Description

The invention relates to the catalytic homopolymerization and copolymerization of ethylene with high activity Mg and Ti containing complex catalysts in a low pressure gas phase fluid bed process to produce polymers having a density of ≥0.94 to ≤0.97 g/cm³, a melt flow ratio of ≥22 to ≤32 and having a relatively round particle shape and a relatively low level of fines.

Ethylene homopolymers having a density of ≥0.96 g/cm³ and a melt index in the range of 5 to 50 g/10 min are useful for injection molding purposes requiring excellent impact strength properties provided that they have a relatively narrow molecular weight distribution. Ethylene polymers having a density of ≥0.96 g/cm³ and a melt index of ≤20 g/cm³ can be made with the catalysts and low pressure gas phase processes described in US—A—3,023,203, 4,003,712 and 3,709,853. The polymers made with the supported chromium oxide, silylchromate and chromocene catalysts, however, have a relatively broad molecular weight distribution as evidenced by melt flow ratio values of ≥35. The polymers of these patents, therefore, have relatively limited use for injection molding applications requiring excellent impact strength properties. It is desirable therefore, to provide catalysts which would enable one to readily prepare, in a gas phase process, ethylene polymers which have a relatively narrow molecular weight distribution.

To be commercially useful in a gas phase process, such as the fluid bed process of US—A—3,709,853, 4,003,712 and 4,011,382, and CA—A—991,798 and BE—A—839,380, the catalyst employed must be a high activity catalyst, that is, it must have a level of productivity of ≥50,000, preferably ≥100,000, kg per polymer per kg of primary metal in the catalyst. This is so because such gas phase processes usually do not employ any catalyst residue removing procedures. Thus, the catalyst residue in the polymer mus be so small that it can be left in the polymer without causing any undue problems in the hands of the resin fabricator and/or ultimate consumer. Low catalyst residue contents are also important where the catalyst is made with chlorine containing materials such as the titanium, magnesium and/or aluminum chlorides used in some so-called Ziegler or Ziegler-Natta catalysts. High residual chlorine values in a molding resin will cause pitting and corrosion on the metal surfaces of the molding devices. Cl residues of the order of ≥200 ppm are not commercially useful.

US—A—3,989,881 discloses the use of a high activity catalyst for the manufacture, under slurry polymerization conditions, of ethylene polymers having a relatively narrow molecular weight distribution (Mw/Mn) of about 2.7 to 3.1. Attempts were made to use catalysts similar to those described in US—A—3,989,881 for the purpose of making polyethylene of narrow molecular weight distribution by polymerizing ethylene alone or with propylene in the gas phase in a fluid bed process using apparatus and conditions similar to those employed in US—A—4,011,382 and BE—A—839,380. These attempts were not successful. In order to avoid the use of the solvents in the slurried catalyst systems of US—A—3,989,881, the Ti/Mg containing components were dried. However, the dried material, a viscous, gummy, pyrophoric composition, could not be readily fed to the reactor because it was not in a free flowing form. Even when blended with silica to improve its free-flowing properties and then added to the reactor the results were commercially unacceptable. The productivity of the catalyst was poor, or the catalyst was pyrophoric and difficult to handle and the polymer product was produced in the form of needle-shaped products which were difficult to fluidize and which exhibited very poor flow properties.

US—A—3,922,322 and 4,035,560 disclose the use of several Ti and Mg containing catalysts for the manufacture of granular ethylene polymers in a gas phase fluid bed process under a pressure ≤69 bar (≤1000 psi). The use of these catalysts in these processes, however, has significant disadvantages. The catalysts of US—A—3,922,322 provide polymers having a very high catalyst residue content, i.e., about 100 ppm of Ti and greater than about 300 ppm Cl, according to the working example of this patent. Further, as disclosed in the working example of US—A—3,922,322, the catalyst is used in the form of a prepolymer, and very high volumes of the catalyst composition must be fed to the reactor relative to the volume of polymer made in the reactor. The preparation and use of this catalyst thus requires the use of relatively large sized equipment for the manufacture, storage and transporting of the catalyst.

The catalysts of US—A—4,035,560 also apparently provide polymers having high catalyst residues, and the catalysts compositions are apparently pyrophoric because of the types and amounts of reducing agents employed in such catalysts.

US—A—4,124,532 discloses the polymerization of ethylene and propylene with high activity catalysts. These catalysts comprise complexes which may contain magnesium and titanium. These complexes are prepared by reacting the halide MX_2 (where M may be Mg) with a compound M'Y (where M' may be Ti and Y is halogen or an organic radical) in an electron donor compound. These complexes are then isolated by either crystallization, by evaporation of the solvent or by precipitation.

Polymerization is carried out with these catalytic complexes and an alkyl aluminum compound.

However, US—A—4,124,532 does not disclose any special techniques or methods of preparing the catalyst in order to achieve the desirable results described in the present invention. The use of the catalysts described in US—A—4,124,532, without these special methods, would not lead to a commercial fluid bed process to produce polyethylenes at commercial rates. In addition the examples in the gas phase do not describe a practical process of copolymerization to produce copolymers with attractive polymer morphology described in the present invention.

EPC—Application 79 100 958.2 discloses that ethylene copolymers, having a density of ≥0.91 to ≤0.94 g/cm³ and a melt flow ratio of ≥22 to ≤32 and which have a relatively low residual catalyst content and a relatively high bulk density and which provide films of good clarity can be produced at relatively high productivities for commercial purposes by a gas phase fluid bed process if the ethylene is copolymerized with one or more C_3 to C_6 α-olefins in the presence of a high activity magnesium-titanium containing complex catalyst prepared under specific activation conditions with an organoaluminum compound and impregnated in a porous inert carrier material.

In the catalyst activation procedure the activation is conducted in at least two stages. In the first stage the precursor composition, impregnated in the silica, is reacted with, and partially activated by, enough activator compound so as to provide a partially activated precursor composition which has an activator compound/Ti molar ratio of >0 to <10:1 and preferably of 4 to 8:1. In order to render the partially activated and impregnated precursor composition active for ethylene polymerization purposes, additional activator compound must also be added to the polymerization reactor to complete, in the reactor, the activation of the precursor composition. The additional activator compound and the partially activated impregnated precursor composition are preferably fed to the reactor through separate feed lines. The additional activator compound may be sprayed into the reactor in the form of a solution thereof in a hydrocarbon solvent such as isopentane, hexane, or mineral oil. This solution usually contains 2 to 30 weight percent of the activator compound.

When the impregnated catalyst of EPC Application 79 100 958.2 was evaluated for the preparation of high density (≥0.94 g/cm³) products at elevated temperatures it was found that the performance of these catalysts was highly dependent on the amount of electron donor $[ED]_q$ in the impregnated precursor composition. Investigations have shown that the level of electron donor in the impregnated precursor can be controlled to some extent by the drying process but it is difficult to control this drying in such a way as to prepare reproducible precursor with precisely the desired level of electron donor.

EPC Application 79 100 957.4 discloses that ethylene homopolymers having a density range of 0.96 to 0.97 g/cm³ and a melt flow ratio of ≥22 to ≤32 and which have a relatively low residual catalyst residue can be produced at relatively high productivities for commercial purposes by a low pressure gas phase fluid bed process if the ethylene is homopolymerized in the presence of a high activity magnesium-titanium complex catalyst blended with an inert carrier material. Although these catalysts have high activity, the polymers produced with this blended catalyst have the disadvantage that the polymer particles formed during the fluid bed polymerization process are irregular in shape and are somewhat difficult to fluidize. Also, the final product contains a relatively high level of fines, i.e., particles having a particle size of ≤125 µm.

It has now been unexpectedly found that ethylene homopolymers and copolymers having a density range of ≥0.94 to ≤0.97 g/cm³ and a melt flow ratio of ≥22 to ≤32 can be produced at relatively high productivities at a relatively high bulk density, with relatively low level of fines and with a relatively round particle shape. These polymers can be produced commercially by a low pressure gas phase fluid bed process if the ethylene is homopolymerized or copolymerized in the presence of a high activity magnesium-titanium complex catalyst, and impregnated in selected amounts in a porous inert carrier material and activated under specific conditions, as is described below.

An object of the present invention is to provide a process for producing, at relatively high productivities and in a low pressure gas phase fluid bed process, ethylene homopolymers and copolymers which have a density of ≥0.94 to ≤0.97 g/cm³, a melt flow ratio of ≥22 to ≤32, a relatively low residual catalyst content and a bulk density of 0.3 to 0.5 g/cm³ (21 to 32 pounds per cubic foot).

Another object of the present invention is to provide granular ethylene polymers which have a particle shape which is round and wherein the final polymer product contains a relatively low level of fines (particles ≤125 µm).

The present invention provides a process for polymerizing ethylene employing a catalyst composition prepared by forming a precursor composition from a magnesium compound, titanium compound and electron donor compound, and then activating the precursor composition with an organoaluminum compound to form the catalyst, which is characterized in that the polymerization is conducted continuously in a fluid bed reactor at a temperature of 30 to 115°C under a pressure of <69 bar (<1000 psi) in the gas phase to produce ethylene homopolymers or ethylene copolymers containing ≥97 mol percent of ethylene and ≤3 mol percent of one or more C_3 to C_8 alpha olefins at a productivity of ≥50,000 kg of polymer per kg of Ti, said polymer being produced in a granular form and having a density of ≥0.94 to ≤0.97 g/cm³ and a melt flow ratio of ≥22 to ≤32, by contacting ethylene, or a mixture of ethylene and at least one C_3 to C_8 alpha olefin, optionally in the presence of hydrogen, with particles of an activated precursor composition having the formula

$$Mg_mTi(OR)_nX_p[ED]_q$$

wherein R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof,

ED is a liquid organic electron donor compound in which said precursor composition and the Ti and

Mg component thereof are soluble or partially soluble and which is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones,

m is ≥0.5 to ≤56,
n is 0, 1 or 2,
p is ≥2 to ≤116, and
q is >1.5 m+2

said precursor composition being impregnated into an inert porous carrier in a weight ratio of 0.033 to 1, being activated with an activator having the formula

$$Al(R'')_cX'_dH_e$$

wherein X' is Cl or OR''', R'' and R''' are the same or different, and are C_1 to C_{14} saturated hydrocarbon radicals, d is 0 to 1.5, e is 1 or 0 and c+d+e=3, activation of said precursor composition being effected by treating the impregnated precursor composition outside the polymerization reactor in a hydrocarbon slurry with >0 to <10 mols of activator compound per mol of titanium compound in said precursor composition, drying the mixture to obtain a free-flowing solid particulate material, and feeding the impregnated precursor composition into the polymerization reactor wherein it is further activated by adding additional activator compound to the reactor in such amounts as to provide ≥10 mols up to a total of ≤400 mols of activator compound per mol of titanium compound in said precursor composition.

The obtained homopolymers and copolymers have high bulk density values and can be readily produced with relatively high productivities. The catalysts used in the claimed process are highly active and improve polymer particle morphology of the resulting polymers (including a relatively low level of fines).

The ethylene polymers obtained according to the invention have a melt flow ratio of ≥22 to ≤32, and preferably of ≥25 to ≤30. The melt flow ratio value is another means of indicating the molecular weight distribution of a polymer. The melt flow ratioe (MFR) range of ≥22 to ≤32 thus corresponds to a Mw/Mn value range of 2.7 to 4.1 and the MFR range of ≥25 to ≤30 corresponds to a Mw/Mn range of 2.8 to 3.6.

The copolymers which may be prepared in the process of the present invention are copolymers of a major mol percent (≥97%) of ethylene, and a minor mol percent (≤3%) of one (copolymer) or more (ter-, tetra-polymers) C_3 to C_8 α-olefins. The C_3 to C_8 α-olefins should not contain any branching on any of their carbon atoms which is closer than the fourth carbon atom. These α-olefins include propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1 and octene-1. The preferred alpha olefins are propylene, butene-1, hexene-1, 4-methylpentene-1 and octene-1.

The ethylene polymers have a density of ≥0.94 to ≤0.97 g/cm³. The density of the copolymer, at a given melt index level of the copolymer, is primarily regulated by the amount of the C_3 to C_8 comonomer which is copolymerized with the ethylene. In the absence of the comonomer, the ethylene would homopolymerize with the catalyst of the present invention to provide homopolymers having a density of about ≥0.96 g/cm³. Thus, the addition of progressively larger amounts of the comonomers to the copolymers results in a progressive lowering of the density of the copolymer. The amount of each of the various C_3 to C_8 comonomers needed to achieve the same result will vary from comonomer to comonomer, under the same conditions.

Thus, to achieve the same results, in the copolymers, in terms of a given density, at a given melt index level, larger molar amounts of the different comonomers would be needed in the order of $C_3>C_4>C_5>C_6>C_7>C_8$.

The melt index of a homopolymer or a copolymer is a reflection of its molecular weight. Polymers having a relatively high molecular weight, have a relatively low melt index. Ultra-high molecular weight ethylene polymers hve a high load (HLMI) melt index of about 0.0 and very high molecular weight ethylene polymers have a high load melt index (HLMI) of about 0.0 to 1.0. Such high molecular weight polymers are difficult, if not impossible to mold in conventional injection molding equipment. The polymers made in the process of the present invention, on the other hand, can be readily molded, in such equipment. They have a standard or normal load melt index of ≥0.0 to 100, and preferably of 0.5 to 80, and a high load melt index (HLMI) of 11 to 2000. The melt index of the polymers which are made in the process of the present invention is a function of a combination of the polymerization temperature of the reaction, the density of the copolymer and the hydrogen/monomer ratio in the reaction system. Thus, the melt index is raised by increasing the polymerization temperature and/or by decreasing the density of the polymer and/or by increasing the hydrogen/monomer ratio. In addition to hydrogen other chain transfer agents such as dialkyl zinc compounds may also be used to further increase the melt index of the polymers.

The polymers obtained according to the present invention have an unsaturated group content of ≤1, and usually ≥0.1 to ≤0.3, C=C/1000 carbon atoms, and a cyclohexane extractables content of less than 3, and preferably less than 2, weight percent.

The polymers obtained according to the present invention have a residual catalyst content, in terms of parts per million of titanium metal, of less than 20 parts per million (ppm) at a productivity level of ≥50,000 kg of polymer per kg of titanium. In terms of Cl, Br or I residues, the polymers obtained according to the present invention typically have a residue content of less than 140 ppm at a productivity of ≥50,000 kg of polymer per kg of titanium.

The polymers obtained according to the present invention are granular materials which have an average particle size of the order of 0.5 to 1.25 mm (0.02 to 0.05 inches), and preferably 0.5 to 1.0 mm (0.02 to 0.4 inches) in diameter. The particle size is important for the purpose of readily fluidizing the polymer particles in the fluid bed reactor, as described below. These granular materials also have a low level of fines (≤4.0 percent of the total polymer product) and these fines are ≤125 µm. Also, these granular materials exhibit a much more spherical shape (as observed by optical microscopy) than the granular materials described in the above mentioned EPC Application 79 100 957.4.

The polymers of the present invention have a bulk density of 0.3 to 0.5 g/cm^3 (21 to 32 pounds per cubic foot).

The compounds used to from the high activity catalyst used in the present invention comprise at least one titanium compound, at least one magnesium compound, at least one electron donor compound, at least one activator compound and at least one inert carrier material, as defined below.

The titanium compound has the structure

$$Ti(OR)_aX_b$$

wherein

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' where R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof,

a is 0, 1 or 2, b is 1 to 4 inclusive and a+b=3 or 4,

R and R' are preferably C_{1-6} alkyl or C_{6-10} aryl; e.g. methyl, ethyl, propyl, i-propyl, butyl, i-butyl, pentyl, hexyl, phenyl, tolyl, xylyl, ethylphenyl, naphthyl.

The titanium compounds can be used individually or in combinations thereof, and would include $TiCl_3$, $TiCl_4$, $Ti(OC_6H_5)Cl_3$, $Ti(OCOCH_3)Cl_3$ and $Ti(OCOC_6H_5)Cl_3$.

The magnesium compound has the structure

$$MgX_2$$

wherein X is selected from the group consisting of Cl, Br, I, or mixtures thereof. Such magnesium compounds can be used individually or in combination thereof and would include $MgCl_2$, $MgBr_2$ and MgI_2. Anhydrous $MgCl_2$ is the particularly preferred magnesium compound.

From ≥0.5 to ≤56, and preferably from 1 to 10 moles of the magnesium compound are used per mol of the titanium compound in preparing the catalyst employed in the present invention.

The titanium compound and the magnesium compound should be used in a form which will facilitate their dissolution in the electron donor compound, as described herein below.

The electron donor compound is an organic compound which is liquid at 25°C and in which the titanium compound and the magnesium compound are partially or completely soluble. The electron donor compounds are known, as such or as Lewis bases.

The electron donor compounds are alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones. Among these electron donor compounds the preferable ones are alkyl esters of C_1 to C_4 saturated aliphatic carboxylic acids; alkyl esters of C_7 to C_8 aromatic carboxylic acids; C_2 to C_8, and most preferably C_3 to C_4, aliphatic ethers; C_3 to C_4 cyclic ethers, and most preferably C_4 cyclic mono- or di-ethers; C_3 to C_6, and most preferably C_3 to C_4, aliphatic ketones. The most preferred of these electron donor compounds would include methyl formate, ethyl acetate, butyl acetate, ethyl ether, hexyl ether, tetrahydrofuran, dioxane, acetone and methyl isobutyl ketone.

The electron donors can be used individually or in combinations thereof.

The level of the electron donor $[ED]_q$ in the precursor composition of the present invention has a value of q is >1.5 m+2 and therefore requires partial activation as a critical step in the formation of a highly active catalyst which produces polymers with attractive particle morphology.

The activator compound has the structure

$$Al(R'')_cX_d'H_e$$

where

X' is Cl or OR''', R'' and R''' are the same or different and are C_1 to C_{14} saturated hydrocarbon radicals,

d is 0 to 1.5, e is 1 or 0 and c+d+e=3,

R'' and R''' are e.g. saturated aliphatic C_{1-14} residues or saturated cycloaliphatic residues with preferably 5—10 carbon atoms such as cyclopentyl, cyclohexyl, cycloheptyl, methylcyclohexyl.

Such activator compounds can be used individually or in combinations thereof and would include $Al(C_2H_5)_3$, $Al(C_2H_5)Cl$, $Al(i\text{-}C_4H_9)_3$, $Al_2(C_2H_5)_3Cl_3$, $Al(i\text{-}C_4H_9)_2H$, $Al(C_6H_{13})_3$, $Al(C_8H_{17})_3$, $Al(C_2H_5)_2H$ and $Al(C_2H_5)_2(OC_2H_5)$.

From 10 to 400, and preferably from 15 to 60, mols of the activator compound are used per mol of the titanium compound in activating the precursor composition employed in the present invention.

The carrier materials used in the present invention are solid, particulate porous materials which are

inert to the other components of the catalyst composition, and to the other active components of the reaction system. These carrier materials would include inorganic materials such as oxides of silicon and/or aluminum. The carrier materials are used in the form of dry powders having an average particle size of 10 to 250, and preferably of 50 to 150 µm. These materials are also porous and have a surface area of ≥3, and preferably of ≥50, square meters per gram. Catalyst activity or productivity is apparently also improved with silica having pore sizes of ≥8 nm and preferably of ≥10 nm. The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material is carried out by heating it at a temperature of ≥600°C. Alternatively, the carrier material dried at a temperature of ≥200°C may be treated with about 1 to 8 weight percent of one or more of the aluminum alkyl compounds described above. This modification of the carrier material by the aluminum alkyl compounds provides the catalyst composition with increased activity and also improves polymer particle morphology of the resulting ethylene polymers.

The catalyst used in the present invention is prepared by first preparing a precursor composition from the titanium compound, the magnesium compound, and the electron donor compound, as described below, and then impregnating the carrier material with the precursor composition and treating the impregnated precursor composition with the activator compound as described below.

The precursor composition is formed by dissolving the titanium compound and the magnesium compound in the electron donor compound at a temperature of 20°C up to the boiling point of the electron donor compound. The titanium compound can be added to the electron donor compound before or after the addition of the magnesium compound, or concurrent therewith. The dissolution of the titanium compound and the magnesium compound can be facilitated by stirring, and in some instances by refluxing these two compounds in the electron donor compound. After the titanium compound and the magnesium compound are dissolved, the precursor composition may be isolated by crystallization or by precipitation with a C_5 to C_8 aliphatic or aromatic hydrocarbon such as hexane, isopentane or benzene.

The crystallized or precipitated precursor composition may be isolated, in the form of fine, free flowing particles having an average particle size of 10 to 100 µm and a settled bulk density of 0.3 to 0.5 g/cm^3 (18 to 33 pounds per cubic foot).

The precursor composition is then impregnated, in a weight ratio of 0.033 to 1, and preferably 0.1 to 0.43, parts of the precursor composition into one part by weight of the carrier material.

The impregnation of the dried (activated) carrier with the precursor composition may be accomplished by dissolving the precursor composition in the electron donor compound, and by then admixing the carrier with the dissolved precursor composition so as to allow the precursor composition to impregnate the carrier. The solvent is then removed by drying at temperatures of ≤70°C.

The carrier may also be impregnated with the precursor composition by adding the carrier to a solution of the chemical raw materials used to form the precursor composition in the electron donor compound, without isolating the precursor composition from said solution. This represents the preferred method because of its simplicity. Most of the excess electron donor compound is then removed by drying at temperature of ≤70°C.

Experience has shown that drying of the impregnated precursor frequently leads to concentrations of the electron donor $[ED]_q$ such that q is >1.5 m+2. It is expeditious in routine production of impregnated precursor to permit some excess (q is >1.5 m+2) electron donor to remain in the impregnated composition rather than risk overdrying and hence thermal decomposition of the precursor.

When thus made as disclosed above the precursor composition so impregnated has the formula

$$Mg_mTi(OR)_nX_p[ED]_q$$

wherein

ED is the electron donor compound,

m is ≥0.5 to ≤56, and preferably ≥1.5 to ≤5,

n is 0, 1 or 2,

p is ≥2 to ≤116, and preferably ≥6 to ≤14,

q is >1.5 m+2

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical and,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof.

In order to be used in the process of the present invention the precursor composition must be completely activated by treatment with sufficient activator compound to transform the Ti atoms in the precursor composition to an active state.

In the catalyst activation procedure of the present invention the activation is conducted in two stages. In the first stage the precursor composition, impregnated in e.g. silica, is first partially activated outside the polymerization reactor by treating it with >0 to <10 mols of activator compound per mol of titanium compound in said precursor composition. This partial activation reaction is carried out in a hydrocarbon solvent slurry followed by drying of the resulting mixture, to remove the solvent, at temperatures between 20 and 70, and preferably of 50 to 70°C. The resulting product is a free-flowing solid particulate material which can be readily fed to the polymerization reactor. The partially activated, impregnated precursor composition, however, is at best, weakly active, as a polymerization catalyst in the process of the present

invention. In order to render the partially activated, impregnated precursor composition active for ethylene polymerization purposes, additional activator compound must also be added to the polymerization reactor to complete, in the reactor, the activation of the precursor composition. The additional activator compound and the partially activated impregnated precursor composition are preferably fed to the reactor through separate feed lines. The additional activator compound may be sprayed into the reactor in the form of a solution thereof in a hydrocarbon solvent such as isopentane, hexane, or mineral oil. This solution usually co[illegible] 2 to 30 weight percent of the activator compound. The additional activator compound is added to th[illegible]n such amounts as to provide, in the reactor, with the amounts of activator compound and tita[illegible]mpound fed with the partially activated and impregnated precursor composition, from ≥10 to ≤40 total mols of activator compound per mol of titanium compound in said precursor composition, preferably from 15 to 60 total mols of activator compound per mol of titanium compound in said precursor composition. The additional amounts of activator compound added to the reactor, react with, and complete the activation of the precursor composition in the reactor.

In the continuous fluid bed process disclosed below, discrete portions of the partially activated precursor composition impregnated on the carrier are continuously fed to the reactor, with discrete portions of any additional activator compound needed to complete the activation of the partially activated precursor composition, during the continuing polymerization process in order to replace active catalyst sites that are expended during the course of the reaction.

The drawing shows a gas phase fluid bed reactor system for carrying out the process of the present invention.

The polymerization reaction is conducted by contacting a stream of the monomer(s), in the fluid bed process described below, and substantially in the absence of catalyst poisons such as moisture, oxygen, carbon monoxide, carbon dioxide and acetylene, with a catalytically effective amount of the completely activated precursor composition (the catalyst) impregnated on a carrier at a temperature and at a pressure sufficient to initiate the polymerization reaction.

A fluidized bed reaction system which can be used in the practice of the process of the present invention is illustrated in Figure 1. With reference thereto the reactor 10 consists of a reaction zone 12 and a velocity reduction zone 14.

The reaction zone 12 comprises a bed of growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components in the form of make-up feed and recycle gas through the reaction zone. To maintain a viable fluidized bed, the mass gas flow rate through the bed must be above the minimum flow required for fluidization, and preferably from 1.5 to 10 times G_{mf} and more preferably from 3 to 6 times G_{mf}. G_{mf} is used in the accepted form as the abbreviation for the minimum mass gas flow required to achieve fluidization, C. Y. Wen and Y. H. Yu, "Mechanics of Fluidization", Chemical Engineering Progress Symposium Series, Vol. 62, p. 110—111 (1966).

It is essential that the bed always contains particles to prevent the formation of localized "hot spots" and to entrap and distribute the particulate catalyst throughout the reaction zone. On start up, the reactor is usually charged with a base of particulate polymer particles before gas flow is initiated. Such particles may be identical in nature to the polymer to be formed or different therefrom. When different, they are withdrawn with the desired formed polymer particles as the first product. Eventually, a fluidized bed of the desired polymer particles supplants the start-up bed.

The partially activated impregnated precursor composition used in the fluidized bed is preferably stored for service in a reservoir 32 under a blanket of a gas which is inert to the stored material, such as nitrogen or argon.

Fluidization is achieved by a high rate of gas recycle to and through the bed, typically in the order of 50 times the rate of feed of make-up gas. The fluidized bed has the general appearance of a dense mass of viable particles in possible free-vortex flow as created by the percolation of gas through the bed. The pressure drop through the bed is equal to or slightly greater than the mass of the bed divided by the cross-sectional area. It is thus dependent on the geometry of the reactor.

Make-up gas is fed to the bed at a rate equal to the rate at which particulate polymer product is withdrawn. The composition of the make-up gas is determined by a gas analyzer 16 positioned above the bed. The gas analyzer determines the composition of the gas being recycled and the composition of the make-up gas is adjusted accordingly to maintain an essentially steady state gaseous composition within the reaction zone.

To insure complete fluidization, the recycle gas and, where desired, part of the make-up gas are returned to the reactor at point 18 below the bed. There exists a gas distribution plate 20 above the point of return to aid fluidizing the bed.

The portion of the gas stream which does not react in the bed constitutes the recycle gas which is removed from the polymerization zone, preferably by passing it into a velocity reduction zone 14 above the bed where entrained particles are given an opportunity to drop back into the bed. Particle return may be aided by a cyclone 22 which may be part of the velocity reduction zone or exterior thereto. Where desired, the recycle gas may then be passed through a filter 24 designed to remove small particles at high gas flow rates to prevent dust from contacting heat transfer surfaces and compressor blades.

The recycle gas is then compressed in a compressor 25 and then passed through a heat exchanger 26

wherein it is stripped of heat of reaction before it is returned to the bed. By constantly removing heat of reaction, no noticeable temperature gradient appears to exist within the upper portion of the bed. A temperature gradient will exist in the bottom of the bed in a layer of 15 to 30 cm (6 to 12 inches), between the temperature of the inlet gas and the temperature of the remainder of the bed. Thus, it has been observed that the bed acts to almost immediately adjust the temperature of the recycle gas above this bottom layer of the bed zone to make it conform to the temperature of the remainder of the bed thereby maintaining itself at an essentially constant temperature under steady conditions. The recycle is then returned to the reactor at its base 18 and to the fluidized bed through distribution plate 20. The compressor can also be placed upstream of the heat exchanger 26.

The distribution plate 20 plays an important role in the operation of the reactor. The fluidized bed contains growing and formed particulate polymer particles as well as catalyst particles. As the polymer particles are hot and possibly active, they must be prevented from settling for if a quiescent mass is allowed to exist, any active catalyst contained therein may continue to react and cause fusion. Diffusing recycle gas through the bed at a rate sufficient to maintain fluidization at the base of the bed is, therefore, important. The distribution plate 20 serves this purpose and may be a screen, slotted plate, perforated plate, a plate of the bubble cap type and the like. The elements of the plate may all be stationary, or the plate may be of the mobile type disclosed in US—A—3,298,792. Whatever its design, it must diffuse the recycle gas through the particles at the base of the bed to keep them in a fluidized condition, and also serve to support a quiescent bed or resin particles when the reactor is not in operation. The mobile elements of the plate may be used to dislodge any polymer particles entrapped in or on the plate.

Hydrogen may be used as a chain transfer agent in the polymerization reaction of the present invention. The ratio of hydrogen/ethylene employed will vary between 0 to 2.0 moles of hydrogen per mole of the monomer in the gas stream.

Any gas inert to the catalyst and reactants can also be present in the gas stream. The activator compound is preferably added to the gas recycle system at the hottest portion thereof. Addition into the recycle line, therefore, downstream from the heat exchanger is preferred, as from dispenser 27 thru line 27A.

Compounds of the structure $Zn(R_a)(R_b)$, wherein R_a and R_b are the same or different C_1 to C_{14} aliphatic or aromatic hydrocarbon radicals, may be used in conjunction with hydrogen, with the catalysts of the present invention as molecular weight control or chain transfer agents, that is, to increase the melt index values of the copolymers that are produced. From 0 to 50, and preferably from 20 to 30 moles of the Zn compound would be used in the gas stream in the reactor per mol of titanium compound in the reactor. The zinc compound would be introduced into the reactor preferably in the form of a dilute solution (2 to 10 weight percent) in a hydrocarbon solvent or absorbed on a solid carrier material, such as silica, in amounts of from 10 to 50 weight percent. These compositions tend to be pyrophoric. The zinc compound may be added into the recycle gas stream from a feeder adjacent to feeder 27.

It is essential to operate the fluid bed reactor at a temperature below the sintering temperature of the polymer particles. To insure that sintering will not occur, operating temperatures below the sintering temperature are desired. For the production of ethylene polymers in the process of the present invention an operating temperature of from 90 to 105°C is preferably used to prepare products having a density of from 0.94 to 0.97 g/cm^3.

The fluid bed reactor is operated at pressures of up to 69 bar (1000 psi), and is preferably operated at a pressure of from 10.3 to 24 bar (150 to 350 psi), with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

The partially activated impregnated precursor composition is injected into the bed at a rate equal to its consumption at a point 30 which is above the distribution plate 20. A gas which is inert to the partially activated impregnated precursor composition such as nitrogen or argon is used to carry the composition into the bed. Injecting the partially activated precursor composition, at a point above the distribution plate is an important feature of this invention. Since the catalysts formed from the impregnated precursor composition used in the practice of the invention are highly active, injection into the area below the distribution plate may cause polymerization to begin there and eventually cause plugging of the distribution plate. Injection into the viable bed, instead, aids in distributing the catalyst throughout the bed and tends to preclude the formation of localized spots of high catalyst concentration which may result in the formation of "hot spots".

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product. Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas velocity.

The particulate polymer product is preferably continuously withdrawn at a point 34 at or close to the distribution plate 20 and in suspension with a portion of the gas stream which is vented before the particles settle to preclude further polymerization and sintering when the particles reach the ultimate collection zone. The suspending gas may also be used, as mentioned above, to drive the product of the reactor to another reactor.

The particulate polymer product is conveniently and preferably withdrawn through the sequential operation of a pair of timed valves 36 and 38 defining a segregation zone 40. While valve 38 is closed, valve 36 is opened to emit a plug of gas and product to the zone 40 between it and valve 36 which is then closed. Valve 38 is then opened to deliver the product to an external recovery zone. Valve 38 is then closed to await the next product recovery operation.

Finally, the fluidized bed reactor is equipped with an adequate venting system to allow venting the bed during start up and shut down. The reactor does not require the use of stirring means and/or wall scraping means.

The highly active impregnated catalyst system of this invention appears to yield a fluid bed product having an average particle size between 0.5 to 1.25 mm (0.02 to 0.05) inches and preferably 0.5 to 1.0 mm (0.02 to 0.04 inches) wherein catalyst residue is unusually low. The polymer particles have a relatively round particle shape and a relatively low level of fines (<125 μm) i.e., ≤4 percent by weight.

The feed stream of gaseous monomer, with or without inert gaseous diluents, is fed into the reactor to achieve a space time yield of 32 to 160 kg/h/m^3 (2 to 10 pounds/hour/cubic foot) of bed volume.

The polymer directly recovered from the polymerization reactor is in granular form ("Virgin" polymer).

The following Examples are designed to illustrate the process of the present invention and are not intended as a limitation upon the scope thereof.

The properties of the polymers produced in the Examples were determined by the following test methods:

Density	ASTM D-1505—A plaque is made and conditioned for one hour at 120°C to approach equilibirum crystallinity and is then quickly cooled to room temperature. Measurement for density is then made in a density gradient column.
Melt Index (MI)	ASTM D-1238—Condition E—Measured at 190°C—reported as grams per 10 minutes.
Flow Rate (HLMI)	ASTM D-1238—Condition F—Measured at 10 times the weight used in the melt index test above.

$$\text{Melt Flow Ratio (MFR)} = \frac{\text{Flow Rate}}{\text{Melt Index}}$$

Productivity	A sample of the resin product is ashed, and the weight percent of ash is determined; since the ash is essentially composed of the catalyst the productivity is thus the kg of polymer produced per kg of total catalyst consumed. The amounts of Ti, Mg and Cl in the ash are determined by elemental analysis.
Bulk Density	The resin is poured via 9,5 mm (3,8") diameter funnel into a 100 ml graduated cylinder to 100 ml line without shaking the cylinder, and weighed by difference.
Average Particle Size	This is calculated from sieve analysis date measured according to ASTM-D-1921 Method A using a 500 g sample. Calculations are based on weight fractions retained on the screens.

Preparation of catalyst

1. Preparation of impregnated precursor

In a 380 l (100 gallon) glass lined autoclave equipped with a mechanical stirrer are placed 6.0 kg (62.83 mol) anhydrous $MgCl_2$ and 195 kg tetrahydrofuran (THF). To this mixture, 3.554 kg (18.73 mol) $TiCl_4$ is added over ½ hour. The mixture is heated to 60°C for about ½ hour in order to completely dissolve the material. To this mixture is added 45 kg of porous silica, dehydrated at 800°C and treated with triethyl aluminum to give 8 wt. % loading of triethyl aluminum. The mixture is stirred for ½ hour. The excess solvent is decanted and the solids are drained on a Sparkler filter. The resulting sludge is dried in a rotary dryer under 20 mbar vacuum with a slow N_2 purge at ≤65°C for about 16 hours to provide a dry, free-flowing solid. The impregnated precursor composition has the formula:

$$TiMg_{2.9}Cl_{9.8}(THF)_{9.3}.$$

In this formula the value of q, calculated according to the formula $q \geq 1.5\ m+2$, is 6.4 which is significantly lower than the 9.3 value experimentally determined.

II. Activation procedure

The desired weights of the impregnated precursor composition and activator compound are added to a mixing tank with sufficient amounts of anhydrous aliphatic hydrocarbon diluent such as isopentane to provide a slurry system.

The activator compound and precursor compound are used in such amounts as to provide a partially activated precursor composition which has an Al/Ti ratio of >0 to <10:1.

The contents of the slurry system are then thoroughly mixed at room temperature and at atmospheric

pressure for about ¼ to ½ hour. The resulting slurry is then dried under a purge of dry inert gas such as nitrogen or argon, at atmospheric pressure and at a temperature of 65±10°C to remove the hydrocarbon diluent. The resulting catalyst is in the form of a partially activated precursor composition which is impregnated within the pores of the silica. The material is a free-flowing particulate material having the size and shape of the silica. It is not pyrophoric unless the aluminum alkyl content exceeds a loading of 10 weight percent. It is stored under a dry inert gas such as nitrogen or argon prior to future use. It is now ready for use by being injected into, and fully activated within, the polymerization reactor.

After completing the activation of the precursor composition, the additional activator compound is fed to the polymerization reactor as a dilute solution in a hydrocarbon solvent such as isopentane. These dilute solutions contain 5 to 30% by volume of the activator compound.

The activator compound is added to the polymerization reactor so as to maintain the Al/Ti ratio in the reactor at a total level of ≥10 to 400:1 and preferably of 15 to 60:1.

Examples 1 to 7

Ethylene was homopolymerized (Examples 1 to 3 and 5 to 7) and copolymerized with butene-1 (Example 4) in these series of examples.

In Examples 1 and 2 the catalyst used was formed as described above except that the partial activation procedure was not used but rather total activation of the precursor composition was accomplished in the polymerization reactor with triethyl aluminum in a five weight percent isopentane solution so as to provide the activated catalyst in the reactor with an Al/Ti mol ratio of 15—40.

In Examples 3 to 7, the impregnated precursor composition was partially activated (see activation procedure above) in a mix tank with the aluminum compound as shown in Tables I to III to provide an Al/Ti ratio as shown in Tables I to III. The completion of the activation of the precursor composition in the polymerization reactor was accomplished with triethyl aluminum in a five weight percent isopentane solution so as to provide the activated catalyst in the reactor with an Al/Ti mol ratio of 15—40.

Each of the polymerization reactions was continuously conducted for >1 hour after equilibrium was reached at 103—105°C and under a pressure of 22 bar (300 psig) with H_2/C_2 mol ratio of 0.35—0.50 and a gas velocity of 3 to 4 times G_{mf} in a fluid bed reactor system at a space time yield of 48 to 96 kg/hr/m³ (3 to 6 lbs/hr/ft³) of bed space. The reaction system was as described above. It has a lower section 3 m (10 feet) high and 34 cm (13½ inches) in (inner) diameter, and an upper section which was 4.8 m (16 feet) high and 49,6 cm (23½ inches) in (inner) diameter.

Tables I to III below list the percent loading of the precursor composition, weight percent of triethyl aluminum used to treat the silica, q measured (actual value), q calculated according to formula q=1.5 m+2, aluminum compound used in the mix tank, Al/Ti mol ratio in the mix tank as well as the residual titanium, bulk density, density, average particle size and fines of the granular resins made in these examples.

TABLE I
Effect of excess (q is >1.5 m+2) electron donor (THF) on activity of impregnated catalyst

Example	1	2	3
Precursor composition			
Loading of precursor composition	20	20	20
Silica treated with triethyl aluminum (wt. percent)	8	8	8
q (measured)	8.0	10.2	9.5
q (calculated)	8.0	7.4	7.5
Activation of precursor composition in mix tank			
Aluminum compound	—	—	Triethylaluminum
Al/Ti	—	—	4
Polymer properties			
Residual titanium (ppm)	9	60	9
Density (g/cm^3)	0.970	0.969	0.966
Bulk density (g/cm^3)	0.449	0.513	0.441
(lbs/ft^3)	28	32	27.5
Particle size (mm)	0.76	0.483	1.02
(in.)	0.03	0.019	0.04
Fines (percent, <125 µm)	1.6	1.2	0.2

The date in Table I show that when q is >1.5 m+2 and there is no partial activation in the mix tank (Example 2) catalyst productivity is very low (Ti=60). However, when q is >1.5 m+2 and there is partial activation in the mix tank (Example 3) according to the process of the invention catalyst productivity is high (Ti=9).

TABLE II
Effect of variables in the catalyst preparation on catalytic activity

Example	3	4	5
Precursor composition			
Percent loading of precursor composition	20	20	28
Silica treated with triethyl aluminum (wt. percent)	8	4	4
q (measured)	9.5	9.5	9.3
q (calculated)	7.5	6.5	6.3
Activation of precursor composition in mix tank			
Aluminum compound	Triethylaluminum	Triethylaluminum	Triethylaluminum
Al/Ti	4	4.5	2
Polymer properties			
Residual titanium (ppm)	9	4	12
Density (g/cm^3)	0.966	0.955	0.967
Bulk density (g/cm^3)	0.441	0.445	0.401
(lbs/ft^3)	27.5	27.8	25
Particle size (mm)	1.02	0.584	0.838
(in.)	0.04	0.023	0.033
Fines (percent <125 μm)	0.2	0.5	0.4

The data of Table II show that by varying the percent loading of the precursor composition, the weight percent of triethyl aluminium employed to treat the silica, q (measured) and Al/Ti ratio in the partially activated precursor composition, catalysts are produced which exhibit high activity and polymers are prepared which exhibit high bulk density and a low level of fines.

TABLE III
Effect of aluminum activating agents on activity of impregnated catalyst

Example	3	6	7
Precursor composition			
...ent loading of precursor ...sition (wt. percent)	20	20	20
...ted with triethyl ...um (wt. percent)	8	4	4
q (measured)	9.5	7.6	7.6
q (calculated)	7.5	6.2	6.2
Partial activation of precursor composition in mix tank			
Aluminum compound	Et_3Al[1]	Et_2AlOEt[2]	$Al(C_6H_{13})_3$
Al/Ti	4	6	3
Polymer properties			
Residual titanium (ppm)	9	14	14
Density (g/cc)	0.966	0.966	0.967
Bulk density (g/cm^3)	0.441	0.439	0.449
(lbs/ft^3)	27.5	27.4	28
Particle size (mm)	1.02	0.533	0.660
(in.)	0.04	0.021	0.026
Fines (percent <125 μm)	0.2	0.8	0.4

(1) Et_3Al=triethyl aluminum
(2) Et_2AlOEt=diethylaluminum ethoxide.

The data of Table III show that by varying the aluminum-compound used to partially activate the precursor composition in the mix tank high activity catalysts based on these aluminum reagents can be prepared and polymers are formed which exhibit high bulk density and a low level of fines.

Claims

1. A process for polymerizing ethylene employing a catalyst composition prepared by forming a precursor composition from a magnesium compound, titanium compound and electron donor compound, and then activating the precursor composition with an organoaluminum compound to form the catalyst, characterized in that the polymerization is conducted continuously in a fluid bed reactor at a temperature of 30 to 115°C under a pressure of <69 bar (<1000 psi) in the gas phase to produce ethylene homopolymers or ethylene copolymers containing ≥97 mol percent of ethylene and ≤3 mol percent of one or more C_3 to C_8 alpha olefins at a productivity of ≥50,000 kg of polymer per kg of Ti, said polymer being produced in a granular form and having a density of ≥0.94 to ≤0.97 g/cm^3 and a melt flow ratio of ≥22 to ≤32, by contacting ethylene, or a mixture of ethylene and at least one C_3 to C_8 alpha olefin, optionally in the presence of hydrogen, with particles of an activated precursor composition having the formula

$$Mg_mTi(OR)_nX_p[ED]_q$$

wherein

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof,

TABLE III
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Example	3	6	7
Precursor composition			
...ent loading of precursor ...sition (wt. percent)	20	20	20
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q (measured)	9.5	7.6	7.6
q (calculated)	7.5	6.2	6.2
Partial activation of precursor composition in mix tank			
Aluminum compound	Et_3Al[1]	Et_2AlOEt[2]	$Al(C_6H_{13})_3$
Al/Ti	4	6	3
Polymer properties			
Residual titanium (ppm)	9	14	14
Density (g/cc)	0.966	0.966	0.967
Bulk density (g/cm^3)	0.441	0.439	0.449
(lbs/ft^3)	27.5	27.4	28
Particle size (mm)	1.02	0.533	0.660
(in.)	0.04	0.021	0.026
Fines (percent <125 μm)	0.2	0.8	0.4

[1] Et_3Al=triethyl aluminum
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The data of Table III show that by varying the aluminum-compound used to partially activate the precursor composition in the mix tank high activity catalysts based on these aluminum reagents can be prepared and polymers are formed which exhibit high bulk density and a low level of fines.

Claims

1. A process for polymerizing ethylene employing a catalyst composition prepared by forming a precursor composition from a magnesium compound, titanium compound and electron donor compound, and then activating the precursor composition with an organoaluminum compound to form the catalyst, characterized in that the polymerization is conducted continuously in a fluid bed reactor at a temperature of 30 to 115°C under a pressure of <69 bar (<1000 psi) in the gas phase to produce ethylene homopolymers or ethylene copolymers containing ≥97 mol percent of ethylene and ≤3 mol percent of one or more C_3 to C_8 alpha olefins at a productivity of ≥50,000 kg of polymer per kg of Ti, said polymer being produced in a granular form and having a density of ≥0.94 to ≤0.97 g/cm^3 and a melt flow ratio of ≥22 to ≤32, by contacting ethylene, or a mixture of ethylene and at least one C_3 to C_8 alpha olefin, optionally in the presence of hydrogen, with particles of an activated precursor composition having the formula

$$Mg_mTi(OR)_nX_p[ED]_q$$

wherein

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof,

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ED is a liquid organic electron donor compound in which said precursor composition and the Ti and Mg component thereof are soluble or partially soluble and which is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones,

m is ≥0.5 to ≤56,

n is 0, 1 or 2,

p is ≥2 to ≤116, and

q is >1.5 m+2,

precursor composition being impregnated into an inert porous carrier in a weight ratio of 0.033 to 1, being activated with an activator having the formula

$$Al(R'')_cX'_dH_e$$

wherein X' is Cl or OR''', R'' and R''' are the same or different, and are C_1 to C_{14} saturated hydrocarbon radicals, d is 0 to 1.5, e is 1 or 0 and c+d+e=3, activation of said precursor composition being effected by treating the impregnated precursor composition outside the polymerization reactor in a hydrocarbon slurry with >0 to <10 mols of activator compound per mol of titanium compound in said precursor composition, drying the mixture to obtain a free-flowing solid particulate material, and feeding the impregnated precursor composition into the polymerization reactor wherein it is further activated by adding additional activator compound to the reactor in such amounts as to provide ≥10 mols up to a total of ≤400 mols of said activator compound per mol of titanium compound in said precursor composition.

2. A process as in claim 1 in which ethylene homopolymer is produced.

3. A process as in claim 1 or 2, in which said magnesium compound comprises $MgCl_2$.

4. A process as in any one of claims 1 to 3 in which said electron donor compound comprises at least one ether, preferably tetrahydrofuran.

5. A process as in any one of claims 1 to 4 in which said titanium compound comprises $TiCl_4$.

6. A process as in any one of claims 1 to 5 wherein the inert porous carrier comprises silica.

7. A process as in claim 6 wherein the silica is treated with at least one activator compound of the formula

$$AlR_3$$

wherein the R's are the same or different, and are C_1 to C_{14} saturated hydrocarbon radicals.

Patentansprüche

1. Verfahren zum Polymerisieren von Ethylen unter Verwendung einer Katalysatorzusammensetzung, hergestellt durch Bildung einer Vorläuferzusammensetzung aus einer Magnesiumverbindung, Titanverbindung und Elektronenspenderverbindung und anschließende Aktivierung der Vorläuferzusammensetzung mit einer Organoaluminiumverbindung zur Bildung des Katalysators, dadurch gekennzeichnet, daß die Polymerisation kontinuierlich in einem Fließbettreaktor bei einer Temperatur von 30 bis 115°C unter einem Druck von <69 bar (<100 psi) in der Gasphase zur Bildung von Ethylenhomopolymerisaten oder Ethylencopolymerisation durchgeführt wird, die ≥97 Mol-% Ethylen und ≤3 Mol-% eines oder mehrerer C_3 bis C_8 α-Olefine bei einer Produktivität von ≥50 000 kg Polymerisat pro kg Ti enthalten, wobei das Polymerisat in granularer Form hergestellt wird und eine Dichte von ≥0,94 bis ≤0,97 g/cm³ und ein Schmelzflußverhältnis von ≥22 bis ≤32 hat, indem man Ethylen oder eine Mischung aus Ethylen und mindestens einem C_3 bis C_8 α-Olefin, wahlweise in Anwesenheit von Wasserstoff, mit Teilchen einer aktivierten Vorläuferzusammensetzung der Formel

$$Mg_mTi(OR)_nX_p[ED]_q$$

in Berührung bringt, in welcher

R ein aliphatischer oder aromatischer C_1 bis C_{14} Kohlenwasserstoffrest oder COR' ist, worin R' ein aliphatischer oder aromatischer C_1 bis C_{14} Kohlenwasserstoffrest ist,

X aus der aus Cl, Br, J oder Mischungen derselben bestehenden Gruppe ausgewählt ist,

ED eine flüssige organische Elektronenspenderverbindung ist, in welcher die Vorläuferzusammensetzung und die Ti und Mg Komponente derselben löslich oder teilweise löslich sind und die aus der aus den Alkylestern aliphatischer und aromatischer Carbonsäuren, aliphatischen Ethern, cyclischen Ethern und aliphatischen Ketonen bestehenden Gruppe ausgewählt ist,

m≥0,5 bis ≤56 ist

n 0, 1 oder 2 ist,

p ≥2 bis ≤116 ist und

q >1,5 m+2 ist,

wobei die Vorläuferzusammensetzung in einem inerten porösen Träger in einem Gewichtsverhältnis von 0,033 bis 1 imprägniert und mit einer Aktivatorverbindung der Formel

$$Al(R'')_cX'_dH_e$$

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aktiviert ist, in welcher X' Cl oder OR''' ist, R'' und R''' gleich oder verschieden sind und gesättigte C_1 bis C_{14} Kohlenwasserstoffreste sind, d 0 bis 1,5 ist, e 1 oder 0 ist und c+d+e=3 ist, wobei die Aktivierung der Vorläuferzusammensetzung durchgeführt wird, indem man die imprägnierte Vorläuferzusammensetzung außerhalb des Polymerisationsreaktors in einer Kohlenwasserstoffaufschlämmung mit >0 bis <10 Mol Aktivatorverbindung pro Mol Titanverbindung in der Vorläuferzusammensetzung behandelt, die Mischng zur Erzielung eines frei fließenden festen, fein zerteilten Materials trocknet und die imprägnierte Vorläufe- sammensetzung in den Polymerisationsreaktokr einführt, in welchem sie weiter aktiviert wird, indem m zusätzliche Aktivatorverbindung in solchen Mengen in den Reaktor einführt, daß sich ≥10 Mol bis zu insgesamt ≤400 Mol dieser Aktivatorverbindung pro Mol Titanverbindung in der Vorläuferzusammensetzung ergeben.

2. Verfahren nach Anspruch 1, in welchem ein Ethylenhomopolymerisat hergestellt wird.

3. Verfahren nach Anspruch 1 oder 2, in welchem die Magnesiumverbindung $MgCl_2$ umfaßt.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem die Elektronenspenderverbindung mindestens einen Ether, vorzugsweise Tetrahydrofuran, umfaßt.

5. Verfahren nach einem der Ansprüche 1 bis 4, in welchem die Titanverbindung $TiCl_4$ umfaßt.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem der inerte poröse Träger Kieselsäure umfaßt.

7. Verfahren nach Anspruch 6, in welchem die Kieselsäure mit mindestens einer Aktivatorverbindung der Formel AlR_3 behandelt ist, in welcher die Substituenten R gleich oder verschieden sind und gesättigte C_1 bis C_{14} Kohlenwasserstoffreste sind.

Revendications

1. Procédé de polymérisation d'éthylène utilisant une composition de catalyseur préparée par formation d'une composition de précurseur à partir d'un composé de magnésium, d'un composé de titane et d'un composé donneur d'électrons, puis activation de la composition de précurseur avec un composé organique d'aluminium pour former le catalyseur, caractérisé en ce que la polymérisation est conduite en continu dans un réacteur à lit fluide à une température de 30 à 115°C sous une pression inférieure à 69 bars (<1000 lb/in^2) dans la phase gazeuse pour produire des homopolymères d'éthylène ou des copolymères d'éthylène contenant 97 ou plus de 97 moles pour-cent d'éthylène et 3 ou moins de 3 moles pour-cent d'une ou plusieurs alpha-oléfines en C_3 à C_8 à une productivité égale ou supérieure à 50 000 kg de polymère par kg de Ti, ledit polymère étant produit sous une forme granulaire et ayant une masse volumique allant d'une valeur supérieure ou égale à 0,94 à une valeur inférieure ou égale à 0,97 g/cm^3 et un rapport d'écoulement à l'état fondu allant d'une valeur supérieure ou égale à 22 à une valeur inférieure ou égale à 32, par mise en contact d'éthylène, ou d'un mélange d'éthylène et d'au moins une alpha-oléfine en C_3—C_8, éventuellement en présence d'hydrogène, avec des particules d'une composition de précurseur activée de formule

$$Mg_mTi(OR)_nX_p[ED]_q$$

dans laquelle

R est un radical hydrocarboné aliphatique ou aromatique en C_1 à C_{14}, ou bien un groupe COR' dans lequel R' est un radical hydrocarboné aliphatique ou aromatique en C_1 à C_{14},

X est choisi entre Cl, Br, I ou leurs mélanges,

ED est un composé organique liquide donneur d'électrons dans lequel ladite composition de précurseur et son composant de Ti et Mg sont solubles ou partiellement solubles et qui est choisi dans le groupe comprenant des esters alkyliques d'acides carboxyliques aliphatiques et aromatiques, d'éthers aliphatiques, d'éthers cycliques et de cétones aliphatiques,

m va d'une valeur égale ou supérieure à 0,5 à une valeur égale ou inférieure à 56,

n est égal à 0, 1 ou 2,

p va d'une valeur égale ou supérieure à 2 à une valeur égale ou inférieure à 116, et

q est supérieur à 1,5 m+2,

ladite composition de précurseur étant imprégnée dans un support poreux inerte dans un rapport en poids de 0,033 à 1 et étant activée avec un activateur de formule

$$Al(R'')_cX'_dH_e$$

dans laquelle X' représente Cl ou un groupe OR''', R'' et R''' étant égaux ou différents et représentant des radicaux hydrocarbonés saturés en C_1 à C_{14}, d a une valeur de 0 à 1,5, e est égal à 0 ou 1 et la somme c+d+e est égale à 3, l'activation de ladite composition de précurseur étant effectuée par traitement de la composition de précurseur imprégnée en dehors du réacteur de polymérisation dans une suspension hydrocarbonée avec une quantité allant de plus de 0 mole à moins de 10 moles de composé activateur par mole de composé de titane dans ladite composition de précurseur, séchage du mélange pour obtenir une matière en particules solides s'écoulant librement et introduction de la composition de précurseur imprégnée dans le réacteur de polymérisation où elle est encore activée par addition au réacteur d'une

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quantité supplémentaire de composé activateur en quantités choisies de manière qu'il y ait 10 ou plus de 10 moles jusqu'à un total de 400 ou moins de 400 moles dudit composé activateur par mole de composé de titane dans ladite composition de précurseur.

2. Procédé suivant la revendication 1, dans lequel un homopolymère d'éthylène est produit.

3. Procédé suivant la revendication 1 ou 2, dans lequel ledit composé de magnésium comprend $MgCl_2$.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel ledit composé donneur d'électrons comprend au moins un éther, de préférence le tétrahydrofuranne.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel ledit composé de titane comprend $TiCl_4$.

6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel le support poreux inerte comprend de la silice.

7. Procédé suivant la revendication 6, dans lequel la silice est traitée avec au moins un composé activateur de formule

$$AlR_3$$

dans laquelle les groupes R sont égaux ou différents et sont des radicaux hydrocarbonés saturés en C_1 à C_{14}.

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