

"CATALYST COMPONENTS FOR THE POLYMERIZATION OF DIENES, CATALYST OBTAINED THEREFROM, AND PROCESS FOR THE PREPARATION OF POLYDIENES USING THE SAME"

The present invention relates to a catalyst component for the preparation of polydienes, which is particularly suitable for the use in non-solution processes.

Polydienes polymers are widely known in the art. In particular, butadiene based elastomers, having a high content of cis-1,4 units are extensively used for the production of tires and other elastomeric products.

Generally these products are obtained by solution polymerization using Z/N catalysts based on Titanium, Cobalt, Nickel or rare earth elements. Although allowing the preparation of products of interest, in particular those having a high content of cis-1,4 units, the solution process is not economical since it requires the removal of large quantities of solvent in order to obtain the solid products. Moreover, the productivity of the process cannot reach very high levels because the increase of the concentration of the polymer makes the viscosity of the polymerization medium so high that stirring becomes impossible.

Accordingly, processes more economical and having a lower environment impact, such as gas-phase processes, would be desirable for the preparation of dienic polymers.

In order to have a viable gas-phase process, the catalyst system used must be capable of providing polymers in high yields and with a good (possibly spherical) morphology.

EP-A-647657 discloses a gas-phase process for the polymerization of conjugated dienes using a catalyst component consisting of a rare earth element compound supported on a particular inorganic solid with certain features of surface area and porosity. According to this patent application, the above catalyst component has an activity higher than that of the catalyst component in which the solid inorganic support is absent. However, a still higher activity would be necessary for an economical carry out of a gas-phase process.

WO 96/04322 discloses a gas-phase process for preparation of polydienes carried out under conditions such as to have the diene monomer(s) in the liquid state and in the presence of an inert particulate material. According to said application, the above process should allow to obtain improved yields and reduced polymer fouling. The catalyst system used in said process comprises a metal component of Ni, Co or Ti supported on a porous inorganic support, while carbon black is used as the inert particulate material in the reactor.

In view of the above, it would be desirable to have a gas-phase process for the preparation of

polydienes characterized by easy operability, high productivity and reduction of fouling. In this connection, the term "easy operability" includes avoiding the use of materials in the reactor other than monomers, catalyst system and fluidization gas, and avoiding the use of restrictive polymerization conditions.

We have surprisingly found that by the use of a catalyst system comprising a specific component and a co-catalyst it is possible to carry out a process of this type.

It is therefore an object of the present invention a catalyst component for the polymerization of dienes, comprising a compound of a metal selected from Co, Ni and rare earth elements, supported on a polymer having a porosity, due to pores with a radius up to 100,000 Å, higher than 0.02 cm³/g measured by the mercury method specified below.

Nickel compounds can be selected from organic compounds of nickel with mono- or bidentate organic ligands containing up to 20 carbon atoms. These organonickel compounds are generally soluble in inert solvents. Representative of organonickel compounds are nickel benzoate, nickel acetate, nickel naphthenate, nickel octanoate, nickel neodecanoate, nickel 2-ethylhexanoate, bis(π -allyl nickel), bis(π -cycloocta-1,5-diene), bis(π -allyl nickel trifluoroacetate), bis(α -furyl dioxime) nickel, nickel palmitate, nickel stearate, nickel acetylacetonate, nickel salicaldehyde, bis(salicylaldehyde) ethylene diimine nickel, bis(cyclopentadiene) nickel, cyclopentadienylnickel nitrosyl and nickel tetracarbonyl. The preferred nickel compounds are selected from nickel salts of carboxylic acids or from nickel organic complexes.

The cobalt compound can be any organic compound such as the cobalt salts of organic acids, cobalt complexes and the like. Preferably, the cobalt compound is selected from the group consisting of cobalt β -ketone complexes, for example, cobalt (II) acetylacetonate and cobalt (III) acetylacetonate; cobalt β -ketoacid ester complexes, for example, cobalt acetylacetonate ethylester complexes; cobalt salts of organic carboxylic acids having 6 or more carbon atoms, for example, cobalt octoate, cobalt naphthenate, and cobalt benzoate; and cobalt halide complexes, for example, cobalt chloride-pyridine complexes; cobalt chloride-ethyl alcohol complexes and cobalt complexes coordinated with butadiene, for example, (1,3-butadiene) [1-(2-methyl-3-butenyl)- π -allyl]-cobalt which may be prepared, for example, by mixing a cobalt compound with an organic aluminum compound, organic lithium compound or alkyl magnesium compound and 1,3-butadiene. Other typical cobalt compounds are cobalt sorbate,

cobalt adipate, cobalt 2-ethylhexoate, cobalt stearate, and the like compounds wherein the organic portion of the molecule contains about 5 to 20, preferably 8 to 18 carbon atoms and one or two carboxylic functions, as well as acetylacetonate.

The rare earth metal compounds can be selected from the group consisting of :

- an alcoholate of formula $(RO)_3M$ (I);
- a carboxylate of formula $(RCO_2)_3M$ (II);
- a complex compound of the rare earth with diketones and/or an addition compound of the halides of the rare earth with an oxygen or nitrogen donor compound corresponding to the following formulae:



and



In the above formulae M is a trivalent element of the rare earth with atomic numbers of 57 to 71; R groups may be the same or different and represent hydrocarbon radicals containing 1 to 20 carbon atoms; L is chlorine, bromine or iodine; and y is from 1 to 6.

Preferred compounds are those in which M is lanthanum, cerium, praseodymium, gadolinium or neodymium or a mixture of elements of the rare earth which contains at least 10% by weight of at least one of the elements lanthanum, cerium, praseodymium or neodymium. Compounds in which M is lanthanum or neodymium or a mixture of rare earth containing at least 30% by weight of lanthanum or neodymium are most preferred.

The substituents R in formulae (I) to (IV) are, in particular, linear or branched alkyl radicals containing 1 to 15 carbon atoms and preferably 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, isopropyl, isobutyl, tert-butyl, 2-ethylhexyl, neopentyl, neoctyl, neodecyl, neododecyl.

Examples of alcoholates of formula (I) are neodymium(III) n-propanolate, neodymium(III) n-butanolate, neodymium(III) n-decanolate, neodymium(III) isopropanolate, neodymium(III) 2-ethylhexanolate, praseodymium(III) n-propanolate, praseodymium(III) n-butanolate, praseodymium(III) n-decanolate, praseodymium(III) isopropanolate, praseodymium(III) 2-ethylhexanolate, lanthanum(III) n-propanolate, lanthanum(III) n-butanolate, lanthanum(III) n-decanolate, lanthanum(III) isopropanolate, lanthanum(III) 2-ethylhexanolate. Preferred compounds are neodymium(III) n-butanolate, neodymium(III) n-decanolate, and neodymium(III) 2-ethylhexanolate.

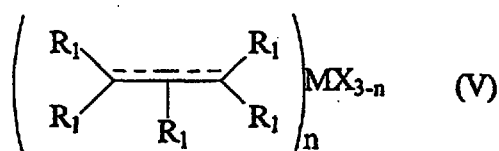
Suitable carboxylates of formula (II) are lanthanum(III) propionate, lanthanum(III) diethyl acetate, lanthanum(III) 2-ethylhexanoate, lanthanum(III) stearate, lanthanum(III) benzoate, lanthanum(III) cyclohexane carboxylate, lanthanum(III) oleate, lanthanum(III) versatate, lanthanum(III) naphthenate, praseodymium(III) propionate, praseodymium(III) diethyl acetate, praseodymium(III) 2-ethylhexanoate, praseodymium(III) stearate, praseodymium(III) benzoate, praseodymium(III) cyclohexane carboxylate, praseodymium(III) oleate, praseodymium(III) versatate, praseodymium(III) naphthenate, neodymium(III) propionate, neodymium(III) diethyl acetate, neodymium(III) 2-ethylhexanoate, neodymium(III) stearate, neodymium(III) benzoate, neodymium(III) cyclohexane carboxylate, neodymium(III) oleate, neodymium(III) versatate, neodymium(III) naphthenate. Preferred compounds are neodymium(III) 2-ethylhexanoate, neodymium(III) versatate, and neodymium(III) naphthenate. Neodymium versatate is particularly preferred.

Suitable complex compounds of formula (III) are lanthanum(III) acetylacetonate, praseodymium(III) acetylacetonate, neodymium(III) acetylacetonate, and preferably neodymium(III) acetylacetonate.

Examples of addition compounds of formula (IV) are, for example, lanthanum(III) chloride with tri-butyl phosphate, lanthanum(III) chloride with tetrahydrofuran, lanthanum(III) chloride with isopropanol, lanthanum(III) chloride with pyridine, lanthanum(III) chloride with 2-ethylhexanol, lanthanum(III) chloride with ethanol, praseodymium(III) chloride with tributyl phosphate, praseodymium(III) chloride with tetrahydrofuran, praseodymium(III) chloride with isopropanol, praseodymium(III) chloride with pyridine, praseodymium(III) chloride with 2-ethylhexanol, praseodymium(III) chloride with ethanol, neodymium(III) chloride with tributyl phosphate, neodymium(III) chloride with tetrahydrofuran, neodymium(III) chloride with isopropanol, neodymium(III) chloride with pyridine, neodymium(III) chloride with 2-ethylhexanol, neodymium(III) chloride with ethanol, lanthanum(III) bromide with tri-butyl phosphate, lanthanum(III) bromide with tetrahydrofuran, lanthanum(III) bromide with isopropanol, lanthanum(III) bromide with pyridine, lanthanum(III) bromide with 2-ethylhexanol, lanthanum(III) bromide with ethanol, praseodymium(III) bromide with tributyl phosphate, praseodymium(III) bromide with tetrahydrofuran, praseodymium(III) bromide with isopropanol, praseodymium(III) bromide with pyridine, praseodymium(III) bromide with 2-ethylhexanol, praseodymium(III) bromide with ethanol, neodymium(III) bromide with tributyl phosphate, neodymium(III) bromide with tetrahydrofuran, neodymium(III) bromide with

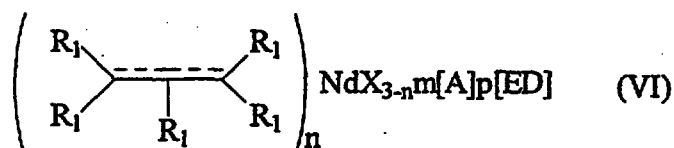
isopropanol, neodymium(III) bromide with pyridine, neodymium(III) bromide with 2-ethylhexanol, neodymium(III) bromide with ethanol. The compounds of the rare earth may be used individually or in admixture with one another.

Another class of compounds usable in the preparation of catalysts for polymerization of dienes is that of the Lanthanide-allyl complexes. These compounds belong to the general formula (V):



where the R_1 groups equal to, or different from, each other are hydrogen or C1-C10 hydrocarbon groups, in particular alkyls; n is 1 or 2; X is selected from halides, carboxylates and alcoholates; and M has the meaning given above.

The complexes in which M is Nd are preferred and, among them, particularly preferred are those of following formula (VI):



where the groups R_1 and n have the same meanings given above, X is Cl or Br, m is an integer from 0 to 2, p is an integer from 0 to 4, A is a salt of a metal belonging to one of the groups from I to IV of the Periodic Table of Elements and ED is an electron donor compound.

The fact that the complexes of the above formula (V) can be found complexed with other molecules is likely a consequence of their preparation methods which often comprise the use of metal-allyl compounds and Nd halides as starting products and certain electron donor compounds as reaction medium. In the above formula (VI) preferred electron donor compounds are ethers and amines, and a preferred metal salts are MgCl_2 and MgBr_2 . When the electron donor is ether it is preferably selected from the group consisting of diethyl ether, dimethoxyethane, tetrahydrofuran (THF) and dioxane.

Examples of usable allyl complexes are $\text{Nd}(\text{Allyl})_2\text{Cl}\cdot 1.5\text{THF}$ and $\text{Nd}(\text{Allyl})\text{Cl}_2\cdot 2\text{THF}$ whose preparation is described in *Journal of Organometallics Chem.* (1998) 552, pag. 195-204; and the complexes of formula $\text{Nd}(\text{Allyl})_2\text{Cl}\cdot 2\text{MgCl}_2\cdot 4\text{THF}$ (described in *Macromol. Symp.* (1998) 128, pag. 53-61) and $\text{Nd}(\text{Allyl})_2\text{Cl}\cdot \text{MgCl}_2\cdot n\text{THF}$ where n is from 1 to 4. Said complexes, in which also MgCl_2 is present, are generally obtainable by the reaction, in an ether solvent, of a Nd trihalide with a halide of Mg-allyl. Preferably the Nd trihalide is NdCl_3 , the ether solvent is tetrahydrofuran and the halide of Mg-allyl is Mg-allyl chloride.

The porous polymer is preferably selected from the group consisting of polyolefin (co)polymers. Preferably it is made up of polyethylene, copolymers of ethylene with proportions less than 20%mol of an olefin selected from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, cyclohexene, styrene; polypropylene with isotacticity index higher than 80%; crystalline copolymers of propylene with smaller amounts (5% mol or less) of ethylene and/or α -olefins such as 1-butene, 1-hexene.

Said porous polyolefin polymer can be prepared by the polymerization of the monomers carried out in the presence of catalyst comprising the product of the reaction between an organo-Al compound and a solid catalyst component comprising a halide of Ti, Zr, or V supported on a MgCl_2 , said solid component having suitable characteristics in terms of porosity and surface area for producing the polymers with the claimed porosity range. Preferably said catalyst components have a spherical form, with particle size from 5 to 200 microns and with surface area (BET) less than $200 \text{ m}^2/\text{g}$ and porosity (mercury method) due to pores with radius up to $10,000 \text{ \AA}$, higher than about $0.5 \text{ cm}^3/\text{g}$ and preferably higher than $0.6 \text{ cm}^3/\text{g}$. Examples of catalyst systems comprising solid components of this type are described for example in EP-A-395083, EP-A-553805, EP-A-553806 and EPA-601525. Said porous polymer can also be in a prepolymerized form that is as a polymer obtained by low conversion polymerization using the catalysts disclosed above. The prepolymer is generally produced in a quantity ranging from 0.5 g per g of solid catalyst component to 2000 g/g. Preferably, however, the amount is between 5 and 500 g per g of solid component and more preferably between 10 and 100 g per g of solid component.

In any case it is essential that the porosity (measured by the mercury method) is higher than $0.02 \text{ cm}^3/\text{g}$ and preferably in the range of from 0.04 to $1.4 \text{ cm}^3/\text{g}$, more preferably of from 0.04 to $1.2 \text{ cm}^3/\text{g}$ measured by the mercury method described below. In particular when a porous prepolymer is used its porosity is preferably from 0.3 to $1.2 \text{ cm}^3/\text{g}$, while when a porous

polymer is used its porosity is preferably from 0.04 to 0.3. The porous polymer used in the present invention is further characterized by a porosity, expressed as void percentage, of higher than 10% preferably higher than 15%. In addition, the porous polymer is also preferably endowed with a spherical form that is obtainable for example by using the catalyst components mentioned above.

The metal compound can be supported on said porous polymer using several methods. The term "metal compound supported" used hereafter and hereabove means the metal compound which is not extractable to an extent higher than 50% with heptane at 80°C for 2 hours.

One method comprises the contact of the support and the metal compound in the presence of a liquid medium that is subsequently removed. The so obtained catalyst component is then reacted with the suitable cocatalyst in order to form the final active catalyst.

According to one preferred embodiment instead, the metal compound is first converted into a final active catalyst by suitable reaction with the co-catalyst and then the whole system is supported on the porous polymer. Therefore, this process of supportation specifically comprises:

- (a) suspending the porous polymer in a hydrocarbon medium, preferably propane;
- (b) contacting the so obtained mixture with a hydrocarbon mixture containing the metal component, the cocatalyst and, optionally, a dienic monomer;
- (c) stirring the resulting mixture and finally,
- (d) removing the liquid hydrocarbon medium.

Step (b) is generally carried out working at a temperature between 0 and 100°C, preferably between 10 and 60°C, while step (c) is carried out for time periods ranging from 1 minute to 10 hours. The use of a low boiling point hydrocarbon medium is preferred since it is then possible to remove it simply by flashing. Preferably, before carrying out the step (a) the porous polymer is contacted with an Al-alkyl compound. The use of diisobutylaluminum hydride (DIBAH) is preferred.

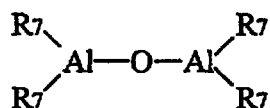
According to another embodiment, the supportation process can be carried out conveniently in a gas-phase loop reactor in which a stream of inert gas keeps the porous polymer moving. The metal compound, optionally dissolved in hydrocarbon solvent, is fed successively, for example using a sprayer, to the gas-phase loop reactor and a smooth-flowing product is obtained at the end of the treatment.

As mentioned above, the active catalysts usable in the polymerization of dienes are formed

upon reaction of the metal components with the suitable cocatalyst compounds.

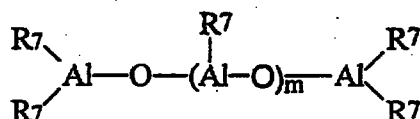
Suitable co-catalysts include organo-Al compounds. In particular, preferred organo-Al compounds are those of formula $\text{AlH}_p\text{R}_q\text{X}$, where R is a hydrocarbon group, preferably an alkyl group, having from 1 to 20 carbon atoms, X is halogen, preferably chlorine, p is from 0 to 2, r is from 1 to 3 and q is from 0 to 2. Specific examples are triethylaluminum (TEAL), triisobutylaluminum (TIBA), tris-2,3-dimethylbutylaluminum diethyl aluminum chloride (DEAC), diisobutylaluminum hydride, and partially hydrolyzed diethyl aluminum chloride (DEACO).

Alumoxanes can also be used as cocatalysts in particular when allyl-Lanthanide complexes are used as catalyst components. In particular, the usable alumoxane is considered to be a linear, branched or cyclic compound containing at least one group of the type:

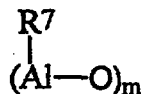


wherein the R^7 substituents, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl and $\text{C}_7\text{-C}_{20}$ arylalkyl radicals, optionally containing Si or Ge atoms, or R^7 is a group $-\text{O}-\text{Al}(\text{R}^7)_2$.

In particular, linear alumoxanes have formula:



wherein m is an integer ranging from 0 to 40 and R^7 has the meaning reported above; and cyclic alumoxanes have formula:



wherein m is an integer ranging from 2 to 40 and R^7 has the meaning reported above.

In the above-mentioned linear and cyclic alumoxanes, R^7 is preferably methyl, ethyl, isobutyl or 2,4,4-trimethyl-pentyl.

Examples of alumoxanes suitable as activating cocatalysts in the catalyst systems according to the present invention are methylalumoxane (MAO), a modified methylalumoxane obtained by

substituting 20-80% of the methyl groups with a C2 to C12 alkyl group preferably isobutyl (MMAO), isobutylalumoxane (TIBAO) 2,4,4-trimethyl-pentylalumoxane (TIOAO) and 2-methyl-pentylalumoxane. Mixtures of different alumoxanes can also be used.

Suitable activating cocatalysts in the catalyst systems of the invention are also the products of the reaction between water and an organometallic aluminum compound, preferably of formula AlR^7_3 or $Al_2R^7_6$, wherein R^7 has the meaning reported above. Particularly suitable are the organometallic aluminum compounds described in EP 0 575 875 (formula (II)) and those described in WO 96/02580 (formula (II)). Non-limiting examples of organometallic aluminum compounds of formula AlR^7_3 or $Al_2R^7_6$ are:

tris(methyl)aluminum, tris(isobutyl)aluminum, tris(isooctyl)aluminum
bis(isobutyl-)aluminum hydride, methyl-bis(isobutyl-)aluminum,
dimethyl(isobutyl-)aluminum, tris(isohexyl)aluminum, tris(benzyl)aluminum,
tris(tolyl)aluminum, tris(2,4,4-trimethylpentyl)aluminum,
bis(2,4,4-trimethylpentyl-)aluminum hydride, isobutyl-bis(2-phenyl-propyl)aluminum,
diisobutyl-(2-phenyl-propyl)aluminum, isobutyl-bis(2,4,4-trimethyl-pentyl)aluminum and
diisobutyl-(2,4,4-trimethyl-pentyl)aluminum.

Particularly preferred aluminum compounds are tris(2,4,4-trimethylpentyl)aluminum (TIOA), and triisobutylaluminum (TIBA).

Mixtures of different organometallic aluminum compounds and/or alumoxanes can also be used.

Suitable activating cocatalysts according to the present invention can also be the compounds of formula Y^+Z^- , wherein Y^+ is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metal compound, and Z^- is a compatible non-coordinating anion, able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate. Preferably, the anion Z^- consists of one or more boron atoms. More preferably, the anion Z^- is an anion of the formula $BAr_4^{(-)}$, wherein the substituents Ar, the same or different from each other, are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of the formula BAr_3 can conveniently be used.

When the metal compound is selected from Ni compounds, the cocatalyst is preferably selected from triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL) diethylaluminum

chloride (DEAC), MAO and mixtures thereof. Furthermore, also promoters, including hydrogen fluoride, boron trifluoride and their etherate derivatives, are preferably used.

When the metal compound is selected from Co compounds, the cocatalyst is preferably selected from ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EADC), partially hydrolized diethylaluminum chloride (DEACO), MAO and mixtures thereof.

When the metal compound is selected from rare earth metal compounds, the cocatalyst is preferably selected from triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL), diisobutylaluminum hydride (DIBAH), MAO and mixtures thereof.

When the catalyst component contains as metal compound the complexes of formulae (V)-(VI) the co-catalyst is preferably MAO.

When the metal compound is selected from those belonging to the formulae (I)-(III) and in particular from Nd carboxylates, the catalyst system is advantageously prepared by reacting the Nd compound with an alkylating agent and with a halogenating agent. The alkylating agent is preferably selected from the trialkyl aluminum compounds like TIBAL, while the halogenating agent is preferably selected from halogenated aluminum alkyls like DEAC or EASC.

Both the Al/Nd and the Cl/Nd molar ratios of the catalyst are somewhat critical for the polymerization activity. Preferably the Al/Nd molar ratio is higher than 10 and more preferably is between 15 and 70. The Cl/Nd molar ratio is preferably higher than 2 and in particular comprised between 2.5 and 5.

It has been observed that when butadiene is to be polymerized the activity of the catalyst system is improved as a consequence of the aging of the catalyst. In particular, aging times higher than 2 days and particularly between 10 and 40 days are suitable to obtain improved very improved yields over the fresh catalyst.

Even the order in which the Nd carboxylate, the alkylating agent and the chlorinating agent are added has an influence on the final properties of the catalyst. Commonly, the catalyst is prepared by first adding the chlorinating agent to the hydrocarbon solution of the Nd carboxylate and then reacting the so obtained slurry mixture with the alkylating agent. In developing this procedure it has been found particularly advantageous, for the increase of the activity, contacting the first mixture with small amounts of the dienine monomer before adding the alkylating agent.

In the alternative and preferred embodiment, the alkylating agent is firstly added to the

hydrocarbon solution of the Nd carboxylate. The so obtained mixture (first mixture) is then aged for a time longer than 4 hours thereby obtaining a homogeneous mixture which is then added with the halogenating agent. This technique allows to obtain a final catalyst system which is completely soluble in the hydrocarbon medium and that is particularly suitable for the supportation on the porous polymer.

The time span of the aging of the first mixture is preferably about 1 day in particular when carboxylates with at least 10 carbon atoms are used. For the lower carboxylates, longer aging times in particular from about 2 to 10 days are preferred. Generally, the use of longer aging times of the first mixture generates a final catalyst system solution capable to remain clear for times longer than 5 days. Also in this case the aging of the final catalyst solution is beneficial for the activity. In particular, aging times from about 2 to 4 days are especially preferred.

The hydrocarbon medium used for the preparation of the catalyst system is generally selected from the group consisting of saturated hydrocarbons like propane, butane, pentane, hexane, heptane or aromatic hydrocarbons such as toluene and benzene.

As explained above, this catalyst system is particularly suited for the preparation of polydienes by polymerization processes carried out in gas-phase. In particular it is very surprising that, as shown in the following examples, with the use of the polymeric porous support of the invention it is possible to obtain improved yields with respect to those obtainable with the same catalyst system supported on silica as disclosed in the prior art.

The gas-phase process can be carried out in a fluidized bed reactor or under conditions in which the polymer is mechanically stirred, and operating in one or more reactors. The polymerization temperature is generally comprised between -10 and 250°C, preferably between 10 and 160°C. The pressure is generally comprised between 0.1 and 50 bar and preferably between 1 and 20 bar.

The molecular weight of the resulting polymers can be regulated by using molecular weight regulator agents, or by using the polymerization conditions.

As polyene units capable of supplying unsaturated units both conjugated and non-conjugated polyene can be used.

Among conjugated dienes 1,3-butadiene, isoprene, pentadiene or dimethyl butadiene may be used. Straight, non-conjugated dienes can be selected from 1,4-(cis or trans)-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, alkenyl or alkylidene-norbornenes, such as

5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene, monocyclic diolefins, such as cis,cis-1,5-cyclooctadiene, 5-methyl-1,5-cyclooctadiene, 4,5,8,9-tetrahydroindene.

As it is known in the art the dienes can also be used in mixtures with other monomers, such as styrene, in order to produce copolymers having specific properties.

The polymers obtained with the catalyst of the invention have a cis-1,4-double bond content of around 60 to 99%. The molecular weight can be adjusted through the composition of the catalyst and by varying the polymerization conditions. Typical molecular weights are in the range from 10^3 to 10^6 , as measured by GPC (gel permeation chromatography).

The Mooney viscosity, ML (1+4', 100°C), is typically in the range from 30 to 180 MU. It is also possible by the gas-phase polymerization to produce polymers of very high molecular weight that would be extremely difficult to obtain by solution polymerization because of the high viscosity and the possibility of transfer reactions through the solvent used.

The polymer obtained may be compounded and vulcanized in the usual way.

The following examples are given in order to better illustrate the invention without limiting it.

EXAMPLES

CHARACTERIZATION

- **Effective density:** ASTM-D 792.

- **Porosity** (due to pores with radius up to 100,000Å): the measure is carried out using a "Porosimeter 2000 series" by Carlo Erba.

The porosity is determined by absorption of mercury under pressure. For this determination use is made of a calibrated dilatometer (diameter 3 mm) CD₃ (Carlo Erba) connected to a reservoir of mercury and to a high-vacuum pump ($1 \cdot 10^{-2}$ mba). 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 10 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.

The porosity (cm³/g), and the distribution of pores is 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 "MILESTONE 200/2.04" program by C. Erba.

The porosity expressed as percentage of voids is calculated from the following formula:

$$X=(100 \cdot V)/V_1$$

where V is the volume of the pores and V_1 is the apparent volume of the sample.

The value of V is directly provided by the instrument that calculates it on the basis of the difference between the initial and final level of the mercury in the. The apparent volume of the sample is given by:

$$V_1=[P_1-(P_2-P)]/D$$

where P is the weight of the sample in grams, P_1 is the weight of the dilatometer+mercury in grams, P_2 is the weight of the dilatometer+mercury+sample in grams and D is the density of mercury (at 25°C = 13.546 g/cm³).

EXAMPLE 1

Supportation of neodymium based catalytic system

9.84 grams of a polyethylene pre-polymer having a porosity of 0.341cm³/g were introduced, under nitrogen and at room temperature, into a 250 ml, 2 neck round bottomed flask, that was then connected under nitrogen to a rotavapor. A solution containing 5 mmoles of DIBAH in 10 ml of hexane was added dropwise in 10 minutes. The flask was allowed to rotate for 1 hour at room temperature under nitrogen. The flask was then disconnected from the rotavapor and the solid was dried under reduced pressure for 30 minutes at room temperature, by gently shaking the flask, until a completely free flowing powder was obtained.

Meanwhile, in a 25 ml Schlenk containing a magnetic stirrer, a solution of 0.523 mmoles of Neodymium versatate (1.65 ml of a 0.317 M solution in hexane), 0.2 mmoles of isoprene, 15 mmoles of DIBAH (10 mL of a 1.5 M solution in toluene) and 0.3 mmoles of EASC (2.5 ml of a 0.121 M solution in hexane) was prepared.

The solution was stirred for 5 minutes and was then cannulated under nitrogen into the flask and homogeneously distributed on the solid support. The solid was dried at reduced pressure for 30 minutes by gently shaking the flask.

The flask was then weighted and the weight of the supported catalyst was calculated to be 12.4 grams.

1,3-butadiene polymerization

The flask, containing the supported catalyst prepared as described in the previous paragraph, was connected to the rotavapor and it was allowed to rotate, at 80–100 rpm, plunged in a water

bath thermostatted at 40°C. 1,3-butadiene, previously flashed twice and passed on a column of molecular sieves, was fed into the rotavapor and continuously discharged at a pressure of 0.26 barg.

After 10 minutes, the gas phase polymerization was discontinued by stopping the feeding of 1,3-butadiene and flushing nitrogen through the flask. 22.8 grams of solid were obtained containing 10.4 grams of polybutadiene (activity 99gpol/mmolNd/h/bar).

Comparative example

Supportation of neodimium based catalytic system

The same procedure disclosed in Example 1 was followed, except that silica was used instead of the polyethylene pre-polymer as the support for the neodimium based catalytic system.

9.24 grams of silica (Grace 955/60) were used as the support, after having been dried at 250°C for 24 hours. 21.04 grams of solid were obtained after the supportation of the catalytic system.

1,3-butadiene polymerization

The polymerization was carried out according to the procedure disclosed in Example 1 with the only difference that the polymerization time lasted 1 hour. At the end of the polymerization 40 grams of solid were recovered corresponding to 18.96 of grams of polybutadiene (activity 30gpol/mmolNd/h/bar).

EXAMPLE 2

Preparation of the homogeneous catalyst solution

A hexane solution containing 0.361mmol of Nd versatate was added with a hexane solution of TIBAL containing 10 mmol of Al. The so obtained solution was left to stand for about one day after which a hexane solution containing 1.08 mmol of DEAC were added. The resulting clear mixture, having a 0.02 molar concentration, was then used in the next step.

Supportation of neodimium based catalytic system

15.3 grams of a polypropylene polymer having a porosity of 0.538 cm³/g were introduced, under nitrogen and at room temperature, into a 250 ml, 2 neck round bottomed flask, containing hexane that was then connected under nitrogen to a rotavapor. The homogeneous catalytic solution prepared as disclosed above was then added dropwise in 10 minutes. The flask was allowed to rotate for 30 min. at room temperature under nitrogen. The flask was then disconnected from the rotavapor and the solid was dried under reduced pressure for 30 minutes

at room temperature, by gently shaking the flask, until a completely free flowing powder was obtained containing 0.34% of Nd.

1,3-butadiene polymerization

The flask, containing 7.85 g of the supported catalyst prepared as described in the previous paragraph, was connected to the rotavapor and it was allowed to rotate, at 80–100 rpm, plunged in a water bath at room temperature. 1,3-butadiene, previously flashed twice and passed on a column of molecular sieves, was fed into the rotavapor until a pressure of about 1.2 atmosphere was reached.

After 15 minutes, the gas phase polymerization was discontinued by stopping the feeding of 1,3-butadiene and flushing nitrogen through the flask. 5 grams of polybutadiene were obtained corresponding to an activity of 88gpol/mmolNd/h/bar.

CLAIMS

1. A solid catalyst component for the (co)polymerization of dienes, comprising a compound of a metal selected from Co, Ni and rare earth elements, supported on a polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method.
2. A solid catalyst component according to claim 1 in which the porous polymer is selected from the group consisting of polyethylene, copolymers of ethylene with proportions less than 20%mol of an olefin selected from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, cyclohexene; polypropylene with isotacticity index above 80%; crystalline copolymers of propylene with up to 5% mol of ethylene and/or α -olefins such as 1-butene, 1-hexene.
3. A solid catalyst component according to claim 2 in which the porous polymer is a prepolymer produced in a quantity of from 0.5 to 2000 g per g of solid catalyst component.
4. A solid catalyst component according to claim 3 in which the porous polymer has a porosity in the range of from 0.04 to 1.4 cm³/g measured by the mercury method.
5. A solid catalyst component according to claim 1 in which the porous polymer is further characterized by porosity, expressed as percentage of voids, of higher than 15%.
6. A solid catalyst component according to any of the preceding claims in which the metal compound is selected from compounds of nickel with mono- or bidentate organic ligands containing up to 20 carbon atoms.
7. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from cobalt salts of organic acids, or cobalt organic complexes.
8. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from rare earth metal compounds belonging to the following classes:
 - an alcoholate of formula (RO)₃M (I);
 - a carboxylate of formula (RCO₂)₃ M (II);
 - complex compound of the rare earth with diketones and/or an addition compound of the halides of the rare earth with an oxygen or nitrogen donor compound corresponding to the formulae
(R-CO-CH-CO-R)₃M (III)

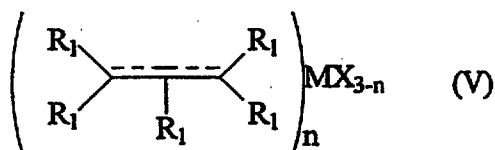
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 $ML_3 \cdot y$ donor (IV),

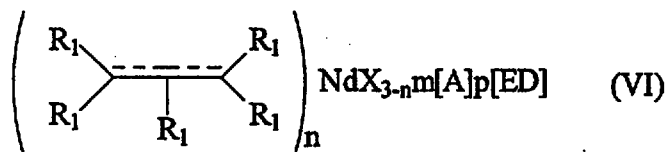
where M is a trivalent element of the rare earth with atomic numbers of 57 to 71; R groups may be the same or different and represent hydrocarbon radicals containing 1 to 10 carbon atoms; L is chlorine, bromine or iodine; and y is from 1 to 6.

9. A solid catalyst component according to claim 8 in which the metal compound is selected from those of formula (II) in which M is neodymium and in which the substituents R are linear or branched alkyl radicals containing 1 to 10 carbon atoms.
10. A solid catalyst component according to claim 9 in which the carboxylates are selected from the group consisting neodymium(III) 2-ethylhexanoate, neodymium(III) versate and neodymium(III) naphthenate.
11. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from rare earth metal compounds of formula (V):



where the R_1 groups equal to, or different from, each other are hydrogen or C1-C10 hydrocarbon groups, in particular alkyls; n is 1 or 2; X is selected from halides, carboxylates and alcoholates; and M has the meaning given above.

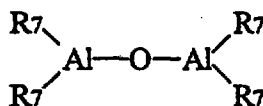
12. A solid catalyst component according to claim 11 in which M is Nd.
13. A solid catalyst component according to claim 12 in which the Nd compound is selected from those of the following formula (VI):



where the groups R_1 and n has the same meanings given above, X is Cl or Br, m is an integer from 0 to 2, p is an integer from 0 to 4, A is a salt of a metal belonging to one of the groups from I to IV of the Periodic Table of Elements and ED is an electron donor compound.



14. A solid catalyst component according to claim 13 in which electron donor compound is selected from ethers and amines, and the metal salt is $MgCl_2$ or $MgBr_2$.
15. A solid catalyst component according to claim 14 in which the electron donor is ether selected from the group consisting of diethyl ether dimethoxyethane, tetrahydrofuran (THF) and dioxane.
16. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to any of the preceding claims with a co-catalyst.
17. Catalyst according to claim 16 in which the cocatalyst is selected from the group consisting of:
 - organo-Al compounds of formula $AlH_pR_qX_r$, where R is a hydrocarbon group, preferably an alkyl group, having from 1 to 20 carbon atoms, X is halogen, preferably chlorine, p is from 0 to 2, r is from 1 to 3 and q is from 0 to 2;
 - alumoxanes containing at least one group of the type:



- wherein the R^7 substituents, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl and C_7 - C_{20} -aryl-alkyl radicals, optionally containing Si or Ge atoms, or R^7 is a group $-O-Al(R^7)_2$;
- compounds of formula Y^+Z^- , wherein Y^+ is a Broensted acid, able to donate a proton and to react irreversibly with a substituent X of the metal compound, and Z^- is a compatible non-coordinating anion, able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate.
18. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to claim 6 and a cocatalyst selected from the group consisting of triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL) diethylaluminum chloride (DEAC), MAO and mixtures thereof.
 19. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to claim 7 and a cocatalyst selected from the group consisting of ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EADC),





- partially hydrolized diethylaluminum chloride (DEACO), MAO and mixtures thereof.
20. Catalyst for the (co)polymerization of dienes comprising the product of the reaction between a solid catalyst component according to any of the claims 8-10 and an alkylating agent and with a halogenating agent.
 21. Catalyst according to claim 26 in which the alkylating agent is selected from the trialkyl aluminum compounds and the halogenating agent is selected from halogenated aluminum alkyls.
 22. Catalyst for the (co)polymerization of dienes comprising the product of the reaction of
 - (a) a porous polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method; and
 - (b) the product of the reaction between (i) a rare earth metal compound belonging to one of the formulae (I)-(III) of claim 12; (ii) an alkylating agent; and (iii) a halogenating agent, said components (i)-(iii) being reacted in a hydrocarbon medium.
 23. Catalyst according to claim 22 in which the alkylating agent is selected from the trialkyl aluminum compounds and the halogenating agent is selected from chlorinated aluminum alkyls.
 24. Catalyst according to claim 23 in which the rare earth metal of formulae (I)-(III) is Nd; the Al/Nd molar ratio is between 30 and 70 and the Cl/Nd molar ratio is between 2.5 and 6.
 25. Catalyst according to claim 28 in which the reaction product (b) is aged for a period longer than 2 days.
 26. Catalyst according to claim 23 in which the component (b) is obtained by reacting the component (iii) with a mixture, obtained by contacting the components (i) and (ii), which has been aged for a period longer than 4 hours.
 27. Catalyst according to claim 26 in which the mixture obtained by contacting the components (i) and (ii) is aged for a period longer than 1 day.
 28. Process for the preparation of a catalyst component according to claims 1-15 comprising contacting, a compound of a metal selected from Co, Ni and rare earth elements, with a polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method.
 29. Process according to claim 28 in which the contact is carried out in a liquid hydrocarbon medium.
 30. Process according to claim 28 in which the contact is carried out in gas-phase.





31. Process for the (co)polymerization of dienes characterized in that it is carried out in the presence of a catalyst system according one or more of the claims 16-27.
32. Process according to claim 31 characterized in that the process is carried out in gas phase.
33. Process according to claim 26 in which the diene is selected from the group consisting of 1,3-butadiene, isoprene, pentadiene or dimethyl butadiene, 1,4-(cis or trans)-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, 5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene, cis,cis-1,5-cyclooctadiene, 5-methyl-1,5-cyclooctadiene, 4,5,8,9-tetrahydroindene.

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