embodiment of the invention the support is based on silica.

Preferably the carrier has been dehydrated by fluidizing with nitrogen and heating.

The support material particles may have any shape. Preferably the shape is approximately spherical and porous.

In the compound having the formula RMgX X is preferably chlorine.

Preferred compounds having the formula RMgX or MgR^1R^2 include magnesium dialkyl and magnesium alkyl chloride. Preferably the alkyl group contains 1-8 carbon-atoms. The alkyl groups may be substituted.

Suitable examples of non-polar solvents in all preparation steps include hydrocarbons. Suitable hydrocarbons include for example iso butane, iso pentane, hexane and heptane.

Preferred compounds which are able to react with unreacted magnesium units are chlorine containing components and/or heteroatom containing components. These compounds prevent by the reaction with alkyl magnesium moieties that the Ti-compound in the third step is reduced.

The chlorine containing component may be (C_1-C_{10}) alkyl chloride or a silicon compound of formula R_mSiCl_{4-m} wherein $0 < m \leq 2$ and R is a hydrocarbon radical containing 1 – 10 carbon atoms.

Preferably the chlorine containing component is (C_1-C_8) alkyl chloride.

Preferably the alkyl chloride is tertiary butyl chloride.

Suitable heteroatom containing components include alcohols, aldehydes, CO_2, H_2O, amines, sulfonates and/or a compound with antistatic properties.

Suitable compound with antistatic properties or antistatic agents include organic compounds or mixture containing at least one electron rich

heteroatom from Group IV, V and/or VI , preferably O or N , and a hydrocarbyl moiety where the hydrocarbyl group is a branched or straight, substituted or un-substituted hydrocarbyl group.

Suitable group IV transition metal components include Ti, Zr and Hf.

Preferably the compound containing a group IV transition metal is $TiCl_4$

The compound containing a group IV transition metal component may additionally be based on a group 16 element for example O and S.

According to another preferred embodiment the group IV transition metal component with a group 16 element is an organic oxygen containing titanium compound.

Suitable organic oxygen containing titanium compound may be represented by the general formula $[TiO_x (OR)_{.4-2x}]_{.n}$ in which R represents an organic radical, x ranges between 0 and 1 and n ranges between 1 and 6.

Suitable examples of organic oxygen-containing titanium compounds include alkoxides, phenoxides, oxyalkoxides, condensed alkoxides, carboxylates and enolates.

According to a preferred embodiment of the invention the organic oxygen-containing titanium compounds is a titanium alkoxide.

Suitable alkoxides include for example Ti $(OC_2H_5)_4$, Ti $(OC_3H_7)_4$, and/or Ti $(OC_4H_9)_4$.

According to a preferred embodiment of the invention the organic oxygen containing titanium compound is Ti $(OC_2H_5)_4$.

Also mixtures of $TiCl_4$ and organic oxygen containing titanium compounds may be applied.

Suitable donors include for example tetrahydrofuran, di methyl formamide and/or ethyl acetate.

The preferred co catalyst is an organo aluminium compound having the formula AlR_3 in which R is a hydrocarbon radical containing 1 – 10 carbon atoms Suitable examples of organo aluminium compound of the formula AlR_3 include for example triethylaluminium alkyl, triisobutyl aluminium alkyl, tri-n-hexyl aluminium and tri octyl aluminium. The resulting activated

catalyst composition results in substantially higher productivity in polymerizing alpha-olefins and in substantially improved higher comonomer incorporation properties.

The preferred promoter is an organo alkyl chloride containing 1-10 carbon atoms or an organo aluminium chloride having the formula AlR_nX_{3-n} wherein X is a halogen and R is a hydrocarbon radical containing 1 – 10 carbon atoms and

$0 \leq n \leq 3$. Suitable examples include ethyl aluminium dichloride, propyl aluminium dichloride, n- butyl aluminium dichloride, iso butyl aluminium dichloride, diethyl aluminium chloride, diisobutyl aluminium chloride and $CHCl_3$.

According to a preferred embodiment of the invention the molar ratio of tetravalent titanium: organo magnesium ranges between 0.2:1 and 3:1.

Preferably the molar ratio of magnesium: halogenide ranges between 2:1 and 1:2.

More preferably the molar ratio of magnesium: halogenide ranges between 1.2:1 and 1: 1.2.

Generally the molar ratio Al: Ti ranges between 0.1: 1 and 10:1.

Generally the average particle size of the catalyst ranges between 20 µm and 70 µm.

According to a preferred embodiment of the invention the catalyst is obtained by a process comprising the following steps:

(1) reacting a silica support with a dialkyl magnesium or a magnesium alkyl chloride having the formula RMgX or MgR^1R^2, wherein R, R^1 and R^2 are selected from the group consisting of alkyl, cycloalkyl, aryl or alkaryl , and X is selected from the group consisting of halogen, OR^3 or $OC(O)R^4$ wherein R^3 and R^4 are an alkyl group containing 2-50 carbon atoms

(2) reacting the magnesium treated support with a chlorine containing component and/or a heteroatom containing component

(3) reacting the obtained product with $TiCl_4$ and/or $Ti(OC_2H_5)_4$ and

(4) optionally adding a donor, a co catalyst and/or a promoter wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

Preferably the titanium loading of the catalyst ranges between 1.2 % by weight and 3.0 % by weight relative to the total weight of the catalyst

According to a preferred embodiment of the invention the catalyst is obtained by a process comprising the following steps:

(1) reacting a silica support with a dialkyl magnesium or a magnesium alkyl chloride having the formula RMgX or MgR^1R^2 wherein the alkyl groups contain 1-8 carbon atoms

(2) reacting the magnesium treated support with t-BuCl

(3) reacting the obtained product with $TiCl_4$ and/or $Ti(OC_2H_5)_4$ and

(4) optionally adding a donor, a co catalyst and/or a promoter

wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

Preferably the titanium loading of the catalyst ranges between 1.2 % by weight and 3.0 % by weight relative to the total weight of the catalyst.

Additional advantages of the catalyst used in the process according to the invention are the easy catalyst preparation procedures, the high catalyst productivity, the low amount of fines, less reactor sheeting and excellent polymer morphology.

The modification of the catalyst may take place with a compound with antistatic properties such as for example Atmer©, Octastats© or Stadis©.

The Ziegler-Natta catalysts obtained with the process according to the invention may be used to produce ethylene homo- and/or copolymers with either a gas phase process or a slurry process under the general conditions. Besides LLDPE also high density polyethylene and bimodal polyethylene may be produced. The obtained particle morphology is excellent, which will be beneficial to all particle forming polymerization processes. HDPE produced with the present catalyst has a density ranging between 910 kg/m^3 and 970 kg/m^3; a melting point ranging between 95^{0}C and 135 ^{0}C and a bulk density ranging between 290 kg/m^3 and 500 kg/m^3

WO03004537 discloses a method for the two step preparation of a procatalyst for an olefin polymerization comprising the steps: a) treating silica by successively contacting said silica with a pair of compounds comprising a moderator compound and a magnesium alkyl compound, wherein said

moderator compound is able of being reduced in a controlled manner by said magnesium alkyl compound, to obtain a modified silica ; b) contacting said modified silica with a chlorine containing titanium compound to obtain a solid procatalyst. The moderator compound serves for moderating the reductive power of the magnesium alkyl compound The moderator compound is a chlorine containing compound such as $SiCl_4$, $TiCl_4$, $ZrCl_4$, $HfCl_4$ or $SnCl_4$ or a gas which contains oxygen. The present invention does not require the treatment of the support with a mixture that must comprise a moderator compound and a magnesium alkyl compound as required by the process according to WO03004537. In contrast to the process according to the present invention the process as disclosed in Example 3 of WO03004537 uses both a specific aluminium alkyl-magnesium alkyl compound and air. WO03004537 does not disclose the preparation of LLDPE.

US2008/058198 discloses a high activity magnesium-based supported catalyst component useful in a catalyst system for the compolymerization of ethylene and alpha-olefin. In the process, alkoxysilane ester is contacted with a halogen-substituted silane to form an organic silicon complex. Optionally, the organic silicon complex is contacted with an aminosilane compound to form an organic silicon complex containing nitrogen. The process according to the present invention does not use an aminosilane. Furthermore this process does not use a silicon complex containing nitrogen. The organic silicon complex containing nitrogen or the organic silicon complex is contacted with a transition metal compound to form an organic silicon complex containing transition metal. The organic silicon complex containing transition metal is then contacted with a substituted aromatic ring nitrogen compound to form a fourth reaction complex, which is then contacted with a magnesium-based composite support that has been prepared in situ by reacting metallic magnesium with an alkyl or aromatic halide to form the catalyst component. Essential differences between US2008/058198 and the present invention are the presence of a substituted aromatic ring nitrogen compound and the aminosilane in the process according to US2008/058198.

US 5424263 discloses a catalyst component useful in the polymerization of olefins especially propylene. The catalyst component

comprises the product obtained by steps of (a) contacting silica with at least one hydrocarbon soluble magnesium-containing compound; (b) contacting the product of step (a) with component (1), a heterocyclic fused ring compound substituted with at least one oxygen atom, and component (2), a modifying compound selected from the group consisting of silicon halides, boron halides, aluminum halides, alkyl silicon halides and mixtures thereof, with the proviso that components (1) and (2) be present such that the molar ratio of component (2) to component (1) is at least about 4:1; and (c) contacting the product of step (b) with a titanium-containing compound having the structural formula $TiX_m(OR)_n$, where X is halogen; R is hydrocarbyl; m is an integer of 1 to 4; and n is 0 or an integer of 1 to 3 with the proviso that the sum of m and n is 4. An essential difference between US 5424263 and the present invention is the presence of a heterocyclic fused ring compound substituted with at least one oxygen atom in the process according to US 5424263 which is not present in the process according to the present invention. US 5424263 is directed to the use of the catalyst in the preparation of polypropylene.US 5424263 does not disclose a polymerisation to obtain LLDPE.

EP2003151 discloses a process for preparing a catalyst useful in gas phase polymerization of olefins wherein the hydrogen response of the catalyst can be improved by using a ketone as the electron donor in the catalyst. The catalyst consists of compounds of Ti, Mg, Al and a ketone. In the process according to the present invention no keton is present to manufacture a copolymer having an MI greater than that prepared in the absence of a ketone.

The invention will be illustrated by the following non-limiting examples.

Examples

All materials were handled in a nitrogen atmosphere using either Schlenk techniques or nitrogen filled glove box. Nitrogen and isopentane were supplied from a plant source and were dried through an additional bed of molecular sieves, if necessary. All other solvents were first dried over molecular sieves and if necessary sodium/potassium amalgam. The catalysts were prepared using temperature controlled to within 0.5° C in a silicon oil bath with stirring.

The properties of the polymers produced in the Examples were determined as follows:

- The Ti, Mg and Al contents were determined via ICP analysis.
- The Flow Index (FI, g/10 min, at 190.degree. C. was determined as specified in ASTM D 1238 using a load of 21.6 kg.
- The density (kg/m^3) was determined as specified in ASTM D 1505-68 with the exception that the density measurement was taken 4 hours instead of 24 hours after the sample was placed in the density column.
- Polymer molecular weight and its distribution (MWD) were determined by Polymer Labs 220 gel permeation chromatograph (GPC). The chromatograms were run at 150 °C using 1, 2, 4-trichlorobenzene as the solvent with a flow rate of 0.9 ml / min. The refractive index detector is used to collect the signal for molecular weights. The co monomer distributions were determined by a FT-IR of Perkin Elmer Spectrum 1. The sample flow is split and approximately 2/3 of it go to the FT-IR and 1/3 goes to the RI detector in parallel measuring mode. The software used is Cirrus from PolyLab for molecular weights from GPC and co monomer distributions from FT-IR. The calibration of the HT-GPC uses a Hamielec type calibration with broad standard and fresh calibration with each sample set. The FT-IR calibration is based on 10 samples of defined branching type and branching frequency available form Polymer Labs.
- The poured bulk density (BD) of the polyethylene powder was determined by measuring the bulk density of the polymer powder according to the procedure outlined in ASTM D1895/A.

Examples I-III

Preparation of the catalyst in a one pot process

In the first step under a dry nitrogen atmosphere, a Schlenk flask was charged to form a slurry with

- silica, previously calcined at 600°C for 4 hours and
- dibutylmagnesium (1M, in heptane) diluted in isopentane

The obtained slurry was kept at 50°C for 0.5 hours.

Next in the second step an isopentane solution of t-BuCl (molar ratio Mg:Cl = 1:2) was added to the above slurry. The flask was kept at 50°C for 0.5 hours.

In the third step an isopentane solution of $TiCl_4$ was added together with $Ti(OEt)_4$ to the slurry and the mixture was kept at 50°C for 0,5 hour.

All solvents were removed under vacuum and a free flow catalyst was obtained.

Table 1

Example	Ti % by weight	Mg% by weight	Al% by weight	Mg/Ti molar ratio	Al/Ti molar ratio	THF% by weight
I	2.06	3.12	0.346	3	0.3	1.57
II	1.87	3.01	0.334	3.16	0.32	1.46
III	1.20	2.40	0.350	3.67	0.33	1.50

Example IV-VI

Preparation of LLDPE

The slurry polymerisation process to prepare ethylene-1-butene copolymer was carried out in deoxygenated isopentane in a two-liter stirred autoclave with use of the catalyst according to Examples I-III. The catalyst was added in an amount of 50 mg.

3 litres hydrogen and 1 ml triethylaluminium (TEAL) were added to the reaction mixture. The temperature was 87 °C and the pressure was 15 bar (15.10^{-6}MPa). Ethylene gas was used to maintain this pressure. Upon completion of the polymerization, the reactor was vented and cooled to ambient temperature to recover the polymer.

Table 2

Example	Productivity (gPE/g-cat.h)	BD (kg/m^3)
IV	6060	350
V	6500	344
VI	3440	330

Comparative Examples A-C

Preparation of the catalyst in a one pot process

The preparations as described in the Examples I-III were repeated with the exception that the titanium loading was outside the range between 1.2 % by weight and 3.0 % by weight relative to the total weight of the catalyst.

Table 3

Example	Ti % by weight	Mg% by weight	Al%	THF%
A	0.87	1.66	3.29	11.73
B	0,92	1.80	3.87	12.74
C	0.98	2.14	2.01	13.98

Comparative Examples D-E

Preparation of LLDPE

The slurry polymerisation process to prepare the ethylene copolymer of ethylene and 1-butene according to Examples IV-VI were repeated with the Catalysts B-C.

Table 4

Example	Productivity (gPE/g-cat.h)	BD (kg/m^3)
D	9320	280
E	11040	210

Examples VII-IX

Gas phase polymerizations were carried out in a fluidized bed reactor at a production rate of 10 kg/hr in the presence of ethylene and 1-butene comonomer. The fluidized bed of reactor was made up of HDPE polyethylene granules. The reactor was passivated with aluminum alkyl. During each run, ethylene and 1-butene comonomer were introduced before the

reactor bed. The individual flows of ethylene, hydrogen and 1-butene comonomer were controlled to maintain target reactor conditions wherein the H_2/C_2 ratio was 10%, the C_4/C_2 ratio was 35% and the C_2 partial pressure was 7 bar (7.10^{-6} MPa).

The concentrations of ethylene and 1-butene were measured by an on-line chromatograph. The examples are directed to samples taken from a 2 days polymerization run on a single gas phase fluidized bed reactor. During the polymerization a catalyst according to Examples I-III was injected directly into the fluidized bed using purified nitrogen wherein the catalyst injection rates were adjusted to maintain a production rate of 10 kg/hr. During each run, the reacting bed of growing polyethylene particles was maintained in a fluidized state by a continuous flow of the make-up feed and recycle gas through the reaction zone. Each polymerization run utilized a reactor temperature of 87 °C. During each run the reactor temperature was maintained at a constant level by adjusting up or down the temperature of the recycle gas to accommodate any changes in the rate of heat generation due to the polymerization.

Table 5

Example	Catalyst	BD (kg/m^3)	MI dg/min
VII	Example I	322	0.93
VIII	Example II	335	0.99
IX	Example III	316	1.55

CLAIMS

1. A catalyst for the production of linear low density polyethylene obtained by an one pot process comprising the steps:

(1) reacting a support with a compound having the formula RMgX or MgR^1R^2, wherein R, R^1 and R^2 are selected from the group consisting of alkyl, cycloalkyl, aryl or alkaryl, and X is selected from the group consisting of halogen, OR^3 or $OC(O)R^4$ wherein R^3 and R^4 are alkyl groups containing 2-50 carbon atoms

(2) reacting the magnesium treated support with a compound which is able to react with unreacted R-Mg moieties and

(3) reacting the product obtained in step (2) with a compound containing a group IV transition metal component

wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6.0 % by weight relative to the total weight of the catalyst.

2. A catalyst according to Claim 1 wherein the process comprises as step (4) adding a donor, a co catalyst and/or a promoter.

3. A catalyst according to any one of Claims 1-2 characterised in that the support includes silica and/or alumina.

4. A catalyst according to any one of Claims 1-3 characterised in that the compound having the formula RMgX or MgR^1R^2 is dialkyl magnesium and/or magnesium alkyl chloride wherein the alkyl group comprises 1-8 carbon atoms.

5. A catalyst according to any one of Claims 1-4 wherein the compound which is able to react with magnesium units is a chlorine containing component and/or a heteroatom containing component.

6. A catalyst according to Claim 5 characterised in that the chlorine containing compound is a $(C_1\text{-}C_{10})$ alkyl chloride or a silicon compound of formula R_mSiCl_{4-m} wherein $0 < m \leq 2$ and R is a hydrocarbon radical containing 1 – 10 carbon atoms.

7. A catalyst according to any one of Claims 1-6 characterised in that the compound containing a group IV transition metal component is $TiCl_4$ or an organic oxygen containing titanium compound.

8. A catalyst according to any one of Claims 1-7 characterised in that the catalyst is obtained by a process comprising the following steps:

(1) reacting a silica support with a dialkyl magnesium or a magnesium alkyl chloride having the formula RMgX or MgR^1R^2 wherein the alkyl groups contain 1-8 carbon atoms

(2) reacting the magnesium treated support with t-BuCl

(3) reacting the obtained product with $TiCl_4$ and/or $Ti(OC_2H_5)_4$ and

(4) optionally adding a donor, a co catalyst and/or a promoter

wherein the titanium loading of the catalyst ranges between 1.2 % by weight and 6..0 % by weight relative to the total weight of the catalyst.

9. A catalyst according to any one of Claims 2-8 characterised in that the donor is tetrahydrofuran, di methyl formamide or ethyl acetate, the cocatalyst is an organo aluminium compound having the formula AlR_3 in which R is a hydrocarbon radical containing 1 – 10 carbon atoms and/or the promoter is an organo alkyl chloride containing 1-10 carbon atoms or an organo aluminium chloride having the formula AlR_nX_{3-n} wherein X is a halogen and R is a hydrocarbon radical containing 1 – 10 carbon atoms and $0 \leq n \leq 3$.

10. A catalyst according to any one of Claims 1-9 characterised in that the titanium loading of the catalyst ranges between 1.2 % by weight and 3.0 % by weight relative to the total weight of the catalyst.

11. A process for the production of linear low density polyethylene having a density ranging between 900 kg/m^3 and 929 kg/m^3; a melting point ranging between 95^{0}C and 135 ^{0}C and a bulk density ranging between 290 kg/m^3 and 500 kg/m^3 in the presence of a Ziegler–Natta catalyst according to any one of Claims 1-10.

12. A process for the production of high density polyethylene having a density ranging between 910 kg/m^3 and 970 kg/m^3; a melting point ranging between 95^{0}C and 135 ^{0}C and a bulk density ranging between 290 kg/m^3 and 500 kg/m^3 in the presence of a Ziegler–Natta catalyst according to any one of Claims 1-10.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/007311

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F4/651 C08F210/16
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/004537 A (BOREALIS TECH OY [FI]; PALMQVIST MAERIT ELISABET HF [SE]; JOHANSSON SO) 16 January 2003 (2003-01-16) examples 1-3 claims 1,3,6,9-16	1-12
Y	page 4, paragraph 3	1-12
X	US 2008/058198 A1 (XU GUANGXUE [US] ET AL) 6 March 2008 (2008-03-06) * comparative example 5, comparative example 12 *	1-12
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 January 2010	25/01/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Gamb, Véronique

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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P,X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LV, XINPING ET AL: "Magnesium compound supported titanium catalyst component for ethylene polymerization" XP002562635 retrieved from STN Database accession no. 2009:1335261 abstract -& CN 101 565 473 A (CHINA PETROLEUM & CHEMICAL CORPORATION, PEOP. REP. CHINA; SINOPEC BEIJ) 28 October 2009 (2009-10-28) -----	1-12
Y	US 5 424 263 A (BUEHLER CHARLES K [US]) 13 June 1995 (1995-06-13) examples 1-22 column 3, line 62 - column 4, line 7 -----	1-12

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Information on patent family members

International application No
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