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(54) Title: CATALYST FOR THE POLYMERIZATION OF OLEFINS

(57) Abstract: The present invention relates to catalysts systems for the polymerization of ethylene and its mixtures with olefins  $\text{CH}_2=\text{CHR}$ , wherein R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, comprising (A) a solid catalyst component comprising Ti, Mg, halogen, and optionally an electron donor compound in a donor/Ti molar ratio lower than 1, (B) an aluminum alkyl compound and (C) a silicon compound of formula  $\text{R}^{\text{I}}\text{mSi}(\text{OR}^{\text{II}})_n$  in which  $\text{R}^{\text{I}}$  is C1 -C20 alkyl group,  $\text{R}^{\text{II}}$  is a secondary or tertiary alkyl group or a cycloalkyl having from 3 to 20 carbon atoms, m is an integer ranging from 0 to 3, and n is (4-m). The catalyst of the invention is suitably used in (co)polymerization processes of ethylene to prepare (co)polymers having narrow Molecular Weight Distribution (MWD) and high activity.



## TITLE

## CATALYST FOR THE POLYMERIZATION OF OLEFINS

The present invention relates to catalysts for the polymerization of olefins, in particular ethylene and its mixtures with olefins  $\text{CH}_2=\text{CHR}$ , wherein R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, comprising a solid catalyst component comprising Ti, Mg, halogen and optionally an electron donor, an aluminum alkyl compound and a particular class of silicon compounds as external electron donor compounds. The catalysts of the invention are suitably used in (co)polymerization processes of ethylene to prepare (co)polymers having narrow Molecular Weight Distribution (MWD) and high activity. The MWD is an important characteristic of ethylene polymers in that it affects both the rheological behavior, and therefore the processability, and the final mechanical properties. In particular, polymers with narrow MWD are suitable for films and injection molding in that deformation and shrinkage problems in the manufactured article are minimized. The width of the molecular weight distribution for the ethylene polymers is generally expressed as melt flow ratio F/E, which is the ratio between the melt index measured by a load of 21.6 Kg (melt index F) and that measured with a load of 2.16 Kg (melt index E). The measurements of melt index are carried out according to ASTM D-1238 and at 190°C. Catalysts for preparing ethylene (co)polymers having narrow MWD are described in the European patent application EP-A-373999. The catalyst comprises a solid catalyst component consisting of a titanium compound supported on magnesium chloride, an alkyl-Al compound and an electron donor compound (external donor) selected from monoethers of the formula  $\text{R}'\text{OR}''$ . Good results in terms of narrow MWD are only obtained when the solid component also contains an internal electron donor compound (diisobutylphthalate). The catalyst activity is unsatisfactory. This latter characteristic is very important in the operation of the plants because it assures competitiveness of the production plant. Hence, it would be highly desirable to have a catalyst capable to produce polymers with narrow molecular weight distribution, in high yields.

JP 6-256413 discloses the copolymerization of ethylene with butene-1 in the presence of a catalyst comprising (A) a solid catalyst component supported on silica and comprising

MgCl<sub>2</sub>, TiCl<sub>3</sub> and an electron donor like tetrahydrofuran, (B) one or more aluminum alkyl compounds optionally halogenated and (C) a specific alkyl trialkoxysilane in which the alkyl is a bulky alkyl of formula  $-C(CH_3)_2-CH(R_2)(R_3)$  where R<sub>2</sub> and R<sub>3</sub> are C1-C3 hydrocarbon groups. The fact that the effect of narrowing the MWD is not particularly pronounced and that the catalyst activity is generally low makes this catalyst system not particularly suitable for industrial use.

The applicant has now found a novel catalyst system for the (co)polymerization of ethylene comprising the product obtained by contacting (A) a solid catalyst component comprising Ti, Mg, halogen, and optionally an electron donor compound in a donor/Ti molar ratio lower than 1, (B) an aluminum alkyl compound and (C) a silicon compound of formula  $R^I_mSi(OR^{II})_n$  in which R<sup>I</sup> is C1-C20 alkyl group, R<sup>II</sup> is a secondary or tertiary alkyl group or a cycloalkyl having from 3 to 20 carbon atoms, m is an integer ranging from 0 to 3, and n is (4-m).

Surprisingly, such a catalyst is able to provide an ethylene (co)polymer with a narrow Molecular Weight Distribution maintaining acceptable activity.

A preferred subgroup of silicon compounds (C) is that in which R<sup>II</sup> is selected from secondary alkyls or cycloalkyl having from 3 to 8 carbon atoms. Moreover, are also preferred the compounds (C) in which m is 2 and n is 2. Among them especially preferred are the compounds in which one of R<sup>I</sup> is Me and the other is selected from Me or a cyclic alkyls having from 3 to 8 carbon atoms and in which the R<sup>II</sup> groups are selected from isopropyl, t-butyl and cyclopentyl.

Preferred compounds are dimethyl di-isopropoxysilane, methyl tri-isopropoxysilane, cyclohexylmethyl di-isopropoxysilane, dimethyl dicyclopentoxysilane, cyclohexylmethyl dicyclopentoxysilane, dicylopentyl(iso-propoxy)silane. Among them particularly preferred compounds are dimethyl di-isopropoxysilane and cyclohexylmethyl di-isopropoxysilane.

The silicon compound (C) is used in amounts such as to give a (B)/(C) molar ratio ranging from 0.1 to 100 preferably from 1 to 50 and more preferably from 5 to 30.

In a preferred aspect the catalyst component of the invention comprises a Ti compound having at least one Ti-halogen bond supported on a magnesium chloride which is preferably magnesium dichloride and more preferably magnesium dichloride in active form. In the context of the present application the term magnesium chloride means magnesium compounds having at least one magnesium chloride bond. As mentioned before, the catalyst component may also contain groups different from halogen, in any case in amounts lower than 0.5 moles for each mole of titanium and preferably lower than 0.3.

Preferably the catalyst component (A) has a porosity  $P_F$  determined with the mercury method higher than 0.3, preferably higher than  $0.40 \text{ cm}^3/\text{g}$  and more preferably higher than  $0.50 \text{ cm}^3/\text{g}$  usually in the range  $0.50\text{-}0.80 \text{ cm}^3/\text{g}$ . The total porosity  $P_T$  can be in the range of  $0.50\text{-}1.50 \text{ cm}^3/\text{g}$ , particularly in the range of from 0.60 and  $1.20 \text{ cm}^3/\text{g}$ .

The surface area measured by the BET method is preferably lower than 80 and in particular comprised between 10 and  $70 \text{ m}^2/\text{g}$ . The porosity measured by the BET method is generally comprised between 0.10 and 0.50, preferably from 0.10 to  $0.40 \text{ cm}^3/\text{g}$ .

In the catalyst component of the invention the average pore radius value, for porosity due to pores up to  $1 \mu\text{m}$ , is in the range from 600 to  $1200 \text{ \AA}$ .

The particles of solid component have substantially spherical morphology and average diameter comprised between 5 and  $150 \mu\text{m}$ , preferably from 20 to  $100 \mu\text{m}$  and more preferably from 30 to  $90 \mu\text{m}$ . As particles having substantially spherical morphology, those are meant wherein the ratio between the greater axis and the smaller axis is equal to or lower than 1.5 and preferably lower than 1.3.

The magnesium dichloride in the active form is characterized by X-ray spectra in which the most intense diffraction line which appears in the spectrum of the non active chloride (lattice distanced of  $2.56 \text{ \AA}$ ) is diminished in intensity and is broadened to such an extent that it becomes totally or partially merged with the reflection line falling at lattice distance (d) of  $2.95 \text{ \AA}$ . When the merging is complete the single broad peak generated has the maximum of intensity which is shifted towards angles lower than those of the most intense line.

The solid components of the invention may in principle comprise an electron donor compound (internal donor), selected for example among ethers, esters, amines and ketones.

However, it has been found particularly advantageous for the present invention to include an electron donor compound only in amount such as to give ED/Ti ratios lower than 1, preferably lower than 0.5 and more preferably not to include any amount of electron donor compound in order for it to be absent in the final solid catalyst component (A).

The preferred titanium compounds have the formula  $\text{Ti}(\text{OR}^{\text{II}})_n\text{X}_{y-n}$ , wherein  $n$  is a number comprised between 0 and 0.5 inclusive,  $y$  is the valence of titanium,  $\text{R}^{\text{II}}$  is an alkyl, cycloalkyl or aryl radical having 1-8 carbon atoms and  $\text{X}$  is halogen. In particular  $\text{R}^{\text{II}}$  can be ethyl, isopropyl, *n*-butyl, isobutyl, 2-ethylhexyl, *n*-octyl and phenyl, (benzyl);  $\text{X}$  is preferably chlorine.

If  $y$  is 4,  $n$  varies preferably from 0 to 0.02; if  $y$  is 3,  $n$  varies preferably from 0 to 0.015.  $\text{TiCl}_4$  is especially preferred. The amount of Ti is typically higher than 1.5% preferably higher than 3% and more preferably equal to, or higher than, 4%wt. Most preferably it ranges from 3.5 to 8%wt.

A method suitable for the preparation of spherical components mentioned above comprises a first step (a) in which a compound  $\text{MgCl}_2.m\text{R}^{\text{III}}\text{OH}$ , wherein  $0.3 \leq m \leq 1.7$  and  $\text{R}^{\text{III}}$  is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms is reacted with the said titanium compound of the formula  $\text{Ti}(\text{OR}^{\text{II}})_n\text{X}_{y-n}$ , in which  $n$ ,  $y$ ,  $\text{X}$  and  $\text{R}^{\text{II}}$  have the same meaning defined above.

In this case  $\text{MgCl}_2.m\text{R}^{\text{III}}\text{OH}$  represents a precursor of Mg dihalide. These kind of compounds can generally be obtained by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Representative methods for the preparation of these spherical adducts are reported for example in USP 4,469,648, USP 4,399,054, and WO98/44009. Another useable method for the spherulization is the spray cooling described for example in USP 5,100,849 and 4,829,034. Adducts having the desired final alcohol content can be obtained by directly using the selected amount of alcohol directly during the adduct preparation. However, if adducts with increased porosity are to be obtained it is convenient to first prepare adducts with more than 1.7 moles of alcohol per mole of  $\text{MgCl}_2$  and then subjecting them to a thermal and/or chemical dealcoholation process. The thermal dealcoholation process is carried out in nitrogen flow at temperatures comprised between 50 and 150°C until the

alcohol content is reduced to the value ranging from 0.3 to 1.7. A process of this type is described in EP 395083.

Generally these dealcoholated adducts are also characterized by a porosity (measured by mercury method ) due to pores with radius up to  $0.1\mu\text{m}$  ranging from  $0.15$  to  $2.5\text{ cm}^3/\text{g}$  preferably from  $0.25$  to  $1.5\text{ cm}^3/\text{g}$ .

In the reaction of step (a) the molar ratio Ti/Mg is stoichiometric or higher; preferably this ratio is higher than 3. Still more preferably a large excess of titanium compound is used. Preferred titanium compounds are titanium tetrahalides, in particular  $\text{TiCl}_4$ . The reaction with the Ti compound can be carried out by suspending the adduct in cold  $\text{TiCl}_4$  (generally  $0^\circ\text{C}$ ); the mixture is heated up to  $80$ - $140^\circ\text{C}$  and kept at this temperature for  $0.5$ - $8$  preferably from  $0.5$  to  $3$  hours. The excess of titanium compound can be separated at high temperatures by filtration or sedimentation and siphoning.

The catalyst component (B) of the invention is selected from Al-alkyl compounds possibly halogenated. In particular, it is selected from Al-trialkyl compounds, for example Al-trimethyl, Al-triethyl, Al-tri-n-butyl, Al-triisobutyl are preferred. The Al/Ti ratio is higher than 1 and is generally comprised between 5 and 800.

The above-mentioned components (A)-(C) can be fed separately into the reactor where, under the polymerization conditions can exploit their activity. It may be advantageous to carry out a pre-contact of the above components, optionally in the presence of small amounts of olefins, for a period of time ranging from  $0.1$  to  $120$  minutes preferably in the range from  $1$  to  $60$  minutes. The pre-contact can be carried out in a liquid diluent at a temperature ranging from  $0$  to  $90^\circ\text{C}$  preferably in the range of  $20$  to  $70^\circ\text{C}$ .

The so formed catalyst system can be used directly in the main polymerization process or alternatively, it can be pre-polymerized beforehand. A pre-polymerization step is usually preferred when the main polymerization process is carried out in the gas phase. The prepolymerization can be carried out with any of the olefins  $\text{CH}_2=\text{CHR}$ , where R is H or a C1-C10 hydrocarbon group. In particular, it is especially preferred to pre-polymerize ethylene, propylene or mixtures thereof with one or more  $\alpha$ -olefins, said mixtures containing up to 20% in moles of  $\alpha$ -olefin, forming amounts of polymer from about  $0.1\text{ g}$  per gram of solid component up to about  $1000\text{ g}$  per gram of solid catalyst component. The pre-polymerization step can be carried out at temperatures from  $0$  to  $80^\circ\text{C}$ , preferably from  $5$  to  $70^\circ\text{C}$ , in the liquid or gas phase. The pre-polymerization step can be performed in-line

as a part of a continuous polymerization process or separately in a batch process. The batch pre-polymerization of the catalyst of the invention with ethylene in order to produce an amount of polymer ranging from 0.5 to 20 g per gram of catalyst component is particularly preferred. The pre-polymerized catalyst component can also be subject to a further treatment with a titanium compound before being used in the main polymerization step. In this case the use of  $\text{TiCl}_4$  is particularly preferred. The reaction with the Ti compound can be carried out by suspending the prepolymerized catalyst component in the liquid Ti compound optionally in mixture with a liquid diluent; the mixture is heated to 60-120°C and kept at this temperature for 0.5-2 hours.

The catalysts of the invention can be used in any kind of polymerization process both in liquid and gas-phase processes. Catalysts having small particle size, (less than 40µm) are particularly suited for slurry polymerization in an inert medium, which can be carried out continuously stirred tank reactor or in loop reactors. Catalysts having larger particle size are particularly suited for gas-phase polymerization processes which can be carried out in agitated or fluidized bed gas-phase reactors.

As already mentioned, the catalysts of the present invention are particularly suitable for preparing ethylene polymers having narrow molecular weight distribution that are characterized by a F/E ratio equal to and preferably lower than 30 in combination with a high polymerization activity.

In addition, to the ethylene homo and copolymers mentioned above the catalysts of the present invention are also suitable for preparing very-low-density and ultra-low-density polyethylenes (VLDPE and ULDPE, having a density lower than 0.920g/cm<sup>3</sup>, to 0.880 g/cm<sup>3</sup>) consisting of copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms, having a mole content of units derived from ethylene of higher than 80%; elastomeric copolymers of ethylene and propylene and elastomeric terpolymers of ethylene and propylene with smaller proportions of a diene having a content by weight of units derived from ethylene of between about 30 and 70%.

The following examples are given in order to further describe the present invention in a non-limiting manner.

### **CHARACTERIZATION**

The properties are determined according to the following methods:

Melt Index:

Melt index (M.I.) are measured at 190°C following ASTM D-1238 over a load of:

2.16 Kg, MI E = MI<sub>2.16</sub>.

21.6 Kg, MI F = MI<sub>21.6</sub>.

The ratio:  $F/E = MI\ F/MI\ E = MI_{21.6}/MI_{2.16}$  is then defined as melt flow ratio (MFR).

MWD.

The molecular weight distribution is also measured by way of Gel Permeation Chromatography which is carried out according to the method based on DIN 55672 under the following conditions:

Solvent: 1, 2, 4-trichlorobenzene, flow: 1 ml/min, temperature: 140°C, calibration using PE standards.

General procedure for the HDPE polymerization test

Into a 1.5 liters stainless steel autoclave, degassed under N<sub>2</sub> stream at 70 °C, 500 ml of anhydrous hexane, the reported amount of catalyst component and 0.17 g of triethylaluminum (TEA) were introduced (or 0.29 g of TIBA). The mixture was stirred, heated to 75 °C and thereafter 3 bar of H<sub>2</sub> and 7 bar of ethylene were fed. The polymerization lasted 2 hours. Ethylene was fed to keep the pressure constant. At the end, the reactor was depressurized and the polymer thus recovered was dried under vacuum at 70 °C.

**EXAMPLE 1-5 and Comparison Example 1****Preparation of the solid component (A)**

A magnesium chloride and alcohol adduct containing about 3 mols of alcohol was prepared following the method described in example 2 of USP 4,399,054, but working at 2000 RPM instead of 10000 RPM. The adduct were subject to a thermal treatment, under nitrogen stream, over a temperature range of 50-150 °C until a weight content of 25% of alcohol was reached.

Into a 2 L four-necked round flask, purged with nitrogen, 1 L of TiCl<sub>4</sub> was introduced at 0°C. Then, at the same temperature, 70 g of a spherical MgCl<sub>2</sub>/EtOH adduct containing 25 %wt of ethanol and prepared as described above were added under stirring. The temperature was raised to 140 °C in 2 h and maintained for 60 min. Then, the stirring was

discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off. The solid residue was then washed once with heptane at 80°C and five times with hexane at 25°C and dried under vacuum at 30 °C and analyzed. Into a 260cm<sup>3</sup> glass reactor provided with stirrer, 351.5 cm<sup>3</sup> of hexane at 20°C and whilst stirring 7 g of the catalyst prepared as above described were introduced at 20°C. Keeping constant the internal temperature, 5.6 cm<sup>3</sup> of tri-n-octylaluminum (TNOA) in hexane (about 370 g/l) were slowly introduced into the reactor and the temperature was brought to 10°C. After 10 minutes stirring, 10 g of propylene were carefully introduced into the reactor at the same temperature during a time of 4 hours. The consumption of propylene in the reactor was monitored and the polymerization was discontinued when a theoretical conversion of 1 g of polymer per g of catalyst was deemed to be reached. Then, the whole content was filtered and washed three times with hexane at a temperature of 20°C (50 g/l). After drying the resulting pre-polymerized catalyst (A) was analyzed and found to contain 1.1 g of polypropylene per g of catalyst.

The pre-polymerized solid catalyst component (A) was employed in the ethylene polymerization according to the general procedure using the type and amount of silicon compound (C) reported in table 1 together with the polymerization results.

**TABLE 1**

| EX.     | Comp. C                               |  | Activity<br>(g/g) | MIE  | F/E | GPC<br>(Mw/Mn) |
|---------|---------------------------------------|--|-------------------|------|-----|----------------|
| 1       | CMDIPS                                |  | 11530             | 0.54 | 30  | 7.9            |
| 2       | DCDIPS                                |  | 7785              | 0.52 | 30  | 5.45           |
| 3       | Me <sub>2</sub> Si(OiPr) <sub>2</sub> |  | 9446              | 0.31 | 27  | 5.48           |
| 4       | DMDCPS                                |  | 7890              | 0.39 | 29  | 5.61           |
| 5       | CMDCPS                                |  | 11648             | 0.49 | 29  | 5.98           |
| Comp. 1 | -                                     |  | 14400             | 0.55 | 34  | 9.87           |

CMDIPS= cyclohexylmethyl di-isopropoxysilane

DMDCPS= dimethyl dicyclopentoxysilane

CMDCPS= cyclohexylmethyl dicyclopentoxysilane

DCDIPS= dicyclopentyl-di(iso-propoxy)silane

## CLAIMS

1. Catalyst system for the (co)polymerization of ethylene comprising the product obtained by contacting (A) a solid catalyst component comprising Ti, Mg, halogen, and optionally an electron donor compound in a donor/Ti molar ratio lower than 1, (B) an aluminum alkyl compound and (C) a silicon compound of formula  $R^I_mSi(OR^{II})_n$  in which  $R^I$  is C1-C20 alkyl group,  $R^{II}$  is a secondary or tertiary alkyl group or a cycloalkyl group having from 3 to 20 carbon atoms, m is an integer ranging from 0 to 3 and n is (4-m).
2. The catalyst system according to claim 1 in which the silicon compound (C) is chosen among those in which  $R^{II}$  is selected from secondary alkyls or cycloalkyl having from 3 to 8 carbon atoms.
3. The catalyst system according to claim 1 in which the silicon compound (C) is chosen among those in which m is 2 and n is 2.
4. The catalyst according to claim 1 in which the silicon compound (C) is chosen among those in which one of  $R^I$  is Me and the other is selected from Me or a cyclic alkyls having from 3 to 8 carbon atoms and in which the  $R^{II}$  groups are selected from isopropyl, t-butyl and cyclopentyl.
5. Process for the preparation of ethylene (co)polymer having a F/E ratio equal to or lower than 30 carried out by polymerizing ethylene, optionally with olefins  $CH_2=CHR$ , wherein R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, in the presence of a catalyst system according to any of claims 1-4.

# INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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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)

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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)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                              | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | FR 2 512 033 A1 (NIPPON OIL CO LTD [JP])<br>4 March 1983 (1983-03-04)<br>example 1<br>comparative example 1<br>example 6<br>comparative example 2<br>example 12<br>comparative example<br>4<br>example 17<br>comparative example 5;<br>* abstract<br>page 12, line 8 - page 13, line 4<br>----- | 1-5                   |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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## INTERNATIONAL SEARCH REPORT

### Information on patent family members

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| FR 2512033                                | A1 | 04-03-1983          | DE<br>GB                   | 3231582 A1<br>2108514 A | 21-04-1983<br>18-05-1983 |
| -----                                     |    |                     |                            |                         |                          |