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(54) COMPOSANTS CATALYSEURS POUR LA POLYMERISATION D'OLEFINES ET CATALYSEUR AINSI OBTENU

(54) CATALYST COMPONENTS FOR THE POLYMERIZATION OF OLEFINS AND CATALYST OBTAINED THEREFROM

(57) La présente invention concerne un composant catalyseur renfermant un composé vanadium avec comme support un polymère poreux doté d'une porosité (mercure) supérieure à 0,02 cc/g. En faisant intervenir les composants catalyseurs susmentionnés, il est possible d'obtenir des copolymères élastomères d'éthylène avec des α-oléfines CH_2=CHR qui renferment éventuellement de faibles doses d'un diène, sans problèmes de salissure.

(57) The present invention provides a catalyst component comprising a vanadium compound supported on a porous polymer having a porosity (mercury) higher than 0.02 cc/g. With the above catalyst components it is possible to prepare elastomeric copolymers of ethylene with α-olefins CH_2=CHR, optionally containing minor proportions of a diene, without fouling problems.

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(57) Abstract

The present invention provides a catalyst component comprising a vanadium compound supported on a porous polymer having a porosity (mercury) higher than 0.02 cc/g. With the above catalyst components it is possible to prepare elastomeric copolymers of ethylene with α-olefins $CH_2{=}CHR$, optionally containing minor proportions of a diene, without fouling problems.

CATALYST COMPONENTS FOR THE POLYMERIZATION OF OLEFINS AND CATALYST OBTAINED THEREFROM

The present invention relates to a vanadium based catalyst component particularly suited for the preparation of elastomeric copolymers of ethylene with α-olefins $CH_2=CHR$, wherein R is an alkyl radical having 1-10 carbon atoms, optionally containing minor proportions of units derived from a diene or a polyene.

The copolymerization of ethylene and α-olefins, optionally in the presence of dienes, has been carried out up to now with several types of catalysts. One of the most known catalyst type is the homogeneous system formed by the reaction product of a vanadium compound, such as vanadium tris-acetylacetonate ($V(AcAc)_3$), with alkylaluminum halides, such as $AlEt_2Cl$.

These catalysts are able to give amorphous copolymers within a wide range of compositions and therefore are suitable for yielding, after vulcanization, elastomeric products showing valuable properties.

Because they are homogeneous systems, these catalysts are not capable of supplying copolymer particles having a controlled morphology. Accordingly, it is not possible to use them in industrial gas-phase polymerization processes for the preparation of EPR/EPDM polymers. Therefore, the catalysts are used in polymerization processes carried out in the presence of an inert hydrocarbon in which the copolymer formed is dissolved, or in liquid propylene, in which the copolymer forms a suspension. However, owing to the rubber-like character of the copolymer obtained, phenomena of adhesion to the reactor walls may occur and agglomerates may be formed, especially in the case of non-solution polymerization processes.

In one attempt to solve these problems, the above catalysts are made heterogeneous by supporting the vanadium compounds on inorganic carriers having a defined morphology. EP 630913 for example, discloses the preparation of EPR/EPDM polymers by gas-phase polymerization using a catalyst comprising a solid component obtained by supporting $V(AcAc)_3$ on silica, an Al-alkylhalide and a chlorinated ester as a promoter. The fouling problems however, are not solved since in order to reduce agglomeration in the gas-phase polymerization it must be used a fluidization aid such as carbon black. This product however, lowers the properties of the polymer since it confers to the elastomeric polymer characteristics that are typical of a filler product. In addition, the supportation on silica carriers suffers from the drawback that it generally leads to catalysts with low activity.

It has been unexpectedly found that by using specific supported catalyst components based on V compounds it is possible to carry out non-solution processes for the preparation of EPR/EPDM polymers without incurring in fouling problems. Further, it has been observed that, compared to the polymerization activity profiles of the catalyst components of the prior art, the catalyst components of the invention show a slower decay rate that makes it possible to obtain higher final yields.

It is therefore an object of the present invention a catalyst component comprising a Vanadium compound supported on a polymer having a porosity, due to pores with a radius up to 100,000Å, higher than 0.02 cm^3/g measured by the mercury method specified below.

Preferably the vanadium compound is selected form the group of vanadium compounds not containing π-V links. Still more preferably the vanadium compound is selected from the group consisting of $V(AcAc)_3$, VCl_4, $VOCl_3$, $VO(OR)_3$, where R is a C1-C8 alkyl group; $V(AcAc)_3$ being the most preferred.

The porous polymer on which the vanadium compound is supported can be any polyolefin (co)polymer known in the art. 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; 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 polymerizing monomers in the presence of a 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 100 microns and with surface area (BET) less than 200 m^2/g and porosity (mercury method) due to pores with radius up to 10,000 Å, higher than about 0.5 cm^3/g and preferably higher than 0.6 cm^3/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. 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 up 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 is higher than 0.02 cm^3/g, preferably ranging from 0.04 to 2 cm^3/g, and more preferably from 0.04 to 1.4 cm^3/g measured by the mercury method described below. In particular when a porous prepolymer is used its porosity is preferably from 0.4 to 1.2 cm^3/g, while when a porous polymer is used its porosity is preferably from 0.04 to 0.4. The porous polymer (including also the prepolymer) used in the present invention is further characterized by a porosity, expressed as void percentage, higher than 10% preferably higher than 15%. In addition, the porous polymer is also preferably endowed with a spherical form which is obtainable for example by using the catalyst components mentioned above.

The vanadium compounds are supported on said porous polymer using the conventional techniques. According to one preferred embodiment, the process of supporting comprises:

(a) suspending the porous polymer in a hydrocarbon medium, preferably propane;

(b) contacting the so obtained mixture with a vanadium compound (neat or as hydrocarbon solution);

(c) stirring the mixture and

(d) removing the liquid hydrocarbon medium.

Step (b) is generally carried out working at 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 low a boiling point hydrocarbon medium is preferred since it is then possible to remove it by flashing.

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

The solid components of the invention form catalysts for the polymerization of olefins by reaction with an organoaluminum compound, and optionally, a halogenated organic compound.

As organoaluminum compounds Al-trialkyls and Al-alkyl halides, are preferably used. In particular the organo-Al compound can be selected from the group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum diethylaluminum chloride, ethylaluminum dichloride, alkylaluminum sesquichlorides and their mixtures.

The Al-alkyl compound is used in amounts corresponding to molar ratios of Al/V from 5 to 500, in particular from 5 to 200, preferably from 15 to 100.

Together with the organo-Al compound, a polymerization promoter may be used in order to further increase the productivity and improve the randomization of the comonomers in the polymer chain.

The promoters generally are halogenated organic compounds belonging to different classes. In particular they can be selected from the following groups:

- halohydrocarbons of R^IX type, in which R^I is an alkyl, cycloalkyl, alkenyl, aryl, arylalkyl or alkylaryl group and X is either Cl or F;
- chlorinated esters of formula $R^{II}COOR^I$ where R^{II} is an halogenated alkyl, cycloalkyl, alkenyl, aryl, arylalkyl or alkylaryl group and R^I has the meaning explained above;
- acyl halides of aliphatic or aromatic carboxylic acids.

Usual examples are: $CHCl_3$, $CFCl_3$, CH_2Cl_2, benzoylchloride, benzylchloride, ethyltrichloroacetate, n-butylperchlorocrotonate (nBPCC), hexachlorocyclopentadiene, hexachloropropylene, 1,2-difluorotetrachloroethylene. Preferably with compounds of AlR_3 type $CHCl_3$ is used and with compounds of AlR_2X type nBPCC is used.

Both the organo-Al compound and the promoter can be supported on porous polymers together with the vanadium compound before the polymerization is carried out. In one preferred method this is obtained by first contacting, in the presence of a liquid hydrocarbon medium, the promoter and the vanadium compound with a porous polymer and then in a second step by contacting the product obtained in the first step with a hydrocarbon solution of the organo-Al compound.

As explained above, this catalyst system is particularly suited for the preparation of elastomeric ethylene copolymers by polymerization processes carried out in bulk or in gas-phase. Very surprisingly, particularly when gas-phase processes are carried out, the use of the claimed catalyst components, differently from those based on silica carriers, allows to avoid fouling problems even in the absence of fluidization aids such as carbon black. Furthermore, unlike the supported vanadium based catalyst of the art, the catalyst of the invention keep the polymerization yields at least at the same level as of yields obtained with the corresponding homogeneous vanadium catalysts.

The gas-phase process is generally 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 80°C, preferably between 20 and 50°C. The pressure is generally comprised between 0.5 and 3 MPa and preferably between 1 and 2 MPa. In liquid monomer the process is carried out under pressures comprised between 1 and 5 MPa, preferably between 1.5 and 3 MPa.

The molecular weight of the resulting polymers can be regulated by using molecular weight regulator agents, such as hydrogen or $ZnEt_2$.

The elastomeric copolymers obtainable by the above processes generally contain from 15 to 85%, and preferably from 35 to 75%, by mole of ethylene units, from 15 to 85%, and preferably from 25 to 65%, of units derived from one or more α-olefins CH_2=CHR where R is a C1-C10 alkyl group; and from 0 to 5%, preferably from 0.5 and 2%, of units derived from the copolymerization of one or more polyenes.

The α-olefins which may be used preferably comprise propylene and 1-butene. As polyene units capable of supplying unsaturated units both conjugated or non conjugated polyene can be used.

Among conjugated dienes 1,3-butadiene and isoprene may be used, while 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 (ENB), 5-isopropylidene-2-norbornene, monocyclic diolefins, such as cis,cis-1,5-cyclooctadiene, 5-methyl-1,5-cyclooctadiene, 4,5,8,9-tetrahydroindene.

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

EXAMPLES

Characterization

Comonomer content: percentage by weight of comonomer determined by IR spectroscopy.

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) CD_3 (Carlo Erba) connected to a reservoir of mercury and to a high-vacuum pump ($1 \cdot 10^{-2}$ mbar). 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/cm^2. 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 (cm^3/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 (ΔH in cm) 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/cm^3).

Intrinsic viscosity (IV): determined in tetrahydronaphthalene at 135°C.

Reactor Fouling: ratio between the weight of polymer particles adhering to each other and to the reactor walls and the weight of the total polymer produced.

EXAMPLE 1

A 4. 25 liters stainless steel reactor was used, which was equipped with a magnetic-drive stirrer, pressure gauge, thermocouple, a window on the side wall for a visual inspection of the polymerization bath, catalyst charging system, monomer feed lines and an external jacket for the thermoregulation of the polymerization bath, in which a vapor/cold water mixture was allowed to circulate. The reactor was purged with propene at 70°C for 1 hour. Propene was then flashed and was replaced with propane at room temperature.

50 g of a polypropylene, having I.V.=1,28 (dl/g), an isotacticity index of 92%, a poured density of 0.4 g/cm^3 and a porosity by mercury of 0.175 (cm^3/g), was charged into the reactor through a hole in the ceiling of the reactor, under propane atmosphere, (Pressure 1bar) at room temperature, without any stirring.

250 g of propane were added at room temperature (pressure of about 10 bar was achieved). A solution of 0.43 mmoles of nBPCC and 15 mg of V(Acac)$_3$ in 5 ml of toluene was injected with a nitrogen overpressure. The suspension in the reactor was stirred for 10 minutes at 40°C. Propane was flashed in about 4-5 minutes. Thereafter, in the reactor were added 250 g of propane and a solution of 2,5 mmoles of DEAC in hexane (10% wt/vol.) under a nitrogen overpressure. The suspension in the reactor was stirred for 2 minutes. The liquid in the reactor was flashed, in about 4-5 minutes.

Polymerization

A mixture of 11,5 g of ethylene and 7,5 g of propylene was fed in 3 minutes and, in this period, the temperature was brought to 50 °C.

7 g of an ethylene/propylene mixture (4.9 g of ethylene and 2.1 g of propylene) were fed in 13 minutes, maintaining the temperature at 50°C and obtaining a total pressure of 4 barg. The total pressure was further increased to 15 barg in 5 minutes, feeding a 70/30 (wt/wt) ethylene/propylene mixture. The suspension in the reactor was stirred at 50°C for 2 hours, keeping the pressure constant by continuously feeding the ethylene/propylene mixture.

The reaction was stopped by quickly degassing the monomers. The reactor was brought to room temperature. 94 g of spherical form polymer were recovered having an ethylene content of 24% wt. The intrinsic viscosity was 2.41 (dl/g). The reactor fouling was about 10%.

EXAMPLE 2

The same porous polymer of Example 1 and the same procedure for its loading in the reactor were used. Then, a solution of 1.15 mmoles of nBPCC and 15 mg of V(Acac)$_3$ in 5 ml of toluene was injected with a nitrogen overpressure. The same procedure of Ex. 1 was then followed, except that 6 mmoles of DEAC (10% wt/vol. solution in hexane) were added.

The polymerization procedure was the same as that disclosed in Ex. 1. After the flash of the liquid in the reactor, 49.5 g of ethylene and 33.2 g of propylene were added in 7 minutes, the temperature was brought to 50°C and the pressure to 15 barg. The pressure was kept constant by feeding an ethylene/propylene mixture (70/30 wt/wt) for a period of 35 minutes. In this period, 3 cc of ENB were continuously added dropwise.

The polymerization was stopped by quickly degassing the monomers. 75 g of spherical form polymer were recovered. The reactor fouling was less than 1%. Analysis showed the polymer contained: ethylene 20.8 wt%, ENB 1 wt%.

EXAMPLE 3

The same reactor disclosed in Example 1 was purged with propene at 70°C for 1 hour. Propene was then flashed and was replaced with propane at room temperature.

50 g of a polypropylene, having I.V.=1,49 (dl/g), an isotacticity index of 96.5%, a poured density of 0.35 g/cm^3 and a porosity by mercury of 0.465 (cm^3/g), was charged into the reactor through a hole in the ceiling of the reactor, under propane atmosphere, (Pressure 1bar) at room temperature, without any stirring.

250 g of propane were added at room temperature (pressure of about 10 bar was achieved). A solution of 0.43 mmoles of nBPCC and 15 mg of V(Acac)$_3$ in 5 ml of toluene was injected with a nitrogen overpressure. The suspension in the reactor was stirred for 10 minutes at 40°C. Propane was flashed in about 4-5 minutes. Thereafter, in the reactor were added 250 g

of propane and a solution of 2,5 mmoles of DEAC in hexane (10% wt/vol.) under a nitrogen overpressure. The suspension in the reactor was stirred for 2 minutes. The liquid in the reactor was flashed, in about 4-5 minutes.

Polymerization

A mixture of 9.3g of ethylene and 11.4g of propylene was fed in 3 minutes and, in this period, the temperature was brought to 50 °C.

10g of an ethylene/propylene mixture (7.5 g of ethylene and 2.5 g of propylene) were fed in 10 minutes, maintaining the temperature at 50°C and obtaining a total pressure of 4 barg. The total pressure was further increased to 15 barg in 5 minutes, feeding a 75/25 (wt/wt) ethylene/propylene mixture. The suspension in the reactor was stirred at 50°C for 2 hours, keeping the pressure constant by continuously feeding the ethylene/propylene mixture.

The reaction was stopped by quickly degassing the monomers. The reactor was brought to room temperature. 125g of spherical form polymer were recovered having an ethylene content of 40% wt. The intrinsic viscosity was 3.59 (dl/g). The reactor fouling was about 5%.

COMPARISON EXAMPLE 4

50 g of silica were loaded into the reactor following the same procedure adopted for Examples 1 and 2. The same procedure, reactants and polymerization conditions of Ex. 1 were used. 55 g of solid were recovered. The reactor fouling was about 100%.

CLAIMS

1. A solid catalyst component comprising a vanadium compound supported on a porous polymer having a porosity, due to pores with a radius up to 100.000Å, higher than 0.02 cm^3/g measured by mercury method.

2. A solid catalyst component according to claim 1 in which the vanadium compound is selected form the group consisting of vanadium compounds not containing π-V links.

3. A solid catalyst component according to claim 2 in which the vanadium compound is selected from the group consisting of $V(AcAc)_3$, VCl_4, $VOCl_3$, $VO(OR)_3$, where R is a C1-C8 alkyl group.

4. A solid catalyst component according to claim 3 in which the vanadium compound is $V(AcAc)_3$.

5. A solid catalyst component according to any of the preceding claims 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.

6. A solid catalyst component according to claim 1 in which the porous polymer is a prepolymer produced in a quantity ranging from 0.5 g per g of solid catalyst component up to 2000 g/g.

7. A solid catalyst component according to claim 1 in which the porous polymer has a porosity in the ranging from 0.04 to 2 cm^3/g measured by the mercury method.

8. A solid catalyst component according to claim 1 in which the porous polymer used in the present invention is further characterized by a porosity, expressed as percentage of voids,

of higher than 10%.

9. A solid catalyst component according to claim 8 in which the percentage of voids is higher than 15%.

10. A catalyst for the polymerization of olefins comprising the product of the reaction of (a) a solid component according to any of the preceding claims; (b) an organoaluminum compound, and optionally, (c) a halogenated organic compound.

11. A catalyst according to claim 10 in which the organo-Al compound is selected from the group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum diethylaluminum chloride, ethylaluminum dichloride, alkylaluminum sesquichlorides and their mixtures.

12. A catalyst according to claim 10 in which the halogenated organic compound is selected from the following classes:
    - halohydrocarbons of R^IX type, in which R^I is an alkyl, cycloalkyl, alkenyl, aryl, arylalkyl or alkylaryl group and X is either Cl or F;
    - chlorinated esters of formula R"COOR"' where R" is an halogenated alkyl, cycloalkyl, alkenyl, aryl, arylalkyl or alkylaryl group and R"' has the same meaning of R";
    - acyl halides of aliphatic or aromatic carboxylic acids.

13. A catalyst according to claim 12 in which the halogenated organic compound is selected from the group consisting of: $CHCl_3$, $CFCl_3$, CH_2Cl_2, benzoylchloride, benzylchloride, ethyltrichloroacetate, n-butylperchlorocrotonate (nBPCC), hexachlorocyclopentadiene, hexachloropropylene, 1,2-difluorotetrachloroethylene.

14. A process for the preparation of elastomeric copolymers of ethylene characterized by the fact that it is carried out in the presence of the catalyst according to any of the claims 10

to13.

15. Process according to claim 14 in which said elastomeric copolymers contain from 15 to 85%, by mole of ethylene units, from 15 to 85% of units derived from one or more α-olefins CH_2=CHR where R is a C1-C10 alkyl group; and from 0 to 5%, of units derived from the copolymerization of one or more polyenes.
16. Process according to claim 15 in which said elastomeric copolymers contain from 35 to 75, %, by mole of ethylene units, from 25 to 65%, of units derived from one or more α-olefins CH_2=CHR where R is a C1-C10 alkyl group, and from 0.5 and 3% of units derived from the copolymerization of one or more polyenes.
17. Process according to claims 14-16 in which the α-olefin is selected from the group consisting of propylene and 1-butene.
18. Process according to any of the claims 14-17 characterized in that it is carried out in gas-phase.