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(54) CATALYST COMPONENTS FOR THE POLYMERIZATION OF OLEFINS

KATALYSATORKOMPONENTEN FÜR DIE POLYMERISATION VON OLEFINEN

COMPOSANTS DE CATALYSEUR POUR LA POLYMÉRISATION DES OLÉFINES

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EP-A1- 2 803 678 **WO-A2-2006/110234**
US-A1- 2011 130 529 **US-A1- 2012 316 299**

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Description

FIELD OF THE INVENTION

[0001] The present disclosure relates to catalyst components for the polymerization of olefins, in particular propylene, comprising a Mg dihalide based support on which are supported Ti atoms and an electron donor compound containing an ester and a carbamate function. The present disclosure further relates to the catalysts obtained from said components and to their use in processes for the polymerization of olefins in particular propylene.

BACKGROUND OF THE INVENTION

[0002] Catalyst components for the stereospecific polymerization of olefins are widely known in the art. Concerning the polymerization of propylene, the most spread out catalyst family belongs to the Ziegler-Natta category which, in general terms, comprises a solid catalyst component, constituted by a magnesium dihalide on which are supported a titanium compound and an internal electron donor compound, used in combination with an Al-alkyl compound. Conventionally however, when a higher cristallinity of the polymer is required, also an external donor (for example an alkoxysilane) is needed in order to obtain higher isotacticity. One of the preferred classes of internal donors is constituted by the esters of phthalic acid, diisobutylphthalate being the most used. The phthalates are used as internal donors in combination with alkylalkoxysilanes as external donor. This catalyst system gives good performances in terms of activity, isotacticity and xylene insolubility.

[0003] One of the problems associated with the use of this catalyst system is that the phthalates have recently raised concerns due to the medical issues associated with their use and some compounds within this class have been classified as source of heavy health problems.

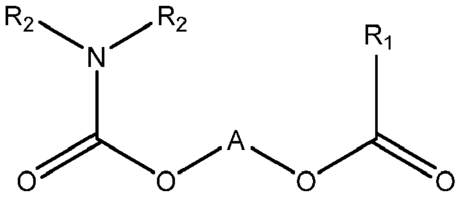
[0004] Consequently, research activities have been devoted to discover alternative classes of internal donors for use in the preparation of catalyst components for propylene polymerization.

[0005] Some of the tested catalysts contain donors structures having contemporaneously amido groups and ester groups. WO2006/110234 describes amino acid derivatives including one carbamate group and one free ester function. The catalysts generated by these structures have very low activity and sterospecificity in bulk propylene polymerization (table 2).

SUMMARY OF THE INVENTION

[0006] Surprisingly, the applicant has found that a class of donors containing both a carbamate and ester function within a specific structure generates catalysts showing an excellent balance of activity and stereospecificity.

[0007] Accordingly, the present disclosure provides a catalyst component for the polymerization of olefins comprising Mg, Ti and an electron donor of formula (I)



(I)

R_1 is selected from C_1-C_{15} hydrocarbon groups, optionally containing a heteroatom selected from halogen, P, S, N and O; R_2 groups, equal to or different from each other, are hydrogen or R_1 groups which can be fused together to form one or more cycles and A is a bivalent bridging group selected from (a) aliphatic, and alicyclic bridging groups, optionally substituted with C_1-C_{15} hydrocarbon groups and/or with heteroatoms selected from halogen, P, S, N, O and Si, and having a bridging chain length ranging from 1 to 6 carbon atoms or (b) phenyl groups, optionally substituted with halogens or C_1-C_{20} alkyl radicals, bridging the oxygen atoms in position 1,2 or 1,3 or 1,4 and naphthalene groups, optionally substituted, bridging the oxygen groups in position 1,2 or 2,3 or 1,8.

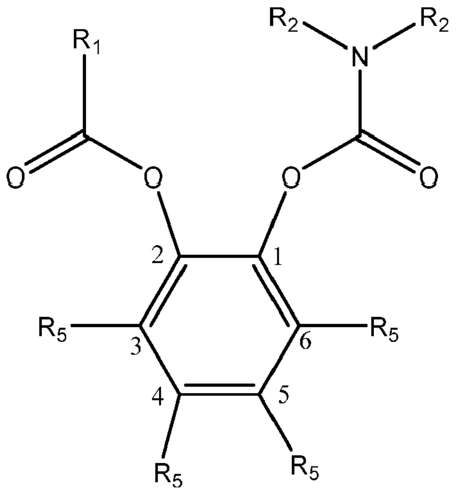
DETAILED DESCRIPTION OF THE INVENTION

[0008] In case of cyclic structures acting as bridging groups the term "chain length" is referred to the shortest sequence of atoms bridging the oxygen atoms of formula (I).

[0009] In a particular embodiment, the said bivalent bridging group is selected from the group consisting of aliphatic, alicyclic radicals, optionally substituted with C_1-C_{15} hydrocarbon groups and/or with heteroatoms selected from halogen, P, S, N, O and Si, and having a bridging chain length ranging from 1 to 6 carbon atoms and especially from 1 to 4 carbon atoms.

[0010] In a particularly preferred embodiment, the bridging group is an aliphatic or alicyclic bridging group having a bridging chain length of 1-6 carbon atoms. Among this class, particularly preferred bridging groups are those of formula $-(CR^4{}_p)_s-$ in which R^4 is independently hydrogen or a C_1-C_{20} hydrocarbon radicals, optionally substituted with heteroatoms selected from halogen, P, S, N, O and Si, which can be fused together to form one or more cycles, p is a number satisfying the available valence of carbon and s is a number from 1 to 6 preferably from 1 to 4. Examples of bridging groups are methylidene, ethane-1,2-diyl, butane-2,3-diyl, pentane-2,4-diyl, 2,2-diisobutylpropane-1,3-diyl, cyclohexane-1,2-diyl, cyclopentane -1,2-diyl. The bridging group pentane-2,4-diyl being the most preferred.

[0011] Another class of preferred bridging group is the one based on phenyl groups, optionally substituted with halogens or C_1-C_{20} alkyl radicals, bridging the oxygen atoms in position 1,2 or 1,3 or 1,4 and the naphthalene groups, optionally substituted bridging the oxygen groups in position 1,2 or 2,3 or 1,8. Among them, particularly preferred are the structure of formula (II) below



(II)

in which R_1 and R_2 have the same meaning previously specified, and R_5, independently, is selected from hydrogen, halogens or C_1-C_{15} hydrocarbon groups optionally substituted with heteroatoms selected from halogen, P, S, N, O and Si, with the proviso that at least one of R_5 is different from hydrogen.

[0012] Preferred structures of formula (II) are those in which at least two of the R_5 groups are different from hydrogen. More preferably the aromatic ring of formula (II) is substituted in position 3,5 and/or 6. Substitution in positions 4, 3, and/or 6 is also preferred. In all these cases, R_5 groups are preferably selected from C_1-C_5 alkyl groups. Particularly preferred is the substitution in position 3 and/or 6 with a primary alkyl group especially methyl, and in position 4 and/or 5 with a tertiary alkyl group especially tert-butyl.

[0013] Specific examples of aromatic bridging groups are 1,2-phenylene, 3-methyl-1,2-phenylene, 4-chloro-1,2-phenylene, 4-(*tert*-butyl)-1,2-phenylene, 3,6-dimethyl-1,2-phenylene, 3,5-dimethyl-1,2-phenylene, 5-(*tert*-butyl)-3-methyl-1,2-phenylene, 3,5-diisopropyl-1,2-phenylene, naphthalene-1,8-diyl, naphthalene-1,2-diyl, naphthalene-2,3-diyl groups.

[0014] Preferably, in the formulas (I) and (II) the R_1 groups are independently selected from C_1-C_{15} alkyl groups, C_6-C_{14} aryl groups, C_3-C_{15} cycloalkyl groups, and C_7-C_{15} arylalkyl or alkylaryl groups; the same applies to R_2 groups which can additionally be hydrogen. More preferably, the R_1 groups in formulae (I) and (II) are aryl or alkylaryl groups in particular phenyl groups preferably substituted with halogen and/or C_1-C_5 alkyl groups.

[0015] Preferably , in the formulas (I) and (II) the R_2 groups are independently selected from hydrogen or C_1-C_{10} alkyl groups and even more preferably from hydrogen or C_1-C_5 alkyl groups in particular ethyl.

[0016] Preferably, the final amount of electron donor compound in the solid catalyst component ranges from 1 to 25% by weight preferably in the range from 3 to 20% by weight.

[0017] Examples of structures of formulas (I) and (II) are the following: 1-((diethylcarbamoyl)oxy)propan-2-yl 4-butylbenzoate, 1-((diethylcarbamoyl)oxy)propan-2-yl 4-chlorobenzoate, 1-((diethylcarbamoyl)oxy)propan-2-yl 4-ethylbenzoate, 1-((diethylcarbamoyl)oxy)propan-2-yl 4-methylbenzoate, 1-((diethylcarbamoyl)oxy)propan-2-yl 4-propylbenzoate, 1-((diethylcarbamoyl)oxy)propan-2-yl benzoate, 2-((diethylcarbamoyl)oxy)ethyl 4-butylbenzoate, 2-((diethylcarbamoyl)oxy)ethyl 4-chlorobenzoate, 2-((diethylcarbamoyl)oxy)ethyl 4-ethylbenzoate, 2-((diethylcarbamoyl)oxy)ethyl 4-methylbenzoate, 2-((diethylcarbamoyl)oxy)ethyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)ethyl benzoate, 2-((diethylcarbamoyl)oxy)propyl 4-butylbenzoate, 2-((diethylcarbamoyl)oxy)propyl 4-chlorobenzoate, 2-((diethylcarbamoyl)oxy)propyl 4-ethylbenzoate, 2-((diethylcarbamoyl)oxy)propyl 4-methylbenzoate, 2-((diethylcarbamoyl)oxy)propyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)propyl benzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl 4-butylbenzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl 4-chlorobenzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl 4-ethylbenzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl 4-methylbenzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl 4-propylbenzoate, 3-((diethylcarbamoyl)oxy)butan-2-yl benzoate, 4-(carbamoyloxy)pentan-2-yl 4-butylbenzoate, 4-(carbamoyloxy)pentan-2-yl 4-chlorobenzoate, 4-(carbamoyloxy)pentan-2-yl 4-ethylbenzoate, 4-(carbamoyloxy)pentan-2-yl 4-methylbenzoate, 4-(carbamoyloxy)pentan-2-yl 4-propylbenzoate, 4-(carbamoyloxy)pentan-2-yl benzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl 4-chlorobenzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl 4-methylbenzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate, 4-((dimethylcarbamoyl)oxy)pentan-2-yl benzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-chlorobenzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-methylbenzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate, 4-((diethylcarbamoyl)oxy)pentan-2-yl benzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl 4-chlorobenzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl 4-methylbenzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate, 4-((diisopropylcarbamoyl)oxy)pentan-2-yl benzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl 4-chlorobenzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl 4-methylbenzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate, 4-((diphenylcarbamoyl)oxy)pentan-2-yl benzoate, 3-((diethylcarbamoyl)oxy)-2,2-dimethylpropyl 4-butylbenzoate, 3-((diethylcarbamoyl)oxy)-2,2-dimethylpropyl 4-chlorobenzoate, 3-((diethylcarbamoyl)oxy)-2,2-dimethylpropyl 4-propylbenzoate, 3-((diethylcarbamoyl)oxy)-2,2-dimethylpropyl benzoate, 2-(((diethylcarbamoyl)oxy)methyl)-2-isopropyl-3-methylbutyl 4-butylbenzoate, 2-(((diethylcarbamoyl)oxy)methyl)-2-isopropyl-3-methylbutyl 4-chlorobenzoate, 2-(((diethylcarbamoyl)oxy)methyl)-2-isopropyl-3-methylbutyl 4-propylbenzoate, 2-(((diethylcarbamoyl)oxy)methyl)-2-isopropyl-3-methylbutyl benzoate, (9-(((diethylcarbamoyl)oxy)methyl)-9H-fluoren-9-yl)methyl 4-butylbenzoate, (9-(((diethylcarbamoyl)oxy)methyl)-9H-fluoren-9-yl)methyl 4-chlorobenzoate, (9-(((diethylcarbamoyl)oxy)methyl)-9H-fluoren-9-yl)methyl 4-propylbenzoate, (9-(((diethylcarbamoyl)oxy)methyl)-9H-fluoren-9-yl)methyl benzoate, 2-((diethylcarbamoyl)oxy)cyclohexyl 4-butylbenzoate, 2-((diethylcarbamoyl)oxy)cyclohexyl 4-chlorobenzoate, 2-((diethylcarbamoyl)oxy)cyclohexyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)cyclohexyl benzoate, 2-((diethylcarbamoyl)oxy)cyclopentyl 4-butylbenzoate, 2-((diethylcarbamoyl)oxy)cyclopentyl 4-chlorobenzoate, 2-((diethylcarbamoyl)oxy)cyclopentyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)cyclopentyl benzoate, 4-(((diethylcarbamoyl)oxy)methyl)-3-isopropyl-5-methylhexyl 4-butylbenzoate, 4-(((diethylcarbamoyl)oxy)methyl)-3-isopropyl-5-methylhexyl 4-chlorobenzoate, 4-(((diethylcarbamoyl)oxy)methyl)-3-isopropyl-5-methylhexyl 4-propylbenzoate, 4-(((diethylcarbamoyl)oxy)methyl)-3-isopropyl-5-methylhexyl benzoate, 2-((diethylcarbamoyl)oxy)phenyl 4-butylbenzoate, 2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate, 2-((diethylcarbamoyl)oxy)phenyl 4-methylbenzoate, 2-((diethylcarbamoyl)oxy)phenyl benzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-butylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-chlorobenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-ethylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-methylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl benzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-butylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-ethylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-methylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-propylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl benzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-butylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-chlorobenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-ethylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-methylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-propylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl benzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-butylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-ethylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-methylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-propylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl benzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 3-chlorobenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 3-chlorobenzoate, 4-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-6-methylphenyl 4-butylbenzoate, 4-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-6-methylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-6-methylphenyl benzoate, 4-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-6-methylphenyl 4-butylbenzoate, 4-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-6-methylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-6-methylphenyl benzoate, 4-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-6-methylphenyl 4-butylbenzoate, 4-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-6-methylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-6-methylphenyl benzoate, 4-(tert-butyl)-2-(carbamoyloxy)-6-methylphenyl 4-butylbenzoate, 4-(tert-butyl)-2-(carbamoyloxy)-6-methylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-(carbamoyloxy)-6-methylphenyl benzoate, 5-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-3-methylphenyl 4-butylbenzoate, 5-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-3-methylphenyl 4-propylbenzoate, 5-(tert-butyl)-2-((diisopropylcarbamoyl)oxy)-3-methylphenyl benzoate, 5-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-3-methylphenyl 4-butylbenzoate, 5-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-3-methylphenyl 4-propylbenzoate, 5-(tert-butyl)-2-((dimethylcarbamoyl)oxy)-3-methylphenyl benzoate, 5-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-3-methylphenyl 4-butylbenzoate, 5-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-3-methylphenyl 4-propylbenzoate, 5-(tert-butyl)-2-((diphenylcarbamoyl)oxy)-3-methylphenyl benzoate, 5-(tert-butyl)-2-(carbamoyloxy)-3-methylphenyl 4-butylbenzoate, 5-(tert-butyl)-2-(carbamoyloxy)-3-methylphenyl 4-propylbenzoate, 5-(tert-butyl)-2-(carbamoyloxy)-3-methylphenyl benzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-butylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-propylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-butylbenzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-propylbenzoate, 1-((diethylcarbamoyl)oxy)naphthalen-2-yl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3,4,6-triisopropylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3,5,6-triisopropylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3,5-diisopropylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3,6-dimethylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3-isopropyl-6-methylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-4,6-diisopropylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-4-isopropyl-3,6-dimethylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-4-methylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-5-isopropyl-3,6-dimethylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-5-methylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-6-isopropyl-3-methylphenyl 4-propylbenzoate, 2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-propylbenzoate, 3,6-di-tert-butyl-2-((diethylcarbamoyl)oxy)phenyl 4-propylbenzoate, 3-((diethylcarbamoyl)oxy)naphthalen-2-yl 4-propylbenzoate, 3-(tert-butyl)-6-((diethylcarbamoyl)oxy)-2,5-dimethylphenyl 4-propylbenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3,6-dimethylphenyl 4-propylbenzoate, 8-((diethylcarbamoyl)oxy)naphthalen-1-yl 4-propylbenzoate 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate , 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate, 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl benzoate, 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl benzoate.

[0018] The compounds falling in formula (I) and (II) can be generally prepared reacting an excess of the starting diol HO-A-OH with a suitable acyl chloride followed by removal of the unreacted diol by aqueous washings, distillation or chromatographic techniques. Then the monoester-monoalcohol is reacted with a suitable carbamoyl chloride. Both steps are carried out in presence of a base and their order can be inverted.

[0019] When unsubstituted or substituted catechols are used as starting diols to prepare the donors according to formula (II), the corresponding monophenol-monocarbamate derivative can be obtained by reacting the starting compounds with diphenyl carbonate and a proper secondary amine. The obtained intermediate is then reacted with a suitable acyl chloride. In such a type of reaction, depending on the type of substitution on the catechol ring, positional isomers can be formed generated by the formation of the carbamic group on one of the two available hydroxyl groups of the catechol. While the presence of two different isomers and their respective ratio can be detected, it has not been possible until now to assign the specific structure to each of the respective isomers which in any case are defined by the formula (II). Therefore, in the examples reported below it has been indicated that the catechol based electron donors are prepared as a mixture of positional isomers.

[0020] In solid catalyst component of the invention the amount of Ti atoms in the solid catalyst component is preferably higher than 2.5%wt more preferably higher than 3.0% with respect to the total weight of said catalyst component.

[0021] As explained above, the catalyst components of the invention comprise, in addition to the above electron donors, Ti, Mg and halogen. In particular, the catalyst components comprise a titanium compound, having at least a Ti-halogen bond and the above mentioned electron donor compounds supported on a Mg halide. The magnesium halide is preferably $MgCl_2$ in active form which is widely known from the patent literature as a support for Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

[0022] The preferred titanium compounds used in the catalyst component of the present invention are $TiCl_4$ and $TiCl_3$; furthermore, also Ti-haloalcoholates of formula $Ti(OR)_{m-y}X_y$ can be used, where m is the valence of titanium, y is a number between 1 and m-1, X is halogen and R is a hydrocarbon radical having from 1 to 10 carbon atoms.

[0023] The preparation of the solid catalyst component can be carried out according to several methods. One method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to USP 4,220,554) and an excess of $TiCl_4$ in the presence of the electron donor compounds at a temperature of about 80 to 120°C.

[0024] According to a preferred method, the solid catalyst component can be prepared by reacting a titanium compound of formula $Ti(OR)_{m-y}X_y$, where m is the valence of titanium and y is a number between 1 and m, preferably $TiCl_4$, with a magnesium chloride deriving from an adduct of formula $MgCl_2 \cdot pROH$, where p is a number between 0.1 and 6, preferably from 2 to 3.5, and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form 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. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054 and USP 4,469,648. The so obtained adduct can be directly reacted with Ti compound or it can be previously subjected to thermal controlled dealcoholation (80-130°C) so as to obtain an adduct in which the number of moles of alcohol is generally lower than 3, preferably between 0.1 and 2.5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold $TiCl_4$ (generally 0°C); the mixture is heated up to 80-130°C and kept at this temperature for 0.5-2 hours. The treatment with $TiCl_4$ can be carried out one or more times. The electron donor compound is preferably added during the treatment with $TiCl_4$. The preparation of catalyst components in spherical form are described for example in European Patent Applications EP-A-395083, EP-A-553805, EP-A-553806, EPA601525 and WO98/44001.

[0025] The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and 500 m^2/g and preferably between 50 and 400 m^2/g, and a total porosity (by B.E.T. method) higher than 0.2 cm^3/g preferably between 0.2 and 0.6 cm^3/g. The porosity (Hg method) due to pores with radius up to 10.000Å generally ranges from 0.3 to 1.5 cm^3/g, preferably from 0.45 to 1 cm^3/g.

[0026] The solid catalyst component has an average particle size ranging from 5 to 120 μm and more preferably from 10 to 100 μm.

[0027] In any of these preparation methods the desired electron donor compounds can be added as such or, in an alternative way, it can be obtained *in situ* by using an appropriate precursor capable to be transformed in the desired electron donor compound by means, for example, of known chemical reactions.

[0028] Regardless of the preparation method used, the final amount of the electron donor compound of formula (I) is such that its molar ratio with respect to the Ti atoms is from 0.01 to 2, preferably from 0.05 to 1.5.

[0029] The solid catalyst components according to the present invention are converted into catalysts for the polymerization of olefins by reacting them with organoaluminum compounds according to known methods.

[0030] In particular, it is an object of the present invention a catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product obtained by contacting:

(i) the solid catalyst component as disclosed above and
(ii) an alkylaluminum compound and optionally,
(iii) an external electron donor compound.

[0031] The alkyl-Al compound (ii) is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides, such as $AlEt_2Cl$ and $Al_2Et_3Cl_3$, possibly in mixture with the above cited trialkylaluminums.

[0032] Suitable external electron-donor compounds include silicon compounds, ethers, esters, amines, heterocyclic compounds and particularly 2,2,6,6-tetramethylpiperidine and ketones.

[0033] Another class of preferred external donor compounds is that of silicon compounds of formula $(R_7)_a(R_8)_bSi(OR_9)_c$, where a and b are integers from 0 to 2, c is an integer from 1 to 4 and the sum (a+b+c) is 4; R_7, R_8, and R_9, are radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R_7 and R_8 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R_9 is a C_1-C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane (C donor), diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane (D donor), diisopropyldimethoxysilane, (2-ethylpiperidinyl)t-butyldimethoxysilane, (2-ethylpiperidinyl)thexyldimethoxysilane, (3,3,3-trifluoro-n-propyl)(2-ethylpiperidinyl)dimethoxysilane, methyl(3,3,3-trifluoro-n-propyl)dimethoxysilane, N,N-diethylaminotriethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R_8 is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R_9 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and thexyltrimethoxysilane.

[0034] The electron donor compound (iii) is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound (iii) of from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100.

[0035] Therefore, it constitutes a further object of the present invention a process for the (co)polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst comprising the product of the reaction between:

(i) the solid catalyst component of the invention;
(ii) an alkylaluminum compound and,
(iii) optionally an electron-donor compound (external donor).

[0036] The polymerization process can be carried out according to known techniques for example slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, it is possible to carry out the polymerization process in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

[0037] The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.5 and 5 MPa, preferably between 1 and 4 MPa. In the bulk polymerization the operating pressure is generally between 1 and 8 MPa, preferably between 1.5 and 5 MPa.

[0038] The following examples are given in order to further illustrate the invention.

CHARACTERIZATIONS

Determination of X.I.

[0039] 2.5 g of polymer and 250 ml of o-xylene were placed in a round-bottomed flask provided with a cooler and a reflux condenser and kept under nitrogen. The obtained mixture was heated to 135°C and was kept under stirring for about 60 minutes. The final solution was allowed to cool to 25°C under continuous stirring, and the insoluble polymer was then filtered. The filtrate was then evaporated in a nitrogen flow at 140°C to reach a constant weight. The content of said xylene-soluble fraction is expressed as a percentage of the original 2.5 grams and then, by difference, the X.I. %.

Determination of donors.

[0040] The content of electron donor has been carried out via gas-chromatography. The solid component was dissolved in acidic water. The solution was extracted with ethyl acetate, an internal standard was added, and a sample of the organic phase was analyzed in a gas chromatograph, to determine the amount of donor present at the starting catalyst compound.

Melt flow rate (MFR)

[0041] The melt flow rate MIL of the polymer was determined according to ISO 1133 (230°C, 2.16 Kg).

EXAMPLES

Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate (Ex.1)

First step: Synthesis of 4-hydroxypentan-2-yl 4-propylbenzoate

[0042] A 1000 mL reaction vessel was charged with 2,4-pentanediol (25 g, 237.8 mmol), triethylamine (31.6 g, 1.3 eq), 4-(dimethylamino)pyridine (0.29 g, 0.01 eq) and THF (600 mL). The mixture was cooled to -5°C and 4-propylbenzoyl chloride (43.5 g, 0.995 eq) was slowly added. The mixture was allowed to stir at ambient temperature for 6 h. The resulting suspension was filtered and the white precipitate was washed 2 times with THF (100 mL in total). The resulting organic phase was concentrated on a rotary evaporator which resulted in the crude product as light yellow oil. It was purified by means of chromatography (SiO_2) - Cyclohexane/ethyl acetate: 10/1 to 2/1. Yield: 42.8 g (71.9 %) - light yellow oil - Syn/Anti=1/1. GC/MS: m/z=250.

Second step: Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate

[0043] A 1000 mL reaction vessel was charged with 4-hydroxypentan-2-yl 4-propylbenzoate (42.8 g, 169.4 mmol), and pyridine (400 mL). Diethylcarbamoyl chloride (34.8 g, 1.5 eq) was slowly added and stirred under reflux for 46 h. Pyridine was concentrated and the resulting oil was diluted with ethyl acetate (100 mL). The resulting solution was washed with a saturated aqueous NH_4Cl solution and a saturated aqueous NaCl solution. The organic phase was dried over $MgSO_4$, filtered and concentrated on a rotary evaporator which resulted in the crude product as oil. It was purified by means of chromatography (SiO_2) - Cyclohexane/ethyl acetate:8/1. Yield: 44.8 g (75.7 %) - light yellow oil - Syn/Anti=1/1. GC/MS: m/z=349.

Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl benzoate (Ex.2)

First step: Synthesis of 4-hydroxypentan-2-yl diethylcarbamate

[0044] A 250 mL reaction vessel was charged with 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate (12.5 g, 35.4 mmol) and toluene (125 mL). Sodium methoxyde (5.8 g, 3 eq) was slowly added at ambient temperature. The mixture was stirred at 60°C for 12 h. The resulting suspension was filtered and the white precipitate was washed 2 times with toluene (60 mL in total). The organic phase was dried over $MgSO_4$, filtered and concentrated on a rotary evaporator which resulted in the crude product as oil. It was purified by means of chromatography (SiO_2) - Cyclohexane/ethyl acetate:6/1. Yield: 5.8 g (79.8 %) - light yellow oil - Syn/Anti=1/1. GC/MS: m/z=203.

Second step: Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl benzoate

[0045] A 250 mL reaction vessel was charged with benzoyl chloride (2.5 g, 21.3 mmol), pyridine (5 mL, 3 eq), THF (100 mL) and 4-hydroxypentan-2-yl diethylcarbamate (4.3 g, 21.3 mmol). The mixture was allowed to stir at 60°C for 2 h. Then the mixture was quenched with diluted HCl and ethyl acetate and the organic layer washed with water until neutral pH. The organic phase was anhydrified, filtered and concentrated on a rotary evaporator which resulted in the pure product. Yield: 6 g - 84 % - light yellow oil - Syn/Anti=1/1. GC/MS: m/z=307.

Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate (Ex.3)

[0046] The synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate is the same of Ex 2 - second step, except that 4-ethylbenzoyl chloride is used instead of benzoyl chloride.

Synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate (Ex.4)

[0047] The synthesis of 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate is the same at Ex 2 - second step, except that 4-butylbenzoyl chloride is used instead of benzoyl chloride

Syntesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate (Ex.5)

First step: Synthesis of a mixture of 4-(tert-butyl)-2-hydroxyphenyl diethylcarbamate and 5-(tert-butyl)-2-hydroxyphenyl diethylcarbamate

[0048] 50 g of 4-t-butylcatechol (300 mmol) are charged in a round bottom flask with THF (300 mL) and 65.5 g of diphenyl carbonate (306 mmol) under nitrogen at room temperature. Then 33 mL of diethylamine (315 mmol) are added slowly dropwise and the mixture is stirred at room temperature until GC analysis shows complete conversion of starting catechol. Then the mixture is diluted with acidic water, extracted with diethyl ether, and organic layer washed with water until neutral pH. Solvent is removed via rotavapor and the obtained oil is dissolved into i-hexane (500 mL) and washed several time with water, until GC analysis show absence of phenol. Solvent is distilled away to afford a mixture of 4-(tert-butyl)-2-hydroxyphenyl diethylcarbamate and 5-(tert-butyl)-2-hydroxyphenyl diethylcarbamate that is used in the next steps without purification.

Second step: Syntesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate

[0049] 4.65 g of a mixture of 4-(tert-butyl)-2-hydroxyphenyl diethylcarbamate and 5-(tert-butyl)-2-hydroxyphenyl diethylcarbamate (17.5 mmol), prepared in the previous step, is charged in a round bottom flask with THF (20 mL) and 2.7 mL of Et3N (19.3 mmol) under nitrogen at room temperature. Then 2.3 mL of 3-chlorobenzoyl chloride (17.9 mmol) are added carefully dropwise. After 1.5 hours acidic water is added and the mixture is extracted with diethyl ether. The organic layer is washed with water until neutral pH, then is anhydrified over Na2SO4 and the solvent is distilled off to afford 7 g of residue (99% of yield) with a GC purity of 99%.

Syntesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate (Ex.6)

[0050] The synthesis is the same of Ex.5 except that in the second step 4-chlorobenzoyl chloride is used instead of

3-chlorobenzoyl chloride.

Syntesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 3-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 3-chlorobenzoate (Ex.7)

[0051] The synthesis is the same of Ex.5 except that 5-(tert-butyl)-3-methylcatechol is used in the first step instead of 4-t-butylcatechol.

Synthesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-chlorobenzoate (Ex.8)

[0052] The synthesis is the same of Ex.7 except that 4-chlorobenzoyl chloride is used in the second step instead of 3-chlorobenzoyl chloride.

Synthesis of a mixture of 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl benzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl benzoate (Ex.9).

[0053] The synthesis is the same of Ex.7 except that benzoyl chloride is used in the second step instead of 3-chlorobenzoyl chloride.

[0054] **N-Z-L-proline methyl ester** used in comparative example 1 is available from Sigma-Aldrich.

General procedure for preparation of the spherical adducts

[0055] An initial amount of microspheroidal $MgCl_2 \cdot 2.8C_2H_5OH$ was prepared according to the method described in Example 2 of WO98/44009, but operating on larger scale.

General procedure for the preparation of the solid catalyst component

[0056] Into a 500 mL round bottom flask, equipped with mechanical stirrer, cooler and thermometer 250 mL of $TiCl_4$ were introduced at room temperature under nitrogen atmosphere. After cooling to 0°C, while stirring, the internal donor and 10.0 g of the spherical adduct (prepared as described above) were sequentially added into the flask. The amount of charged internal donor was such to charge a Mg/donor molar ratio of 6. The temperature was raised to 100°C and maintained for 2 hours. Thereafter, stirring was stopped, the solid product was allowed to settle and the supernatant liquid was siphoned off at 100°C. After the supernatant was removed, additional fresh $TiCl_4$ was added to reach the initial liquid volume again. The mixture was then heated at 120°C and kept at this temperature for 1 hour. Stirring was stopped again, the solid was allowed to settle and the supernatant liquid was siphoned off.

[0057] The solid was washed with anhydrous hexane six times (6 x 100 mL) in temperature gradient down to 60°C and one time (100 mL) at room temperature. The obtained solid was then dried under vacuum and analyzed.

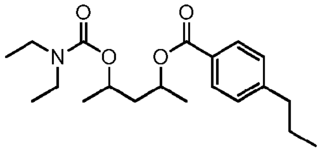
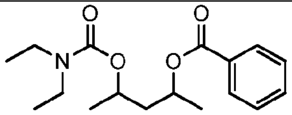
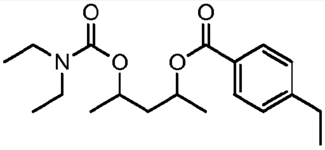
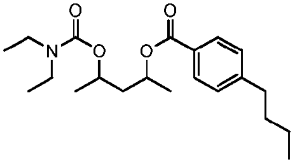
General procedure for the polymerization of propylene

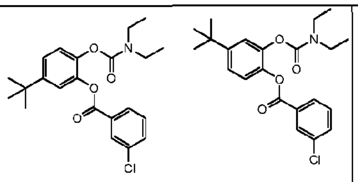
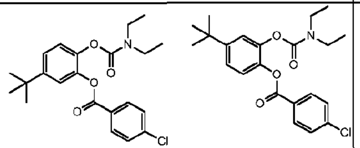
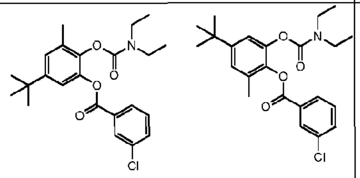
[0058] A 4-litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst feeding system, monomer feeding lines and thermostating jacket, was purged with nitrogen flow at 70°C for one hour. Then, at 30°C under propylene flow, were charged in sequence with 75 mL of anhydrous hexane, 0.76 g of $AlEt_3$, the external electron donor indicated in Table 1 (if used) and 0.006÷0.010 g of solid catalyst component. The autoclave was closed; subsequently 2.0 NL of hydrogen were added. Then, under stirring, 1.2 kg of liquid propylene was fed. The temperature was raised to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. At the end of the polymerization, the non-reacted propylene was removed; the polymer was recovered and dried at 70°C under vacuum for three hours. Then the polymer was weighed and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction.

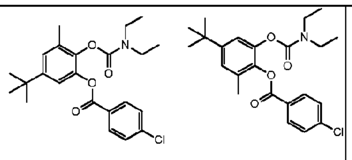
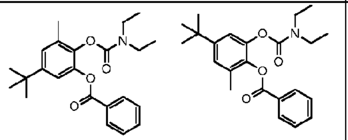
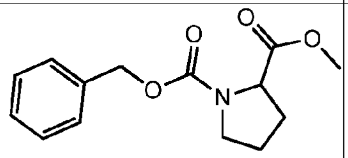
Examples 1-9 and Comparative 1

[0059] The catalyst components were prepared according to the general procedure using the donors indicated in Table 1. The so obtained solid catalyst components were analyzed for their composition, and were tested in polymerization of propylene, using the procedure described above. The results are listed in Table 1.

Table 1

	Catalyst compostion			Polymerization			
	Internal Donor		Ti	ED	Mileage	XI	MIL
	Name	%wt	%wt		kg/g	%wt	g/10'
1	 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-propylbenzoate	9.1	4.0	D	74	98.3	1.7
2	 4-((diethylcarbamoyl)oxy)pentan-2-yl benzoate	8.1	4.3	D	59	97.5	1.2
3	 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-ethylbenzoate	8.8	4.2	D	61	98.4	0.5
4	 4-((diethylcarbamoyl)oxy)pentan-2-yl 4-butylbenzoate	12.9	4.3	D	75	98.7	0.4

5	 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 3-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)ph	17.1	4.9	D	73	98.0	0.6
6	 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)phenyl 4-chlorobenzoate	8.1	4.1	D	64	97.5	0.2
7	 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 3-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 3-chlorobenzoate	14.6	4.7	D	65	98.6	0.4

8	 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl 4-chlorobenzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl 4-chlorobenzoate	17.3	4.6	D	98	97.7	0.3
9	 4-(tert-butyl)-2-((diethylcarbamoyl)oxy)-6-methylphenyl benzoate and 5-(tert-butyl)-2-((diethylcarbamoyl)oxy)-3-methylphenyl benzoate	n.d.	4.8	D	65	96.3	0.6
C 1	 N-L-Z-Proline methyl ester	n.d.	5.4	D	13	93.1	6.9

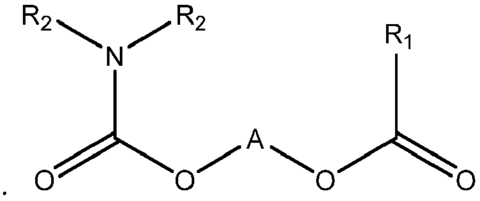
ED: External Donor.

D: dicyclopentyldimethoxysilane

nd: not determined

Claims

1. A solid catalyst component for the polymerization of olefins comprising Mg, Ti and an electron donor of formula (I)



where R_1 is selected from C_1-C_{15} hydrocarbon groups, optionally containing a heteroatom selected from halogen, P, S, N and O; R_2 groups, equal to or different from each other, are hydrogen or R_1 groups which can be fused together to form one or more cycles and A is a bivalent bridging group selected from (a) aliphatic and alicyclic bridging groups, optionally substituted with C_1-C_{15} hydrocarbon groups and/or with heteroatoms selected from halogen, P, S, N, O and Si, and having a bridging chain length ranging from 1 to 6 carbon atoms or (b) phenyl groups, optionally substituted with halogens or C_1-C_{20} alkyl radicals, bridging the oxygen atoms in position 1,2 or 1,3 or 1,4 and naphthalene groups, optionally substituted, bridging the oxygen groups in position 1,2 or 2,3 or 1,8.

2. The solid catalyst component according to claim 1 in which the bridging group has formula - $(CR^4{}_p)_s$- in which R^4 is, independently, hydrogen or a C_1-C_{20} hydrocarbon radical, optionally substituted with heteroatoms selected from halogen, P, S, N, O and Si, which can be fused together to form one or more cycles, p is a number satisfying the available valence of carbon and s is a number from 1 to 6.

3. The solid catalyst component according to claim 2 in which the bridging group is selected from the group consisting of methylidene, ethane-1,2-diyl, butane-2,3-diyl, pentane-2,4-diyl, 2,2-diisobutylpropane-1,3-diyl, cyclohexane-1,2-diyl, cyclopentane -1,2-diyl.

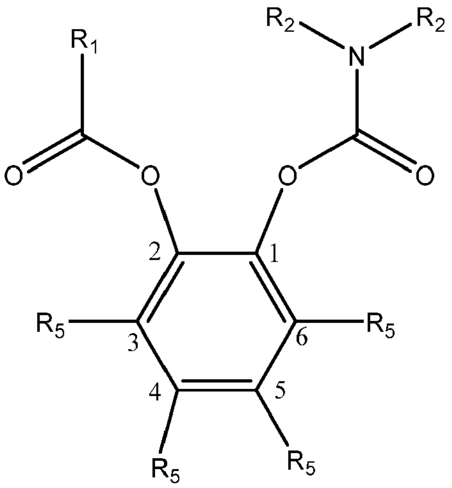
4. The solid catalyst component according to claim 1 in which R_1 groups are selected from aryl and alkylaryl groups.

5. The solid catalyst component according to claim 4 in which R_1 groups are selected from phenyl groups.

6. The solid catalyst component according to claim 5 in which the phenyl groups are substituted with halogen and/or C_1-C_5 alkyl groups.

7. The solid catalyst component according to claim 1 in which R_2 groups are independently selected from hydrogen or C_1-C_{10} alkyl groups.

8. The solid catalyst component according to claim 1 in which the electron donor is selected from those having the following formula (II):



(II)

in which R_1 and R_2 have the same meaning according to claim 1, and R_5, independently, is selected from hydrogen, halogens or C_1-C_{15} hydrocarbon groups optionally substituted with heteroatoms selected from halogen, P, S, N, O and Si, with the proviso that at least one of R_5 is different from hydrogen.

9. A catalyst for the polymerization of olefins comprising the product of the reaction between:

(i) the solid catalyst component according to any of the preceding claims and
(ii) an alkylaluminum compound and optionally,
(iii) an external electron donor compound.

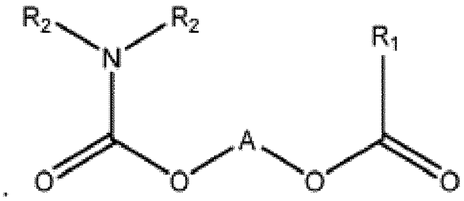
10. The catalyst according to claim 9 further comprising an external electron donor compound.

11. A process for the (co)polymerization of olefins CH_2=CHR, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst system comprising the product of the reaction between:

i. the solid catalyst component according to any of the claims 1- 8;
ii. an alkylaluminum compound and,
iii. optionally an external donor compound.

Patentansprüche

1. Feste Katalysatorkomponente für die Polymerisation von Olefinen, umfassend Mg, Ti und einen Elektronendonor mit der Formel (I)



wobei R_1 ausgewählt ist aus C_1-C_{15}-Kohlenwasserstoffgruppen, die gegebenenfalls ein Heteroatom ausgewählt aus Halogen, P, S, N und O enthalten; die Gruppen R_2, die gleich oder voneinander verschieden sein können, Wasserstoff oder Gruppen R_1 sind, die unter Bildung von einem oder mehreren Cyclen miteinander kondensiert sein können, und A eine zweiwertige Brückengruppe ist, die ausgewählt ist aus (a) aliphatischen und alicyclischen Brückengruppen, die gegebenenfalls mit C_1-C_{15}-Kohlenwasserstoffgruppen substituiert sind, und/oder mit Heteroatomen ausgewählt aus Halogen, P, S, N, O und Si, und mit einer Brückenkettenlänge von 1 bis 6 Kohlenstoffatomen, oder (b) Phenylgruppen, die gegebenenfalls mit Halogenen oder C_1-C_{20}-Alkylresten substituiert sind, welche die Sauerstoffatome in Position 1,2 oder 1,3 oder 1,4 verbrücken, und Naphthalingruppen, die gegebenenfalls substituiert sind, welche die Sauerstoffgruppen in Position 1,2 oder 2,3 oder 1,8 verbrücken.

2. Feste Katalysatorkomponente nach Anspruch 1, wobei die Brückengruppe die Formel $-(CR^4_p)_s-$ hat, in der R^4 unabhängig Wasserstoff oder ein C_1-C_{20}-Kohlenwasserstoffrest ist, der gegebenenfalls mit Heteroatomen ausgewählt aus Halogen, P, S, N, O und Si substituiert ist, die unter Bildung von einem oder mehreren Cyclen miteinander kondensiert sein können, p eine Zahl ist, die die verfügbare Wertigkeit von Kohlenstoff absättigt, und s eine Zahl von 1 bis 6 ist.

3. Feste Katalysatorkomponente nach Anspruch 2, wobei die Brückengruppe ausgewählt ist aus der Gruppe bestehend aus Methyliden, Ethan-1,2-diyl, Butan-2,3-diyl, Pentan-2,4-diyl, 2,2-Diisobutylpropan-1,3-diyl, Cyclohexan-1,2-diyl, Cyclopentan-1,2-diyl.

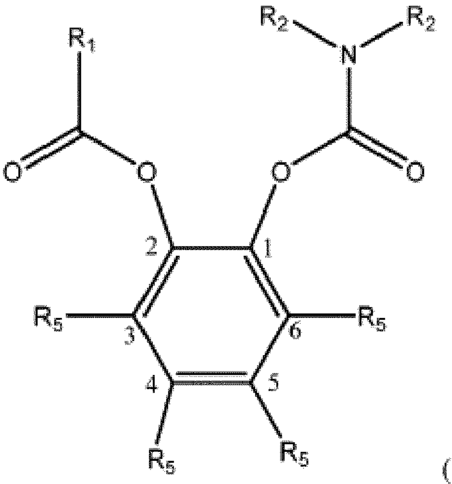
4. Feste Katalysatorkomponente nach Anspruch 1, wobei die Gruppen R_1 ausgewählt sind aus Aryl- und Alkylarylgruppen.

5. Feste Katalysatorkomponente nach Anspruch 4, wobei die Gruppen R_1 ausgewählt sind aus Phenylgruppen.

6. Feste Katalysatorkomponente nach Anspruch 5, wobei die Phenylgruppen mit Halogen und/oder C_1-C_5-Alkylgruppen substituiert sind.

7. Feste Katalysatorkomponente nach Anspruch 1, wobei die Gruppen R_2 unabhängig ausgewählt sind aus Wasserstoff oder C_1-C_{10}-Alkylgruppen.

8. Feste Katalysatorkomponente nach Anspruch 1, wobei der Elektronendonor ausgewählt ist aus jenen der Formel (II):



(II)

wobei R_1 und R_2 die gleiche Bedeutung wie in Anspruch 1 haben, und R_5 unabhängig ausgewählt ist aus Wasserstoff, Halogenen oder C_1-C_{15} Kohlenwasserstoffgruppen, die gegebenenfalls mit Heteroatomen ausgewählt aus Halogen, P, S, N, O und Si substituiert sind, mit der Maßgabe, dass mindestens einer von R_5 von Wasserstoff verschieden ist.

9. Katalysator zur Polymerisation von Olefinen, umfassend das Produkt der Reaktion zwischen:

(i) der festen Katalysatorkomponente gemäß einem der vorhergehenden Ansprüche und
(ii) einer Alkylaluminiumverbindung und gegebenenfalls
(iii) einer externen Elektronendonorverbindung.

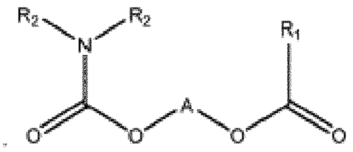
10. Katalysator nach Anspruch 9, ferner umfassend eine externe Elektronendonorverbindung.

11. Verfahren zur (Co)polymerisation von Olefinen CH_2=CHR, wobei R Wasserstoff oder ein Kohlenwasserstoffrest mit 1 bis 12 Kohlenstoffatomen ist, welches in Gegenwart eines Katalysatorsystems durchgeführt wird, welches das Produkt der Reaktion zwischen:

i. der festen Katalysatorkomponente nach einem der Ansprüche 1 bis 8;
ii. einer Alkylaluminiumverbindung und
iii. gegebenenfalls einer externen Donorverbindung umfasst.

Revendications

1. Composant de catalyseur solide pour la polymérisation d'oléfines comprenant Mg, Ti et un donneur d'électrons de formule (I)



où R_1 est choisi parmi les groupes hydrocarbonés en C_1-C_{15} contenant optionnellement un hétéroatome choisi parmi halogène, P, S, N et O ; les groupes R_2, identiques ou différents les uns des autres, sont l'hydrogène ou des groupes R_1 qui peuvent être fusionnés ensemble pour former un ou plusieurs cycles et A est un groupe de pontage bivalent choisi parmi (a) des groupes de pontage aliphatiques et alicycliques, optionnellement substitués par des groupes hydrocarbonés en C_1-C_{15} et/ou par des hétéroatomes choisis parmi halogène, P, S, N, O et Si, et ayant une longueur de chaîne de pontage allant de 1 à 6 atomes de carbone ou (b) des groupes phényle, optionnellement substitués par des halogènes ou des radicaux alkyle en C_1-C_{20}, servant de pont entre les atomes d'oxygène en position 1,2 ou 1,3 ou 1,4 et des groupes naphtalène, optionnellement substitués, servant de pont aux groupes oxygène en position 1,2 ou 2,3 ou 1,8.

2. Composant de catalyseur solide selon la revendication 1 dans lequel le groupe de pontage a la formule-- $(CR^4{}_p)_s$- dans lequel R^4 est, indépendamment, hydrogène ou un radical hydrocarboné en C_1-C_{20} optionnellement substitué par des hétéroatomes choisis parmi halogène, P, S, N, O et Si, qui peuvent être fusionnés ensemble pour former un ou plusieurs cycles, p est un nombre satisfaisant la valence de carbone disponible et s est un nombre de 1 à 6.

3. Composant de catalyseur solide selon la revendication 2 dans lequel le groupe de pontage est choisi dans le groupe constitué par le méthylidène, l'éthane-1,2-diyle, le butane-2,3-diyle, le pentane-2,4-diyle, le 2,2-diisobutylpropane-1,3-diyle, le cyclohexane-1,2-diyle, le cyclopentane-1,2-diyle.

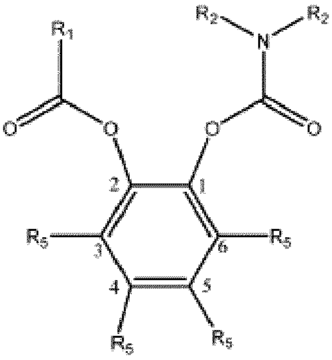
4. Composant de catalyseur solide selon la revendication 1, dans lequel les groupes R_1 sont choisis parmi des groupes aryle et alkylaryle.

5. Composant de catalyseur solide selon la revendication 4 dans lequel les groupes R_1 sont choisis parmi les groupes phényle.

6. Composant de catalyseur solide selon la revendication 5 dans lequel les groupes phényle sont substitués par des groupes halogénés et/ou des groupes alkyle en C_1-C_5.

7. Composant de catalyseur solide selon la revendication 1 dans lequel les groupes R_2 sont indépendamment choisis parmi hydrogène ou des groupes alkyle en C_1-C_{10}.

8. Composant de catalyseur solide selon la revendication 1 dans lequel le donneur d'électrons est choisi parmi ceux ayant la formule suivante (II) :



(II)

dans laquelle R_1 et R_2 ont la même signification selon la revendication 1, et R_5, indépendamment, est choisi parmi hydrogène, des halogènes ou des groupes hydrocarbonés en C_1-C_{15} optionnellement substitués par des hétéroatomes choisis parmi halogène, P, S, N, O et Si, à condition qu'au moins l'un de R_5 soit différent de l'hydrogène.

9. Catalyseur pour la polymérisation d'oléfines comprenant le produit de la réaction entre :

(i) le composant de catalyseur solide selon l'une quelconque des revendications précédentes et
(ii) un composé de l'alkylaluminium et optionnellement,
(iii) un composé donneur d'électrons externe.

10. Catalyseur selon la revendication 9 comprenant, en outre, un composé donneur d'électrons externe.

11. Procédé pour la (co)polymérisation d'oléfines CH_2=CHR, dans lesquelles R est hydrogène ou un radical hydrocarbyle ayant de 1 à 12 atomes de carbone, réalisée en présence d'un système catalyseur comprenant le produit de la réaction entre :

i. le composant de catalyseur solide selon l'une quelconque des revendications 1 à 8 ;
ii. un composé de l'alkylaluminium et,
iii. optionnellement, un composé donneur externe.

REFERENCES CITED IN THE DESCRIPTION

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