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(71) Applicant: BASELL POLIOLEFINE ITALIA S.R.L.

[IT/IT]; Via Pontaccio 10, 20121 Milano (IT).

(72) Inventors: GADDI, Benedetta; C/O Basell Poliolefine

Italia S.r.l., P.le G. Donegani, 12, 44122 Ferrara (IT). COL-

LINA, Gianni; C/O Basell Poliolefine Italia S.r.l., P.le

G. Donegani, 12, 44122 Ferrara (IT). EVANGELISTI,

Daniele; C/O Basell Poliolefine Italia S.r.l., P.le G. Done-

gani, 12, 44122 Ferrara (IT). FUSCO, Ofelia; C/O Basell

Poliolefine Italia S.r.l., P.le G. Donegani, 12, 44122 Ferrara

(IT). GESSI, Piero; C/O Basell Poliolefine Italia S.r.l., P.le

G. Donegani, 12, 44122 Ferrara (IT).

(74) Agent: GIBERTI, Stefano; c/o Basell Poliolefine Italia

S.r.l., Intellectual Property, P.le G. Donegani 12, 44122 Fer-

rara (IT).

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(54) Title: CATALYST COMPONENTS FOR THE POLYMERIZATION OF OLEFINS

(57) Abstract: A solid catalyst component for the polymerization of olefins comprising Mg, Ti, halogen, and an electron donor compound selected from glutarates said catalyst being characterized by specific porosity features and being able to produce olefin polymers endowed with low bulk density and relatively high porosity.

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CATALYST COMPONENTS FOR THE POLYMERIZATION OF OLEFINS

FIELD OF THE PRESENT DISCLOSURE

[0001] The present disclosure relates to the field of chemistry. In particular, it relates to catalyst components for the polymerization of olefins, which are characterized by specific chemical and physical properties. The disclosed catalysts are particularly useful in the preparation of porous propylene polymers.

BACKGROUND OF THE INVENTION

[0002] One of the most important families of propylene polymers is constituted by the so called heterophasic copolymers compositions made of a relatively high crystallinity propylene polymer fraction and a low crystallinity elastomeric component (for instance, a propylene-ethylene copolymer).

[0003] Although these compositions could be prepared by mechanical blending of the two main components, they are more commonly prepared via the sequential polymerization technique where the relatively high crystalline propylene polymer (sometimes called crystalline matrix) is prepared in a first polymerization reactor and then transferred to a successive polymerization reactor, where the low crystallinity elastomeric component is formed.

[0004] In this type of process, the porosity of the relatively high crystallinity polymer matrix may affect the incorporation of the elastomeric fraction into the crystalline matrix.

[0005] As a general rule in fact, the higher is the porosity of the polymer matrix produced in the first step, the higher is the amount of elastomeric component that can be incorporated, within said matrix, in the second polymerization step.

[0006] On the other hand, if the porosity of the matrix is poor, the presence of an excessive amount of elastomeric polymer fraction on the particles surface considerably increases the tackiness of said particles which gives raise to agglomeration phenomena possibly causing reactor downsides such as reactor wall sheeting, plugging or even clogging.

[0007] A macroscopic measurement of the polymer porosity is given by the polymer bulk density. The bulk density or apparent density is the mass per unit of volume of a material, including voids inherent in the material of interest. In case of polymer particles of regular morphology,

relatively low values of bulk density indicate a relatively high porosity of the polymer powder. Thus, at least for certain applications it would be desired to produce in the first polymerization step a propylene polymer endowed with both higher porosity (lower bulk density) and high crystallinity.

[0008] One option to produce crystalline polymers with a certain level of porosity is to polymerize propylene with a catalyst already having a certain level of porosity.

[0009] As disclosed in EP 395083, such catalyst can be obtained starting from adducts of formula $\text{MgCl}_2 \cdot m\text{EtOH} \cdot n\text{H}_2\text{O}$ where m is between 1 and 6 and n is between 0.01 and 0.6 from which a certain amount of alcohol is removed thereby creating a porous precursor which is then converted into a catalyst component by reaction with a titanium compound containing at least one Ti-Cl bond.

[0010] As a drawback, the increase of the catalyst porosity may lead to a corresponding decrease of the catalyst performances in terms of polymerization activity.

[0011] In WO2004/026920 it is proposed to prepare adducts having an increased amount of alcohol and characterized by a particular X-ray diffraction spectrum. These adducts once converted into catalyst component containing phthalates as internal donor are able to generate catalysts with increased activity or, if the adducts are partially dealcoholated before reaction with the Ti compound, with higher porosity with respect to that generated by adducts having the same amount of alcohol obtained directly in preparation and not dealcoholated. Notwithstanding that, there is the need of a catalyst able to produce crystalline polypropylene with a still increased porosity.

[0012] The applicant has now found catalyst components able to generate propylene polymers having at the same time low bulk density, high porosity and high crystallinity.

SUMMARY OF THE INVENTION

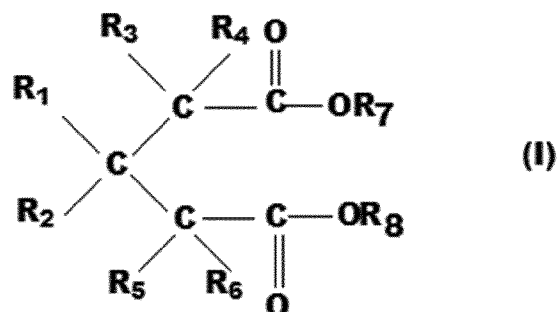
Accordingly, the present disclosure regards a solid catalyst component for the polymerization of olefins comprising Mg, Ti, halogen, and an electron donor compound selected from glutarates said catalyst being characterized by a total porosity (measured by mercury intrusion method) deriving from pores with radius up to 1000 nm of at least $0.20 \text{ cm}^3/\text{g}$ with the proviso that more than 50% of said porosity derives from pores having radius from 1 to 100 nm.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In a preferred embodiment of the present disclosure the total mercury porosity of the adduct ranges from 0.25 to 0.80 cm³/g, preferably from 0.35 to 0.60 cm³/g.

[0014] The porosity fraction deriving from pores having radius from 1 to 100nm preferably ranges from at least 50% to 90% of the total porosity, preferably from 55.0 to 85% and more preferably from 60 to 80% of the total porosity.

[0015] Preferred glutarates are those of formula (I):



[0016] wherein the radicals R₁ to R₈ equal to or different from each other, are H or a C₁-C₂₀ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups, optionally containing heteroatoms, and two or more of said radicals can also be joined to form a cycle, with the provisions that R⁷ and R⁸ are both different from hydrogen.

[0017] An interesting class of substituted glutarates is that in which R₁ is H and R₂ is selected from linear or branched C₁-C₁₀ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. Preferably, R₂ is selected from linear or branched C₁-C₁₀ alkyls, cycloalkyl, and arylalkyl groups.

[0018] In a preferred embodiment, in the compounds of formula (I) both R₁ and R₂ are different from hydrogen and are selected from linear or branched C₁-C₁₀ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. More preferably, both R₁ and R₂ are selected from C₂-C₅ linear alkyl groups.

[0019] R₇ and R₈ are preferably primary alkyl, arylalkyl or alkylaryl groups having from 1 to 10 carbon atoms. More preferably they are primary branched alkyl groups having from 1 to 8 carbon atoms. Examples of suitable R₇ and R₈ groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, neopentyl, 2-ethylhexyl.

[0020] Specific examples of β-monosubstituted glutarate compounds are diisobutyl 3-methylglutarate, diisobutyl 3-phenylglutarate, diethyl 3-ethylglutarate, diethyl 3-n-propylglutarate, diethyl 3-isopropylglutarate, diethyl 3-isobutylglutarate, diethyl 3-

phenylglutarate, diisobutyl 3-ethylglutarate, diisobutyl 3-isopropylglutarate, diisobutyl 3-isobutylglutarate, diethyl 3-(3,3,3-trifluoropropyl)glutarate, diethyl 3-cyclohexylmethyl glutarate, diethyl 3-tertbutyl glutarate.

[0021] Specific examples of di or tri substituted glutarates are: diethyl 3,3-dimethylglutarate, diisobutyl 3,3-dimethylglutarate, diethyl 3-methyl-3-isobutyl glutarate, diethyl 3-methyl-3-t-butyl glutarate, diisobutyl 3-methyl-3-isobutyl glutarate, diethyl 3-methyl-3-phenyl glutarate, diethyl 3,3-di-n-propyl glutarate, diisobutyl 3,3-di-n-propyl glutarate, diethyl 3,3-diisobutyl glutarate, diethyl 3-methyl-3-butyl glutarate, diethyl 3,3-diphenyl glutarate, diethyl 3-methyl-3-ethyl glutarate, diethyl 3,3-diethylglutarate, diethyl 3-methyl-3-isopropyl glutarate, diethyl 3-phenyl-3-n-butyl glutarate, diethyl 3-methyl-3-t-butyl glutarate, diethyl 3,3-diisopropyl glutarate diisobutyl 3-methyl-3-phenyl glutarate, diisobutyl 3,3-diisobutyl glutarate, diisobutyl 3-methyl-3-butyl glutarate, diisobutyl 3,3-diphenyl glutarate, diisobutyl 3-methyl-3-ethyl glutarate, diisobutyl 3,3-diethylglutarate, diisobutyl 3-methyl-3-isopropyl glutarate, diisobutyl 3-phenyl-3-n-butyl glutarate, diisobutyl 3-methyl-3-t-butyl glutarate, diisobutyl 3,3-diisopropyl glutarate, diethyl 3-ethyl-3 n butyl glutarate, diisobutyl 3-ethyl-3- n-butyl glutarate, diethyl 3-i-propyl-3-n-butyl glutarate, diisobutyl 3-i-propyl-3-n-butyl glutarate, diethyl 3-(2-methyl-butyl)-3-ethyl glutarate, diisobutyl 3-(2-methyl-butyl)-3-ethyl glutarate, diethyl 3-n-propyl-3-phenyl glutarate, diisobutyl 3-n-propyl-3-phenyl glutarate diethyl 2-methyl-3-phenyl glutarate, diethyl 2,2-dimethyl-3-phenyl glutarate, diethyl 2-methyl-3,3-diisobutyl glutarate, diethyl 2-ethyl-3-isopropylglutarate, diisobutyl 2-methyl-3-phenyl glutarate, diisobutyl 2,4-dimethyl-3-phenyl glutarate, diisobutyl 2-methyl-3,3-diisobutyl glutarate, diisobutyl 2-ethyl-3-isopropylglutarate. Among them, diethyl 3,3-di-n-propyl glutarate and diisobutyl 3,3-di-n-propyl glutarate are most preferred.

[0022] Specific examples of glutarates in which the substituents R₁ and R₂ are linked to form a cycle are 9,9-bis(ethoxyacetyl)fluorene, 1,1-bis(ethoxyacetyl)cyclopentane, 1,1-bis(ethoxyacetyl)cyclohexane, 1,3-bis(ethoxycarbonyl)-1,2,2-trimethylcyclopentane.

[0023] The catalyst components of the present disclosure precursor having the above-mentioned features can be obtained according several methods. According to the preferred one, an adduct between magnesium chloride and alcohol (in particular ethanol) containing from 3.5 to 4.5 moles of alcohol per mole of Mg is prepared.

[0024] The adduct can be prepared by contacting MgCl₂ and alcohol in the absence of the inert liquid dispersant, heating the system at the melting temperature of MgCl₂-alcohol adduct or above,

and maintaining said conditions so as to obtain a completely melted adduct. In particular, the adduct is preferably kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period equal to, or greater than, 1 hour, preferably from 2 to 15 hours, more preferably from 5 to 10 hours. Said molten adduct is then emulsified in a liquid medium which is immiscible with and chemically inert to it and finally quenched by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct. It is also preferable, before recovering the solid particles, to leave them in the cooling liquid at a temperature ranging from -10 to 25°C for a time ranging from 1 to 24 hours. Particularly in this method the solidification of the adduct in spherical particles can be obtained by spraying the MgCl_2 -alcohol adduct, not emulsified, in an environment having a temperature so low as to cause rapid solidification of the particles.

[0025] In a variant to this method, MgCl_2 particles can be dispersed in an inert liquid immiscible with and chemically inert to the molten adduct, heating the system at temperature equal to or higher than the melting temperature of MgCl_2 -ethanol adduct and then adding the desired amount of alcohol in vapor phase. The temperature is kept at values such that the adduct is completely melted for a time ranging from 10 minutes to 10 hours. The molten adduct is then treated as disclosed above. The liquid in which the MgCl_2 is dispersed, or the adduct emulsified, can be any liquid immiscible with and chemically inert to the molten adduct. For example, aliphatic, aromatic or cycloaliphatic hydrocarbons can be used as well as silicone oils. Aliphatic hydrocarbons such as vaseline oil are particularly preferred.

[0026] The quenching liquid is preferably selected from hydrocarbons that are liquid at temperatures ranging from -30 to 30°C. Among them preferred are pentane, hexane, heptane or mixtures thereof.

[0027] In another variant, the obtained molten adduct is solidified in discrete particles by using spray cooling technique in which the solution is sprayed by a nozzle in a cold atmosphere where immediate solidification occurs.

[0028] The so obtained solid adducts are made of compact particles with low mercury porosity which may range from 0.05 to 0.12 cm³/g.

[0029] The mercury porosity can be increased by a dealcoholation step carried out according to known methodologies such as those described in EP-A-395083 in which dealcoholation is obtained by keeping the adduct particles in an open cycle fluidized bed created by the flowing of

warm nitrogen which after removal of the alcohol from the adduct particles is directed out of the system. In this open cycle treatment, the dealcoholation is carried out at increasing temperature gradient until the particles have reached the desired alcohol content which is in any case at least 10% (molar amount) lower than the initial amount.

[0030] The so obtained partially dealcoholated adducts may show a porosity ranging from 0.15 to 1.5 cm³/g depending on the extent of alcohol removed.

[0031] The particles collected at the end of the treatment form, are then reacted with a titanium compound and the glutarate in order to form the final solid catalyst component. Particularly preferred titanium compounds are those of formula $Ti(OR^a)_nX_{y-n}$ in which n is comprised between 0 and y; y is the valence of titanium; X is chlorine and R^a is an hydrocarbon radical, preferably alkyl, radical having 1-10 carbon atoms or a COR^a group. Among them, particularly preferred are titanium compounds having at least one Ti-Cl bond such as titanium tetrachlorides or chloroalcoholates. Preferred specific titanium compounds are TiCl₃, TiCl₄, Ti(OBu)₄, Ti(OBu)Cl₃, Ti(OBu)₂Cl₂, Ti(OBu)₃Cl. Preferably, the reaction is carried out by suspending the adduct in cold TiCl₄ (generally 0°C or lower); then the so obtained mixture is heated up to 80-130°C and kept at this temperature for 0.5-2 hours. After that, the excess of TiCl₄ is removed and the solid component is recovered. The treatment with TiCl₄ can be carried out one or more times.

[0032] The solid catalyst component described in the present application can contain Ti atoms in an amount higher than 0.5%wt more preferably higher than 1.0%wt and especially higher than 1.5%wt with respect to the total weight of said catalyst component. An amount ranging from 1.50 to 5%wt of titanium with respect to the total weight of said catalyst component is especially preferred.

[0033] The solid catalyst component may also contain a small amounts of additional metal compounds selected from those containing elements belonging to group 1-15 preferably groups 11-15 of the periodic table of elements (Iupac version).

[0034] Most preferably, said compounds include elements selected from Cu, Zn, and Bi not containing metal-carbon bonds. Preferred compounds are the oxides, carbonates, alkoxylates, carboxylates and halides of said metals. Among them, ZnO, ZnCl₂, CuO, CuCl₂, and Cu diacetate, BiCl₃, Bi carbonates and Bi carboxylates are preferred.

[0035] The said compounds can be added either during the preparation of the previously described magnesium-alcohol adduct or they can be introduced into the catalysts by dispersing them into the titanium compound in liquid form which is then reacted with the adduct.

[0036] Whichever the method used, the final amount of said metals into the final catalyst component ranges from 0.1 to 10%wt, preferably from 0.3 to 8% and most preferably from 0.5 to 5% wt with respect to the total weight of solid catalyst component.

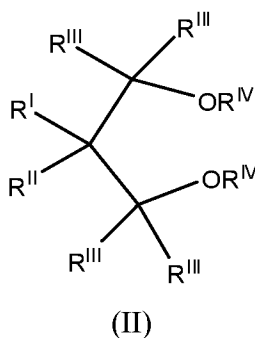
[0037] The electron donor compound (glutarate as internal donor) can be added during the reaction between titanium compound and the adduct in an amount such that the ratio glutarate:Mg ranges from 1:4 and 1:20.

[0038] In a preferred embodiment the electron donor compound is added during the first treatment with TiCl_4 .

[0039] Regardless of the preparation method used, the final amount of glutarate in the solid catalyst component is such that its molar ratio with respect to the Ti atoms is from 0.01:1 to 2:1, preferably from 0.05:1 to 1.2:1.

[0040] The glutarate donor can be added as such during the catalyst preparation process or, in the alternative, in the form of precursors that, due to reaction with other catalyst ingredients, are able to transform in the compounds of formula (I). In addition to the glutarate, the solid catalyst components can also contain additional donors. Although there is no limitation on the type of additional donors which can be selected from esters, ethers, carbamates, thioesters, amides and ketones.

[0041] Among the above classes, particularly preferred are the 1,3-diethers of formula (II)

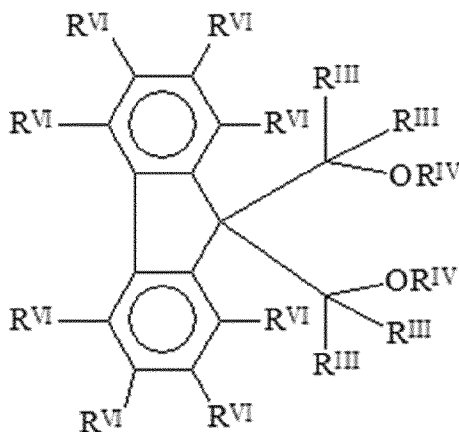


[0042] where R^{I} and R^{II} are the same or different and are hydrogen or linear or branched C_1 - C_{18} hydrocarbon groups which can also form one or more cyclic structures; R^{III} groups, equal or different from each other, are hydrogen or C_1 - C_{18} hydrocarbon groups; R^{IV} groups equal or

different from each other, have the same meaning of R^{III} except that they cannot be hydrogen; each of R^I to R^{IV} groups can contain heteroatoms selected from halogens, N, O, S and Si.

[0043] Preferably, R^{IV} is a 1-6 carbon atom alkyl radical and more particularly a methyl while the R^{III} radicals are preferably hydrogen. Moreover, when R^I is methyl, ethyl, propyl, or isopropyl, R^{II} can be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, isopentyl, 2-ethylhexyl, cyclopentyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl; when R^I is hydrogen, R^{II} can be ethyl, butyl, sec-butyl, tert-butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, 1-decahydronaphthyl; R^I and R^{II} can also be the same and can be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, neopentyl, phenyl, benzyl, cyclohexyl, cyclopentyl.

[0044] . Especially preferred are the compounds of formula (III):



(III)

[0045] where the R^{VI} radicals equal or different are hydrogen; halogens, preferably Cl and F; Cl-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl radicals, optionally containing one or more heteroatoms selected from the group consisting of N, O, S, P, Si and halogens, in particular Cl and F, as substitutes for carbon or hydrogen atoms, or both; the radicals R^{III} and R^{IV} are as defined above for formula (II).

[0046] Surprisingly, the catalyst components of the present disclosure, are capable to produce polymers having higher porosity (lower bulk density), with respect to the catalyst components prepared from the precursor not having the combination of described features notwithstanding the similar level of total porosity.

[0047] The catalyst components of the present disclosure form catalysts for the polymerization of alpha-olefins $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, by reaction with Al-alkyl compounds. The alkyl-Al compound 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 $\text{Al}_2\text{Et}_3\text{Cl}_3$ optionally in mixture with said trialkyl aluminum compounds.

[0048] The molar ratio between alkyl-Al compound and Ti of the solid catalyst component may range from 20:1 to 2000:1.

[0049] In the case of the stereoregular polymerization of α -olefins such as for example propylene and 1-butene, an electron donor compound (external donor) which can be the same or different from the compound used as internal donor can be used in the preparation of the catalysts disclosed above. In case the internal donor is an ester of a polycarboxylic acid, in particular a phthalate, the external donor is preferably selected from the silicon compounds containing at least a Si-OR link, having the formula $\text{R}_a^1\text{R}_b^2\text{Si}(\text{OR}^3)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1 , R^2 , and R^3 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^1 and R^2 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R^3 is a C_1 - C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butylldimethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R^2 is a branched alkyl or cycloalkyl group and R^3 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.

[0050] As previously indicated the components of the present disclosure and catalysts obtained therefrom find applications in the processes for the (co)polymerization of olefins of formula $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms.

[0051] The catalysts of the present disclosure can be used in any of the olefin polymerization processes known in the art. They can be used for example in slurry polymerization using as diluent an inert hydrocarbon solvent or bulk polymerization using the liquid monomer (for example

propylene) as a reaction medium. Moreover, they can also be used in the polymerization process carried out in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

[0052] 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 0.1 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa.

[0053] The following examples are given to illustrate and not to limit the present disclosure itself.

CHARACTERIZATION

[0054] Porosity and surface area with nitrogen: are determined according to the B.E.T. method (apparatus used SORPTOMATIC 1900 by Carlo Erba).

[0055] Porosity and surface area with mercury:

[0056] The measure is carried out using a "Pascal 240" series porosimeter by Carlo Erba.

[0057] The porosity is determined by intrusion of mercury under pressure. For this determination use is made of a calibrated dilatometer (capillary diameter 3 mm) CD3P (by Carlo Erba) connected to a reservoir of mercury and to a high-vacuum pump. A weighed amount of sample is placed in the dilatometer. The apparatus is then placed under high vacuum (<0.1 mm Hg) and is maintained in these conditions for 20 minutes. The dilatometer is then connected to the mercury reservoir and the mercury is allowed to flow slowly into it until it reaches the level marked on the dilatometer at a height of 10 cm. The valve that connects the dilatometer to the vacuum pump is closed and then the mercury pressure is gradually increased with nitrogen up to 140 kg/cm². Under the effect of the pressure, the mercury enters the pores and the level goes down according to the porosity of the material.

[0058] The porosity (cm³/g) (for supports and catalysts only deriving from pores up to 1000 nm and for polymer up to 10000 nm) and the pore distribution curve, are directly calculated from the integral pore distribution curve, which is function of the volume reduction of the mercury and applied pressure values (all these data are provided and elaborated by the porosimeter associated computer which is equipped with a dedicated Pascal software supplied by C. Erba).

[0059] The average pore size is determined as the weighted average by the pore distribution curve and it calculated summing up all the values obtained by multiplying the relative volume (%)

of each pore fraction in the range 0-1000 nm of the curve by the average pore radius of the said fraction and dividing by 100 the so obtained sum.

EXAMPLES

[0060] General procedure for the preparation of the catalyst component

Into a 1l steel reactor provided with stirrer, 500 cm³ of TiCl₄ were introduced at room temperature, at 0°C and whilst stirring 20 g of the adduct (prepared according to the examples illustrated below) were introduced containing BiCl₃ (in amount to have a Mg/Bi molar ratio of 60); at 40°C temperature an amount of diethyl 3,3-di-n-propylglutarate as internal donor so as to give a Mg/donor molar ratio of 14 was introduced. The whole was heated to 110°C over 58 minutes and these conditions were maintained over 50 minutes. The stirring was stopped and after 10 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 110°C. A further treatment of the solid was carried out adding 500 cm³ of TiCl₄ and an amount of diethyl 3,3-di-n-propylglutarate as internal donor so as to give a Mg/donor molar ratio of 14. The mixture was heated at 110°C over 10 min. and maintaining said conditions for 30 min under stirring conditions (500 rpm). The stirring was then discontinued and after 30 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 110°C. A further treatment of the solid was carried out adding 500 cm³ of TiCl₄ and heating the mixture at 110°C over 10 min. and maintaining said conditions for 15 min under stirring conditions (500 rpm). The stirring was then discontinued and after 10 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 110°C. Thereafter, 5 washings with 500 cm³ of anhydrous hexane at 90°C and 1 washings with 500 cm³ of anhydrous hexane at room temperature were carried out. The solid catalyst component obtained was then dried under vacuum in nitrogen environment at a temperature ranging from 40-45°C.

[0061] General procedure for the propylene polymerization test.

[0062] A 4 litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst feeding system, monomer feeding lines and thermostating jacket, was used. The reactor was charged with 0.01 gr. of solid catalyst component 0.76 g of TEAL, 0.06g of cyclohexylmethyldimethoxysilane, 3.2 l of propylene, and 2.0 l of hydrogen. The system was heated to 70°C over 10 min. under stirring, and maintained under these conditions for 120 min. At

the end of the polymerization, the polymer was recovered by removing any unreacted monomers and was dried under vacuum.

[0063] Example 1

In a vessel reactor equipped with a IKA RE 166 stirrer containing 963 g of anhydrous EtOH at -8°C were introduced under stirring 530 g of MgCl_2 and 14 g of water. Once the addition of MgCl_2 was completed, the temperature was raised up to 108°C and kept at this value for 20 hrs. After that, while keeping the temperature at 108°C , the melt was fed by volumetric pump set to 62 ml/min together with OB55 oil fed by volumetric pump set to 225 ml/min, to an emulsification unit operating at 2800 rpm and producing an emulsion of the melt into the oil. While melt and oil were fed in continuous, the mixture at about 108°C was continuously discharged into a vessel containing 22 liters of cold hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C . After 24 hours, the solid particles of the adduct recovered were then washed with hexane and dried at 40°C under vacuum. The compositional analysis showed that the particles contained 61.8 % by weight of EtOH, 1.15% bw of water, the remaining being MgCl_2 .

The adduct was then thermally dealcoholated in a fluidized bed under increasing temperature nitrogen flow until the content of EtOH reached a chemical composition of 57.3%wt EtOH 1.2%wt H_2O , a total porosity deriving from pores up to 1000 nm of $0.18\text{ cm}^3/\text{g}$ and with the fraction of porosity deriving from pores with radius up to 100 nm accounting for 47.1% of the total porosity. Then, a sample of said dealcoholated adduct was used to prepare, according to the general procedure previously reported, the catalyst component which was characterized by containing 16%wt of Mg, 1.8%wt of Ti, 1.1%wt of Bi, 10%wt of glutarate, a total porosity deriving from pores up to 1000 nm of $0.273\text{ cm}^3/\text{g}$ and a fraction of porosity deriving from pores with radius up to 100 nm accounting for 66.6 % of the total porosity.

The so obtained catalyst was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

[0064] Comparative example 1

The same procedure disclosed for example 1 was used with the difference that diisobutyl phthalate was used instead of diethyl 3,3-di-n-propylglutarate in the preparation of the solid catalyst component. This latter was characterized by containing 17.5%wt of Mg, 1.4% wt of Ti, 2.7%wt of Bi, 8.5% wt of phthalate.

The so obtained catalyst was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

[0065] Example 2

The adduct containing 57.3 % by weight of EtOH and 1.2%wt of water prepared in example 1 was thermally dealcoholated in a fluidized bed under increasing temperature nitrogen flow until the content of EtOH reached a chemical composition of 50%wt EtOH, 1.2%wt H₂O, a total porosity deriving from pores up to 1000 nm of 0.35 cm³/g and with the fraction of porosity deriving from pores with radius up to 100 nm accounting for 29.1% of the total porosity.

[0066] Then, a sample of said dealcoholated adduct was used to prepare, according to the general procedure previously reported, the catalyst component which was characterized by containing 16%wt of Mg, 1.7%wt of Ti, 1.1% wt of Bi, 7.9%wt of glutarate, a total porosity deriving from pores up to 1000 nm of 0.517 cm³/g and a fraction of porosity deriving from pores with radius up to 100 nm accounting for 60.2 % of the total porosity.

The so obtained catalyst was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

[0067] Comparative Example 2

An initial amount of MgCl₂·2.8C₂H₅OH adduct was prepared according to the methodology described in Example 2 of PCT Publication No. WO98/44009, but operating on larger scale.

The adduct was then thermally dealcoholated under increasing temperature nitrogen flow until the content of EtOH reached a chemical composition of 49.8%wt EtOH and 1.3% wt of water.

[0068] Then, a sample of said dealcoholated adduct was used to prepare, according to the general procedure previously reported, the catalyst component which was characterized by containing 15.5%wt of Mg, 1.5%wt of Ti, 0.9%wt Bi, 9.1%wt of glutarate, a total porosity deriving from pores up to 1000 nm of 0.545 cm³/g and a fraction of porosity deriving from pores with radius up to 100 nm accounting for 46.6 % of the total porosity.

The so obtained catalyst was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

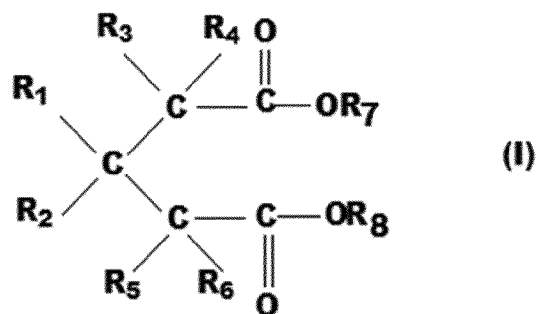
TABLE 1

Example	I.I.	Melt Index g/10'	Polymer Porosity (cm³/g)	Polymer bulk Density g/cm³
1	98.9	1.1	0.20	0.42
Comp.1	99.4	1.2	0.17	0.44
2	99.0	1.4	0.30	0.40
Comp.2	98.9	1.8	0.21	0.42

CLAIMS

What is claimed is:

1. A solid catalyst component for the polymerization of olefins comprising Mg, Ti, halogen, and an electron donor compound selected from glutarates said catalyst being characterized by a total porosity (measured by mercury intrusion method) deriving from pores with radius up to 1000 nm of at least $0.20 \text{ cm}^3/\text{g}$ with the proviso that more than 50% of said porosity derives from pores having radius from 1 to 100 nm.
2. The solid catalyst precursor of claim 1 in which the total mercury porosity ranges from 0.25 to $0.80 \text{ cm}^3/\text{g}$.
3. The solid catalyst precursor according to claim 1 in which the porosity fraction deriving from pores having radius from 1 to 100nm ranges from at least 50% to 90% of the total porosity.
4. The solid catalyst precursor according to claim 3 in which the porosity fraction deriving from pores having radius from 1 to 100 nm ranges from 55% to 85% of the total porosity.
5. The solid catalyst precursor of claim 1 in which the electron donor is selected from glutarates of formula (I)



wherein the radicals R_1 to R_8 equal to or different from each other, are H or a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups, optionally containing heteroatoms, and two or more of said radicals can also be joined to form a cycle, with the provisions that R^7 and R^8 are both different from hydrogen.

6. The solid catalyst precursor of claim 5 in which R_1 is H and R_2 is selected from linear or branched C_1 - C_{10} alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups.
7. The solid catalyst precursor of claim 5 in which both R_1 and R_2 are different from hydrogen

and are selected from linear or branched C₁-C₁₀ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups.

8. The solid catalyst precursor of claim 7 in which both R₁ and R₂ are selected from C₂-C₅ linear alkyl groups.
9. The solid catalyst precursor of claim 5 in which R₇ and R₈ are primary alkyl, arylalkyl or alkylaryl groups having from 1 to 10 carbon atoms.
10. The solid catalyst components according to claim 1 in which the Ti atom belong to titanium compounds of formula Ti(OR^a)_nX_{y-n} in which n is comprised between 0 and y; y is the valence of titanium; X is chlorine and R^a is a hydrocarbon radical.
11. The solid catalyst components according to claim 1 further comprising compounds of metals selected from Cu, Zn, and Bi said compounds being free from metal-carbon bonds.
12. The solid catalyst components according to claim 1 further comprising an additional donor selected esters, ethers, carbamates, thioesters, amides and ketones.
13. Catalyst for the polymerization of olefins comprising the product of the reaction between a catalyst component according to anyone of the claims 1 to 12, and an organoaluminum compound.
14. The catalyst for the polymerization of olefins according to claim 13 further comprising an external donor.
15. Process for the polymerization of olefins of formula CH₂=CHR, in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in the presence of a catalyst according to any one of the claims 13-14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/086195

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F4/657 C08F4/651 C08F110/06
ADD.

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 practicable, search terms used)

EPO-Internal, 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 2017/042058 A1 (BASELL POLIOLEFINE ITALIA SRL [IT]) 16 March 2017 (2017-03-16) paragraph [0067] - paragraph [0070] examples 19-24; table 2 claims 1-15	1-15
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X	----- WO 00/55215 A1 (MONTELL TECHNOLOGY COMPANY BV [NL]; MORINI GIAMPIERO [IT] ET AL.) 21 September 2000 (2000-09-21) page 6, paragraph third examples 1-16; tables 1,2 ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Gamb, Véronique

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	US 2014/316083 A1 (BRITA DIEGO [IT] ET AL) 23 October 2014 (2014-10-23) comparative example 1 and example 2 -----	1-15
A	WO 2004/026920 A1 (BASELL POLIOLEFINE SPA [IT]; EVANGELISTI DANIELE [IT] ET AL.) 1 April 2004 (2004-04-01) cited in the application examples 1-3; tables 1,2 -----	1-15

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