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(54) Title: CATALYST

(57) Abstract: This invention relates to a process for making single site catalysts using surfactants free from perfluorinated octanoic acid and perfluorinated octanoic acid related compounds. The invention also relates to the use of such catalysts for the production of polyolefins as well as to the solid catalysts themselves.



Catalyst

Field of invention

5 The present invention relates to a process for making single site catalysts using surfactants free from perfluorinated octanoic acid and perfluorinated octanoic acid related compounds. The invention also relates to the use of such catalysts for the production of polyolefins as well as to the solid catalysts themselves.

Background of Invention

10 Single site catalysts have been used to manufacture polyolefins for many years. Countless academic and patent publications describe the use of these catalysts in olefin polymerisation. One big group of single site catalysts are metallocenes, which are nowadays used industrially and polyethylenes and polypropylenes in particular are often produced using cyclopentadienyl based catalyst systems with different substitution patterns.

15 In slurry and gas phase processes alike, catalysts need to be made of solid, uniform particles of appropriate particle size, morphology and mechanical stability to avoid reactor fouling, sheeting and line plugging. The use therefore of a catalyst support is common place. Metallocenes are conventionally supported on a carrier such as silica, for example. The use however of supported catalysts is associated with problems such as silica residues in the final
20 product.

In WO 03/051934, the inventors proposed an alternative form of catalyst which is provided in solid form but does not require a conventional external carrier material such as silica. The invention is based on the finding that a homogeneous catalyst system containing an organometallic compound of a transition metal can be converted, in a controlled way, to
25 solid, uniform catalyst particles by first forming a liquid/liquid emulsion system, which comprises as the dispersed phase, said solution of the homogeneous catalyst system, and as the continuous phase a solvent immiscible therewith, and then solidifying said dispersed droplets to form solid particles comprising the said catalyst.

The invention described in WO 03/051934 enabled the formation of solid spherical
30 catalyst particles of said organotransition metal catalyst without using e.g. external porous carrier particles, such as silica, normally required in the art. Thus, problems relating to catalyst silica residues can be solved by this type of catalyst. Further, it could be seen that catalyst particles having improved morphology, will give, due to the replica effect, polymer particles having improved morphology as well.

The standard procedure for the manufacture of said solid unsupported single site catalysts does however pose certain environmental concerns. Production of the catalyst in this way conventionally makes use of highly fluorinated surfactants, such as highly fluorinated heptanol, octanol, and nonanol as described in WO 03/051934. WO 2006/069733 also
5 discloses hydrocarbon-based surfactants which are preferably semi- or highly-fluorinated hydrocarbons.

A recent REACH Annex XV report submitted by the German and Norwegian authorities proposes a restriction on the manufacture, use or placing on the market of perfluorinated octanoic acid (PFOA) and PFOA-related compounds. There is therefore a
10 need to design a new process, following the principles outlined in WO 03/051934, but which avoids the use of highly fluorinated octanoic acid surfactants.

Highly fluorinated surfactants such as perfluorooctanesulfonic acid and/or perfluorooctanoic acid were used in WO 2011/076443, WO 2011/076617 and WO 2011/076618. These applications all disclose surfactants based around a perfluoroalkyl
15 ethylacrylate ester core.

There remains therefore a need for alternative surfactants that address the environmental concerns. These new surfactants must possess at least the same performance as the typical highly fluorinated surfactants, and also be suitable for use in the manufacture of solid olefin catalysts, which are not supported on an external carrier, and which processes
20 lead to uniform catalyst particles and thus to uniform polymers having desired morphology. These surfactants must also be easily synthesised and economically viable on a commercial scale.

The present inventors have now found a new class of commercially available compounds to be used as alternative surfactants to the highly/perfluorinated surfactants
25 conventionally used in making catalysts by the method following the basic principles as described in WO 03/051934 as described above.

These compounds are non-persistent and non-bioaccumulative, and thus pose reduced environmental, health and safety risks than the highly fluorinated alternatives of the prior art. In particular, these compounds used as surfactants have been shown to demonstrate
30 at least the same performance as the conventional highly fluorinated compounds but without the environmental concerns in the process as described herein.

Summary of the Invention

Thus, viewed from one aspect the invention provides a process for producing an olefin polymerisation catalyst comprising an organometallic compound of a transition metal of Group 3 to 10 of the Periodic Table (IUPAC), or of an actinide or lanthanide, having the formula (I):



wherein

“M” is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007) or of an actinide or lanthanide,

each “X” is independently a monoanionic ligand, such as a σ -ligand,

each “L” is independently an organic ligand which coordinates to the transition metal “M”,

“R” is a bridging group linking said organic ligands (L),

“m” is 1, 2 or 3, preferably 2

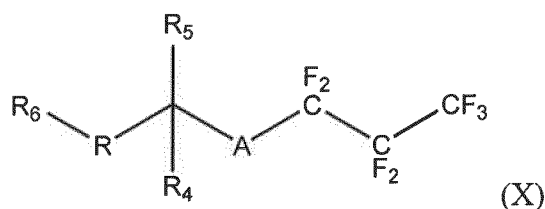
“n” is 0, 1 or 2, preferably 1,

“q” is 1, 2 or 3, preferably 2 and

m+q is equal to the valency of the transition metal (M); in the form of solid particles, comprising the steps of:

- a) preparing a homogenous solution of one or more catalyst components including said organometallic compound of formula (I);
- b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;
- c) solidifying said dispersed phase to convert said droplets to solid particles, and
- d) optionally recovering said particles to obtain said catalyst;

characterised in that an emulsifying agent is present during the formation of said emulsion system and said emulsifying agent comprises a compound of formula (X):



wherein

R_6 is HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C-, or CF₃(O)C-

A is -O-, a covalent bond or CF₂;

R_4 is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

R_5 is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

5 R is -CF₂-, (-CH₂)_n-, -CF₂CF₂-, or a covalent bond

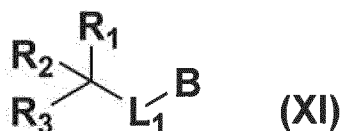
n is 1 to 2;

with the proviso that compound (X) is not a perfluoroalcohol or perfluorocarboxylic acid;

or a salt thereof, e.g. a NH₄⁺, Na⁺, or K⁺ salt;

10

or a compound of formula (XI)



15

wherein

R_1 , R_2 , and R_3 are independently selected from any one of F, -CF₃ or CF₃CF₂- provided at least one R group is -CF₃;

L_1 is a linear or branched C₁₋₆ alkyl group wherein each C atom is substituted with 0, 1, 2, or 3 F atoms, and optionally said alkyl group contains an ether linkage;

20

B is selected from HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C- or CF₃(O)C-; or a salt thereof.

Viewed from another aspect the invention provides a process for producing an olefin polymerisation catalyst comprising an organometallic compound of a transition metal of Group 3 to 10 of the Periodic Table (IUPAC), having the formula (I):

25



wherein

“M” is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007) or an actinide or lanthanide,

30

each “X” is independently a monoanionic ligand, such as a σ-ligand,

each “L” is independently an organic ligand which coordinates to the transition metal “M”,

“R” is a bridging group linking said organic ligands (L),

“m” is 1, 2 or 3, preferably 2

“n” is 0, 1 or 2, preferably 1,

“q” is 1, 2 or 3, preferably 2 and

5 m+q is equal to the valency of the transition metal (M); in the form of solid particles, comprising the steps of:

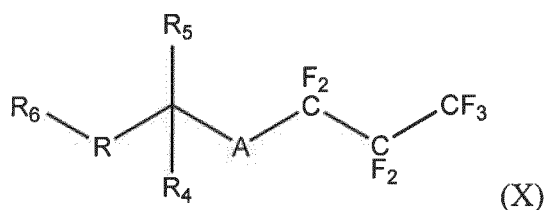
a) preparing a homogenous solution of one or more catalyst components including said organometallic compound of formula (I);

10 b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;

c) solidifying said dispersed phase to convert said droplets to solid particles, and

d) optionally recovering said particles to obtain said catalyst; characterised in that

15 an emulsifying agent is present during the formation of said emulsion system and said emulsifying agent comprises the reaction product of (i) a compound of formula (X):



wherein

20 R₆ is HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C-, or CF₃(O)C-

A is -O-, a covalent bond or CF₂;

R₄ is -H, -F, -CF₃, -Me, CF₂CF₃, or ethyl;

R₅ is -H, -F, -CF₃, -Me, CF₂CF₃, or ethyl;

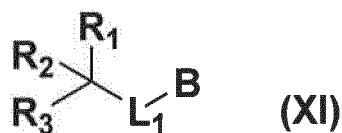
R is -CF₂, (-CH₂)_n, -CF₂CF₂, or a covalent bond

25 n is 1 to 2;

with the proviso that compound (X) is not a perfluoroalcohol or perfluorocarboxylic acid;

or a salt thereof, e.g. a NH₄⁺, Na⁺, K⁺ salt

30 or a compound of formula (XI)



wherein

5 R_1 , R_2 , and R_3 are independently selected from any one of F, $-CF_3$ or CF_3CF_2- provided at least one R group is $-CF_3$;

L_1 is a linear or branched C_{1-6} alkyl group wherein each C atom is substituted with 0, 1, 2 or 3 F atoms, and optionally said alkyl group contains an ether linkage;

B is selected from $HO-$, $HO(O)C-$, $H(O)C-$, $F(O)C-$, $CH_3(O)C-$ or $CF_3(O)C-$;

10 or a salt thereof; and

(ii) a cocatalyst.

Viewed from another aspect the invention provides a catalyst obtainable by a process as hereinbefore described.

15 Viewed from a yet further aspect the invention provides a process for the preparation of polyolefin comprising polymerising at least one olefin in the presence of an olefin polymerisation catalyst as hereinbefore defined.

20 Viewed from another aspect the invention provides use of the catalyst as hereinbefore defined for the homo- or copolymerisation of olefins, in particular C_2 to C_{10} α -olefins, preferably propene or ethylene or a mixture of ethylene or propene with one or more α -olefin(s).

Viewed from another aspect the invention provides the use a compound of formula (X) or (XI) or the use of the reaction product of a compound of formula (X) or (XI) as hereinbefore defined and a cocatalyst as an emulsifying agent in a process comprising

- 25 a) preparing a homogenous solution of one or more catalyst components;
- b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;
- c) solidifying said dispersed phase to convert said droplets to solid particles, and
- 30 d) optionally recovering said particles to obtain said catalyst.

One of the main advantages of the invention is that the surfactant used in the preparation of the catalyst system does not contain environmentally non-desired components.

A further advantage of the present invention is that said catalyst system shows desirable catalytic activity.

Description of the Invention

- 5 The present invention relates to the use of certain surfactants or the use of the reaction product of certain surfactants and a cocatalyst as emulsifying agents to prepare solid catalysts particles. The surfactants of the invention can be added to the process directly or can be added having been pre-reacted with a cocatalyst. The invention is based on the finding that a homogeneous catalyst system containing an organometallic compound of a transition metal
10 can be converted, in a controlled way, to solid, uniform catalyst particles by first forming a liquid/liquid emulsion system, which comprises as the dispersed phase, a solution of the homogeneous catalyst system, and as the continuous phase a solvent immiscible therewith, and then solidifying said dispersed droplets to form solid particles comprising the said catalyst.
- 15 The invention enables the formation solid spherical catalyst particles of said organotransition metal catalyst without using e.g. external porous carrier particles, such as silica, normally required in the prior art. A uniform distribution of the chemical composition, both intra- and interparticles, can thus be obtained. Advantageously, the catalyst particles of the invention have a uniform catalytical behaviour in a polymerisation process. E.g. the
20 catalyst can provide a uniform start-up of the polymerisation in a polymerisation process.

Emulsion

- By the term “emulsion” is meant a multiphasic, i.e. at least two phase emulsion system. The emulsion may be formed by any means known in the art, e.g. by stirring, shaking
25 or sonicating the dispersed phase (e.g. the solution of the catalyst component(s)) with a solvent substantially immiscible therewith. An emulsifying agent is used in the manufacture of the emulsion. When the emulsion forms, the solution which contains, or will contain, the catalyst/catalyst component(s) forms the dispersed phase, which can also be called the discontinuous phase, and the liquid medium, with which it is immiscible forms the
30 continuous phase.

The dispersed phase will be in the emulsion as liquid droplets, where the catalyst formation occurs.

Catalyst Components

The homogeneous solution of catalyst components comprises a transition metal compound of formula (I) and optionally a cocatalyst comprising a compound of a group 13 metal, e.g. aluminium and/or boron.

5 Catalyst

The polymerisation catalyst of the invention comprises an organometallic compound of a transition metal of Group 3 to 10 of the Periodic Table, or of an actinide or lanthanide. Preferably, said transition metal is selected from Groups 4 to 10, more preferably from Groups 4 to 6 of the Periodic Table, most preferably it is Ti, Zr or Hf.

10 The organometallic compound (C) preferably comprises a transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007). The term "an organometallic compound (C)" in accordance with the present invention includes any metallocene or non-metallocene compound of a transition metal which bears at least one organic (coordination) ligand and exhibits the catalytic activity alone or together with a cocatalyst. The transition metal
15 compounds are well known in the art and the present invention covers compounds of metals from Group 3 to 10, e.g. Group 3 to 7, or 3 to 6, such as Group 4 to 6 of the Periodic Table, (IUPAC 2007).

In an embodiment the organometallic compound (C) has the following formula (C):



wherein

"M" is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007),

each "X" is independently a monoanionic ligand, such as a σ -ligand,

25 each "L" is independently an organic ligand which coordinates to the transition metal "M",

"R" is a bridging group linking said organic ligands (L),

"m" is 1, 2 or 3, preferably 2

"n" is 0, 1 or 2, preferably 1,

30 "q" is 1, 2 or 3, preferably 2 and

m+q is equal to the valency of the transition metal (M).

"M" is preferably selected from the group consisting of zirconium (Zr), hafnium (Hf), or titanium (Ti), more preferably selected from the group consisting of zirconium (Zr) and hafnium (Hf).

In a more preferred definition, each organic ligand (L) is independently

- (a) a substituted or unsubstituted cyclopentadienyl or a bi- or multicyclic derivative of a cyclopentadienyl which optionally bear further substituents and/or one or more hetero ring atoms from a Group 13 to 16 of the Periodic Table (IUPAC); or
- 5 (b) an acyclic η^1 - to η^4 - or η^6 -ligand composed of atoms from Groups 13 to 16 of the Periodic Table, and in which the open chain ligand may be fused with one or two, preferably two, aromatic or non-aromatic rings and/or bear further substituents; or
- (c) a cyclic η^1 - to η^4 - or η^6 -, mono-, bi- or multidentate ligand composed of unsubstituted or substituted mono-, bi- or multicyclic ring systems selected from aromatic or
- 10 non-aromatic or partially saturated ring systems, such ring systems containing optionally one or more heteroatoms selected from Groups 15 and 16 of the Periodic Table.

Organometallic compounds (C), preferably used in the present invention, have at least one organic ligand (L) belonging to the group (a) above. Such organometallic compounds are called metallocenes.

15 More preferably at least one of the organic ligands (L), preferably both organic ligands (L), is (are) selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, which can be independently substituted or unsubstituted.

Further, in case the organic ligands (L) are substituted it is preferred that at least one organic ligand (L), preferably both organic ligands (L), comprise one or more substituents

20 independently selected from C_1 to C_{20} hydrocarbyl or silyl groups, which optionally contain one or more heteroatoms selected from groups 14 to 16 and/or are optionally substituted by halogen atom(s),

The term C_1 to C_{20} hydrocarbyl group, whenever used in the present application, includes C_1 to C_{20} alkyl, C_2 to C_{20} alkenyl, C_2 to C_{20} alkynyl, C_3 to C_{20} cycloalkyl, C_3 to C_{20} cycloalkenyl, C_6 to C_{20} aryl, C_7 to C_{20} alkylaryl or C_7 to C_{20} arylalkyl groups or mixtures of

25 these groups such as cycloalkyl substituted by alkyl.

Further, two substituents, which can be same or different, attached to adjacent C-atoms of a ring of the ligands (L) can also taken together form a further mono or multicyclic ring fused to the ring.

30 Preferred hydrocarbyl groups are independently selected from linear or branched C_1 to C_{10} alkyl groups, optionally interrupted by one or more heteroatoms of groups 14 to 16, like O, N or S, and substituted or unsubstituted C_6 to C_{20} aryl groups.

Linear or branched C₁ to C₁₀ alkyl groups, optionally interrupted by one or more heteroatoms of groups 14 to 16, are more preferably selected from methyl, ethyl, propyl, isopropyl, tertbutyl, isobutyl, C₅₋₆ cycloalkyl, OR, SR, where R is C₁ to C₁₀ alkyl group,

C₆ to C₂₀ aryl groups are more preferably phenyl groups, optionally substituted with 1
5 or 2 C₁ to C₁₀ alkyl groups as defined above.

By "σ-ligand" is meant throughout the invention a group bonded to the transition metal (M) via a sigma bond.

Further, the ligands "X" are preferably independently selected from the group consisting of hydrogen, halogen, C₁ to C₂₀ alkyl, C₁ to C₂₀ alkoxy, C₂ to C₂₀ alkenyl, C₂ to C₂₀ alkynyl, C₃ to C₁₂ cycloalkyl, C₆ to C₂₀ aryl, C₆ to C₂₀ aryloxy, C₇ to C₂₀ arylalkyl, C₇ to C₂₀ arylalkenyl, -SR", -PR"₃, -SiR"₃, -OSiR"₃ and -NR"₂, wherein each R" is independently hydrogen, C₁ to C₂₀ alkyl, C₂ to C₂₀ alkenyl, C₂ to C₂₀ alkynyl, C₃ to C₁₂ cycloalkyl or C₆ to C₂₀ aryl.

More preferably "X" ligands are selected from halogen, C₁ to C₆ alkyl, C₅ to C₆
15 cycloalkyl, C₁ to C₆ alkoxy, phenyl and benzyl groups.

The bridging group "R" may be a divalent bridge, preferably selected from -R'₂C-, -R'₂C-CR'₂-, -R'₂Si-, -R'₂Si-Si R'₂-, -R'₂Ge-, wherein each R' is independently a hydrogen atom, C₁ to C₂₀ alkyl, C₂ to C₁₀ cycloalkyl, tri(C₁-C₂₀-alkyl)silyl, C₆- C₂₀-aryl, C₇- C₂₀ arylalkyl and C₇- C₂₀-alkylaryl .

More preferably the bridging group "R" is a divalent bridge selected from -R'₂C-, -R'₂Si-, wherein each R' is independently a hydrogen atom, C₁ to C₂₀ alkyl, C₂ to C₁₀
20 cycloalkyl, C₆- C₂₀-aryl, C₇- C₂₀ arylalkyl and C₇- C₂₀-alkylaryl .

A preferred metallocene is therefore a compound of formula (III)

25
$$(\text{Cp})_m\text{R}_n\text{MX}_q \quad (\text{III})$$

wherein

each Cp independently is substituted or unsubstituted cyclopentadienyl or a bi- or multicyclic derivative of a cyclopentadienyl which optionally bear further substituents;

30 R is a divalent bridge selected from -R'₂C-, -R'₂Si-, wherein each R' is independently a hydrogen atom, C₁ to C₂₀ alkyl, C₂ to C₁₀ cycloalkyl, C₆- C₂₀-aryl, C₇- C₂₀ arylalkyl and C₇- C₂₀-alkylaryl;

M is a transition metal of Group 4 to 6, such as Group 4, e.g. Ti, Zr or Hf,

each X is independently a sigma-ligand,

n is 0, or 1, e.g. 1;
m is 1, 2 or 3, e.g. 1 or 2, preferably 2;
q is 1, 2 or 3, e.g. 2 or 3, preferably 2;
wherein $m+q$ is equal to the valency of M.

5 Another subgroup of the organometallic compounds (C) of formula (I) is known as non-metallocenes wherein the transition metal (M), preferably a Group 4 to 6 transition metal, suitably Ti, Zr or Hf, has a coordination ligand other than a cyclopentadienyl ligand.

The term "non-metallocene" used herein means compounds, which bear no cyclopentadienyl ligands or fused derivatives thereof, but one or more non-cyclopentadienyl
10 η -, or σ -, mono-, bi- or multidentate ligand. Such ligands can be chosen e.g. from the groups (b) and (c) as defined above and described e.g. in WO 01/70395, WO 97/10248, WO 99/41290, and WO 99/10353), and further in V. C. Gibson et al., in Angew. Chem. Int. Ed., engl., vol 38, 1999, pp 428 447, the disclosures of which are incorporated herein by reference.

15 However, the organometallic compound (C) of the present invention is preferably a metallocene as defined above.

Metallocenes are described in numerous patents. In the following just a few examples are listed; EP 260 130, WO 97/28170, WO 98/46616, WO 98/49208, WO 98/040331, WO 99/12981, WO 99/19335, WO 98/56831, WO 00/34341, WO00/148034, EP 423 101,
20 EP 537 130, WO2002/02576, WO2005/105863, WO 2006097497, WO2007/116034, WO2007/107448, WO2009/027075, WO2009/054832, WO 2012/001052, and EP 2532687, the disclosures of which are incorporated herein by reference. Further, metallocenes are described widely in academic and scientific articles.

25 **Cocatalyst**

In addition to the transition metal compounds, the catalyst may contain additional compounds, such as cocatalysts, activators, internal donors, and any reaction products of transition metal compounds and cocatalysts. As typical cocatalysts conventional activators are used, e.g. compounds of Group 13, e.g. organoaluminum compounds, such as alkyl
30 aluminium compounds, e.g. trialkylaluminum, or aluminoxane compounds, which are commonly used with single site catalysts. In addition non-coordination ionic cocatalysts, such as boron activators can be used.

Preferred cocatalysts are the aluminoxanes, in particular the C_{1-10} alkylaluminoxanes, most particularly methylaluminoxane (MAO). Such aluminoxanes can be used as the sole

cocatalyst or together with other cocatalyst(s). Thus besides, or in addition to, aluminoxanes, other cation complex forming catalyst activators can be used. In this regard mention may be made particularly to boron compounds known in the art. The activators may be commercially available or can be prepared according to the prior art literature.

5 Further aluminoxane cocatalysts are described in WO-A-94/28034 which is incorporated herein by reference. These are linear or cyclic oligomers having up to 40, preferably 3 to 20-(Al(R''')O)- repeat units (wherein R''' is hydrogen, C₁₋₁₀ alkyl (preferably methyl) or C₆₋₁₈ aryl or mixtures thereof).

10 Use of an amount of such activators is within the knowledge of a man skilled in the field. As an example, with the boron activators, 5:1 to 1:5, preferably 2:1 to 1:2, such as 1:1, ratio of the transition metal to boron activator may be used. In the case of aluminoxanes, such as methylaluminoxane (MAO), the amount of Al, provided by aluminoxane, can be chosen to provide an Al:transition metal molar ratio e.g. in the range of 1:1 to 10000:1, suitable 5:1 to 8000:1, preferably 10:1 to 7000:1, e.g. 100:1 to 4000:1, as normally used for homogeneous
15 catalyst systems, or alternatively 10:1 to 500:1, such as 100:1 to 300:1 as normally used for heterogeneous catalyst systems.

The use of both Al and B cocatalysts is also preferred for the catalysts of the invention.

20 The quantity of cocatalyst to be employed in the catalyst of the invention is thus variable and depends on the conditions and the particular transition metal compound chosen but will be well known to a person skilled in the art. Any additional components to be contained in the solution comprising the catalyst may be added to said solution before or, alternatively, after the dispersing step.

25 The ratio of the solution of the catalyst components, e.g. in toluene, and the liquid medium with which it is immiscible, is such that the solution of the catalyst forms the discontinuous phase. Typically the volume of dispersed phase is in the range of 1 to 50 vol%, preferably 5 to 40 vol%, more preferably 10-30 vol%, most preferably 15-25 vol%, e.g. 20 vol% dispersed phase.

30 Catalyst Manufacture

The catalyst of the present invention is preferably used in combination with the cocatalysts as a catalyst for the polymerization of olefins. The catalyst of the invention is in solid, preferably in unsupported form. Thus, no external carrier is used but the catalyst is still

presented in solid particulate form. Thus, no external support material such as inert organic or inorganic carrier, for example silica is employed.

In order to provide the catalyst of the invention in solid form but without using an external carrier, a liquid/liquid emulsion system is used. The process involves dispersing catalyst components (e.g. the organometallic compound and the cocatalyst(s)) in a solvent, adding an immiscible solvent to create an emulsion and solidifying said dispersed droplets to form solid particles. A particular emulsifying agent is used to ensure the formation of an emulsion.

In particular, the method involves preparing a solution of the catalyst components and a particular emulsifying agent; dispersing said solution in an immiscible solvent to form an emulsion in which said one or more catalyst components are present in the droplets of the dispersed phase; immobilising the catalyst components in the dispersed droplets, in the absence of an external particulate porous support, to form solid particles comprising the said catalyst, and optionally recovering said particles.

This process enables the manufacture of active catalyst particles with improved morphology, e.g. with a predetermined particle size, spherical shape, compact structure, excellent surface properties and without using any added external porous support material, such as an inorganic oxide, e.g. silica. The catalyst particles can have a smooth surface, they may be compact in nature and catalyst active components can be distributed uniformly thorough the catalyst particles.

The catalyst forming compounds may be combined in one solution which is dispersed in the immiscible solvent, or, alternatively, at least two separate catalyst solutions for each part of the catalyst forming compounds may be prepared, which are then dispersed successively to the immiscible solvent.

In a preferred method for forming the catalyst at least two separate solutions for each or part of said catalyst may be prepared, which are then dispersed successively to the immiscible solvent.

More preferably, a solution of the complex comprising the transition metal compound and the cocatalysts is combined with the immiscible solvent to form an emulsion wherein that inert immiscible solvent forms the continuous liquid phase and the solution comprising the catalyst components forms the dispersed phase (discontinuous phase) in the form of dispersed droplets. The droplets are then solidified to form solid catalyst particles, and the solid particles are separated from the liquid and optionally washed and/or dried. The solvent

forming the continuous phase may be immiscible to the catalyst solution at least at the conditions (e. g. temperatures) used during the dispersing step.

The term "immiscible with the catalyst solution" means that the solvent (continuous phase) is fully immiscible or partly immiscible i.e. not fully miscible with the dispersed phase solution.

Preferably said solvent is inert in relation to the compounds of the catalyst system to be produced. Full disclosure of the necessary process can be found in WO03/051934 which is herein incorporated by reference.

The inert immiscible solvent must be chemically inert at least at the conditions (e.g. temperature) used during the dispersing step. Preferably, the solvent of said continuous phase does not contain dissolved therein any significant amounts of catalyst forming compounds. Thus, the solid particles of the catalyst are formed in the droplets from the compounds which originate from the dispersed phase (i.e. are provided to the emulsion in a solution dispersed into the continuous phase).

The terms "immobilisation" and "solidification" are used herein interchangeably for the same purpose, i.e. for forming free flowing solid catalyst particles in the absence of an external porous particulate carrier, such as silica. The solidification happens thus within the droplets. Said step can be effected in various ways as disclosed in said WO03/051934. Preferably solidification is caused by an external stimulus to the emulsion system such as a temperature change to cause the solidification. Thus in said step the catalyst component (s) remain "fixed" within the formed solid particles. It is also possible that one or more of the catalyst components may take part in the solidification/immobilisation reaction.

Accordingly, solid, compositionally uniform particles having a predetermined particle size range can be obtained.

Furthermore, the particle size of the catalyst particles of the invention can be controlled by the size of the droplets in the solution, and spherical particles with a uniform particle size distribution can be obtained.

The invention is also industrially advantageous, since it enables the preparation of the solid particles to be carried out as a one-pot procedure. Continuous or semicontinuous processes are also possible for producing the catalyst.

Dispersed Phase

The principles for preparing two phase emulsion systems are as such known in the chemical field. Thus, in order to form the two phase liquid system, the solution of the catalyst component (s) and the solvent used as the continuous liquid phase have to be essentially immiscible at least during the dispersing step. This can be achieved in a known manner e.g. by choosing said two liquids and/or the temperature of the dispersing step/solidifying step accordingly.

A solvent may be employed to form the solution of the catalyst component (s). Said solvent is chosen so that it dissolves said catalyst component (s). The solvent can be preferably an organic solvent such as used in the field, comprising an optionally substituted hydrocarbon such as linear or branched aliphatic, alicyclic or aromatic hydrocarbon, such as a linear or cyclic alkane, an aromatic hydrocarbon and/or a halogen containing hydrocarbon.

Examples of aromatic hydrocarbons are toluene, benzene, ethylbenzene, propylbenzene, butylbenzene and xylene. Toluene is a preferred solvent. The solution may comprise one or more solvents. Such a solvent can thus be used to facilitate the emulsion formation, and usually does not form part of the solidified particles, but e.g. is removed after the solidification step together with the continuous phase.

Alternatively, a solvent may take part in the solidification, e.g. an inert hydrocarbon having a high melting point (waxes), such as above 40°C, suitably above 70°C, e. g. above 80°C or 90°C, may be used as solvents of the dispersed phase to immobilise the catalyst compounds within the formed droplets.

In another embodiment, the solvent consists partly or completely of a liquid monomer, e.g. liquid olefin monomer designed to be polymerised in a "prepolymerisation" immobilisation step.

Continuous Phase

The solvent used to form the continuous liquid phase is a single solvent or a mixture of different solvents and may be immiscible with the solution of the catalyst components at least at the conditions (e.g. temperatures) used during the dispersing step. Preferably said solvent is inert in relation to said compounds.

The term "inert in relation to said compounds" means herein that the solvent of the continuous phase is chemically inert, i.e. undergoes no chemical reaction with any catalyst forming component. Thus, the solid particles of the catalyst are formed in the droplets from the compounds which originate from the dispersed phase, i.e. are provided to the emulsion in a solution dispersed into the continuous phase.

It is preferred that the catalyst components used for forming the solid catalyst will not be soluble in the solvent of the continuous liquid phase. Preferably, said catalyst components are essentially insoluble in said continuous phase forming solvent.

Solidification takes place essentially after the droplets are formed, i.e. the solidification is effected within the droplets e.g. by causing a solidifying reaction among the compounds present in the droplets. Furthermore, even if some solidifying agent is added to the system separately, it reacts within the droplet phase and no catalyst forming components go into the continuous phase.

The term "emulsion" used herein covers both bi-and multiphasic liquid systems.

In a preferred embodiment said solvent forming the continuous phase is an inert solvent including a halogenated organic solvent or mixtures thereof, preferably fluorinated organic solvents and particularly semi, highly or perfluorinated organic solvents and functionalised derivatives thereof. Examples of the above-mentioned solvents are semi, highly or perfluorinated hydrocarbons, such as alkanes, alkenes and cycloalkanes, ethers, e.g. perfluorinated ethers and amines, particularly tertiary amines, and functionalised derivatives thereof. Preferred are semi, highly or perfluorinated, particularly perfluorinated hydrocarbons, e.g. perfluorohydrocarbons of e.g. C3-C30, such as C4-C10. Specific examples of suitable perfluoroalkanes and perfluorocycloalkanes include perfluoro-hexane, -heptane, -octane and -(methylcyclohexane). Semi fluorinated hydrocarbons relates particularly to semifluorinated n-alkanes, such as perfluoroalkyl-alkane.

In the present application the commonly used definitions are used as follows: "Semi fluorinated" hydrocarbons also include such hydrocarbons wherein blocks of -C-F and -C-H alternate. "Highly fluorinated" means that the majority of the -C-H units are replaced with -C-F units. "Perfluorinated" means that all -C-H units are replaced with -C-F units.

Dispersing step

The emulsion can be formed by any means known in the art: by mixing, such as by stirring said solution vigorously to said solvent forming the continuous phase or by means of mixing mills, or by means of ultrasonic wave. The mixing may be effected at lower or elevated temperatures, e.g. between 0 and 100 °C, depending i.a. on the used solvents, and is chosen accordingly.

A further possibility is to use a so called phase change method for preparing the emulsion by first forming a homogeneous system which is then transferred by changing the temperature of the system to a at least biphasic system so that droplets will be formed. If

needed, part of the catalyst forming compounds may be added after the emulsion system is formed,

The emulsion formation via said "one phase" change may be one preferable method, especially when e.g. fluorinated solvents are used as the continuous phase, since the miscibility of the fluorinated solvents, in particular perfluorinated solvents, with common organic solvents (e.g. alkane, such as pentane, hexane, chloroform, toluene) is dependent on the temperature so that a one phase system (homogeneous phase) of the fluorous solvent and a common organic solvent can be formed above a certain critical temperature. The ratio of the first (e.g. fluorous solvent) and the second solvent (catalyst solution) is chosen so that the first solution forms the discontinuous phase (droplets) in the at least two phase system. The two phase state is maintained during the emulsion formation step and the solidification step, as for example, by appropriate stirring.

It is a feature of the invention that emulsifying agents (which can also be called as emulsion stabilisers) can be used, for facilitating the formation and/or stability of the emulsion. These surfactants can be added to the catalyst solution, which forms the dispersed phase of the emulsion, to facilitate the forming of the emulsion and to stabilize the emulsion.

According to a preferred alternative, an emulsifying and/or emulsion stabilising agent is formed by reacting a surfactant bearing at least one functional group with a compound reactive with said functional group and present in the catalyst solution or in the solvent forming the continuous phase. The obtained reaction product acts as the actual emulsifying agent and/or stabiliser in the formed emulsion system.

The compound reacting with such surfactant is preferably contained in the catalyst solution and may be a further additive or one or more of the catalyst forming compounds. Such compound is e.g. a compound of group 13 (e.g. MAO and/or an aluminium alkyl compound and/or a transition metal compound). Thus, according to the preferred alternative emulsifying agent is formed by pre-reacting the surfactant with a cocatalyst.

If a pre-reacted surfactant is used, the surfactant is preferably first reacted with a compound of the catalyst solution before the addition of the transition metal compound. In the preferred embodiment the surfactant is reacted with a cocatalyst to form the "actual" emulsifying agent. Then, an additional amount of cocatalyst and the transition metal compound is added to said solution and the obtained solution is dispersed to the solvent forming the continuous phase. The "actual" surfactant solution may be prepared before the dispersing step or in the dispersed system. If said solution is made before the dispersing step, then the prepared "actual" surfactant solution and the transition metal solution may be

dispersed successively (e.g. the surfactant solution first) to the immiscible solvent, or be combined together before the dispersing step.

Surfactant

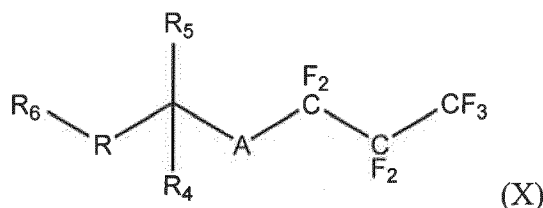
5 “Surfactants” according to this invention are agents that lower the surface tension of a liquid and lower the interfacial tension between two phases.

The present invention relies on the use of certain surfactants for forming the emulsion. These surfactants can be added to the process to form the emulsion or preferably the surfactant is pre-reacted with a cocatalyst to create the emulsifying agent.

10 After the formation of the emulsion system, the catalyst system is formed *in situ* from the catalyst components, e.g. the organometallic compounds of a transition metal of formula (I) and a cocatalyst comprising a compound of a group 13 metal, e.g. aluminium and/or boron in the solvent.

The surfactants according to the invention comprise a compound of formula (X):

15



wherein

R₆ is HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C-, or CF₃(O)C-

A is -O-, a covalent bond or CF₂;

20 R₄ is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

R₅ is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

R is -CF₂, (-CH₂)_n-CF₂CF₂- or a covalent bond

n is 1 to 2;

or a salt thereof, e.g. a NH₄⁺, Na⁺, K⁺ salt, provided that the compound (X) cannot

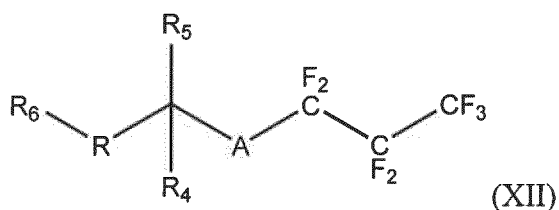
25 represent a perfluoroalcohol or perfluorocarboxylic acid.

It is preferred if R₆ is HO-, HO(O)C-, or F(O)C-.

It is preferred if R₄ is -H, -F, or -CF₃.

It is preferred if R₅ is -H, -F, or -CF₃. If R₄ is H then it is preferred if R₅ is H. If R₄ is F then it is preferred if R₅ is F or CF₃.

30 In a preferred embodiment, the surfactant is of formula (XII)



wherein,

R₆ is HO-, HO(O)C-, or F(O)C-;

A is -O-;

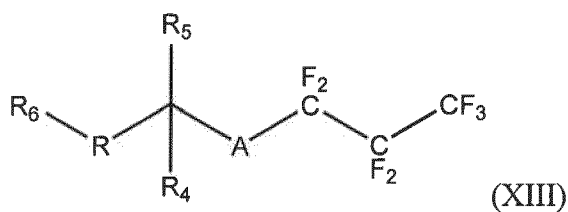
R₄ is -F, or -CF₃;

R₅ is -F or -CF₃;

R is (-CH₂)- or a covalent bond

or a salt thereof.

In a preferred embodiment, the surfactant is of formula (XIII)



wherein

R₆ is HO-, HO(O)C-, or F(O)C-;

A is a covalent bond or CF₂;

R₄ is -H, or -F;

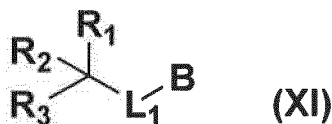
R₅ is -H, or -F;

R is (-CH₂)_n or a covalent bond

n is 1 to 2;

or a salt thereof, e.g. a NH₄⁺, Na⁺, K⁺ salt, provided that formula (XIII) cannot represent a perfluoroalcohol or perfluorocarboxylic acid. By perfluoroalcohol or perfluorocarboxylic acid is meant a compound in which the C-H atoms of an alcohol or the C-H atoms of a carboxylic acid are replaced by C-F. No other functional groups are present (e.g. if A is O and R₆ is OH, then the molecule is not deemed a perfluoroalcohol).

In a second embodiment, the surfactant is of formula (XI)



wherein

5 R_1 , R_2 , and R_3 are independently selected from any one of F, CF_3 or CF_3CF_2 - provided at least one R group is CF_3 ;

L_1 is a linear or branched C_{1-6} alkylene group wherein each C atom is substituted with 0, 1, 2 or 3F atoms, and optionally said alkyl group contains an ether linkage;

B is selected from HO-, HO(O)C-, H(O)C-, F(O)C-, $CH_3(O)C$ -, or $CF_3(O)C$ -;
 10 or a salt thereof.

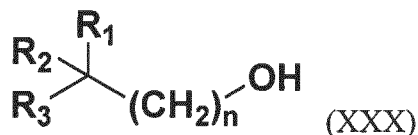
It is preferred if B is OH.

It is preferred if each C atom in L_1 is substituted with 0, 1 or 2 F atoms.

It is preferred if the L_1 group is free of F atoms. It is preferred if L_1 is linear. It is preferred if L_1 is a C1-3-alkylene group, such as methylene or ethylene group.

15 It is preferred if two of R_1 , R_2 , and R_3 are CF_3 . It is preferred if all of R_1 , R_2 , and R_3 are CF_3 .

It is preferred if the surfactant is of formula (XXX)

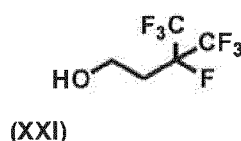
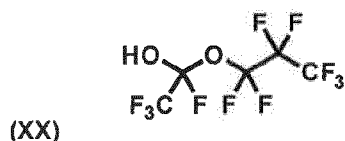
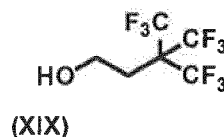
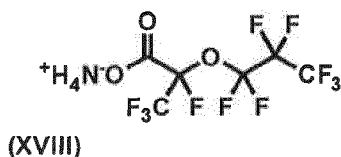
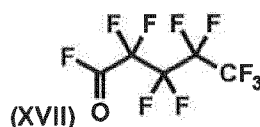
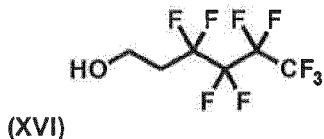
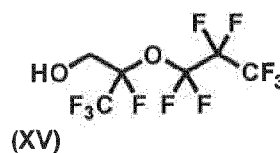
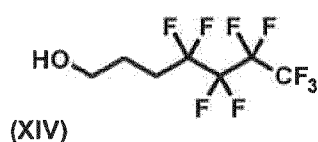


20 R_1 , R_2 , and R_3 are independently selected from any one of F, CF_3 or CF_3CF_2 - provided at least one R group is CF_3 ; and

n is 1 to 3.

In any surfactant of the invention, it is preferred if there are 12 F atoms or fewer, such as 11 atoms or fewer in the molecule.

25 It is preferred if the surfactant is a liquid at room temperature. Preferably the emulsifying agent is a surfactant selected from formulas (XIV) to (XXI) or a reaction product of a surfactant of formulas (XIV) to (XXI) with a cocatalyst. Preferred surfactants include:



More preferably, the surfactant is:

XIX	XXI	XX
3-(Nonafluoro-tert-butyl)propan-1-ol	3,4,4,4-Tetrafluoro-3-(trifluoromethyl)butan-1-ol	1H,1H-Perfluoro(2-methyl-3-oxahexan-1-ol)

- In a preferred embodiment, the surfactant reacts with a compound contained in the catalyst solution. Such compound is preferably e.g. a cocatalyst, suitably an organoaluminium compound, such as an aluminium alkyl compound optionally comprising halogen or, preferably, in case of metallocenes, an aluminoxane compound (e.g. as known in the art). In one embodiment, this reaction is effected before the surfactant is added to the homogeneous solution of catalyst components. In the pre-reaction with the cocatalyst, especially aluminum compound, the molar ratio of the Al:surfactant is in the range of 10:1 to 5000:1, preferably in the range of 50:1 to 2000:1, more preferably in the range of 100:1 to 1000:1, especially in the range of 100:1 to 500:1. Thus, the addition of the pre-reacted surfactant may be added e.g. before the dispersing step of the catalyst solution. However, the surfactant may also be added to the formed emulsion system, whereby, preferably, the transition metal compound, e.g. a metallocene, is added to the dispersed phase after the

formation of the reaction product of the surfactant and said compound, e.g. a cocatalyst, of the emulsion system. After said reaction, if needed, the amount of said compound, e.g. a cocatalyst, in the catalyst solution may be increased with a further addition of the compound, either separately or e.g. together with the transition metal compound.

5 Preferably, the surfactant is reacted with a compound of the catalyst solution before the addition of the transition metal compound. In a preferred embodiment the surfactant is reacted with a cocatalyst, in the present invention preferably aluminoxane, present in the catalyst solution to form the "actual" surfactant. Then, an additional amount of cocatalyst and the transition metal compound, e.g. a metallocene, is added to said solution and the obtained
10 solution is dispersed to the solvent forming the continuous phase. The "actual" surfactant solution may be prepared before the dispersing step or in the dispersed system. If said solution is made before the dispersing step, then the prepared "actual" surfactant solution and the transition metal solution may be dispersed successively (e.g. the surfactant solution first) to the immiscible solvent, or be combined together before the dispersing step.

15 It is within the scope of the invention to use other emulsifying agents in addition to the surfactants defined above but this is not preferred.

Preparation of a Liquid/Liquid Emulsion

Suitable processes for dispersing the solution of catalyst components in the liquid
20 medium to form an emulsion is the use of a mechanical device as well as the use of ultrasound for mixing, as known to the skilled person. The process parameters, such as time of mixing, intensity of mixing, type of mixing, power employed for mixing, such as mixer velocity or wavelength of ultrasound employed, viscosity of solvent phase are used for adjusting the size of the catalyst system.

25 Regardless of the method used to form the emulsion, its temperature prior to solidifying the droplets is preferably -20 to +50 °C, more preferably -10 to +40 °C, yet more preferably -5 to 30 °C, and still more preferably 0 to 20 °C. Suitable temperature is dependent on the solvents used.

30 Droplet Size and Distribution

The droplet size and distribution of the formed dispersed phase can be selected or controlled in a manner known in the art, for example, by the choice of the device for emulsion formation and by the energy put into the emulsification. This, advantageously, may also allow for the size of the catalyst particles to be controlled. For instance, large droplets of

discontinuous phase will generally give rise to larger catalyst particles than smaller droplets. The droplet size needed to obtain any particular catalyst particle size may be readily deduced by the skilled man in the art.

5 Solidification

The solidification of the catalyst component(s) in the dispersed droplets can be effected in various ways, e.g. by causing or accelerating the formation of said solid catalyst forming reaction products of the compounds present in the droplets. This can be effected, depending on the used compounds and/or the desired solidification rate, with or without an external stimulus, such as a temperature change of the system.

In a particularly preferred embodiment, the solidification is effected after the emulsion system is formed by subjecting the system to an external stimulus, such as a temperature change. Temperature differences of e.g. 5 to 100°C, such as 10 to 100°C, or 20 to 90°C, such as 50 to 90°C are preferred.

The emulsion system may be subjected to a rapid temperature change to cause a fast solidification in the dispersed system. The dispersed phase may e. g. be subjected to an immediate (within milliseconds to few seconds) temperature change in order to achieve an instant solidification of the component (s) within the droplets. The appropriate temperature change, i. e. an increase or a decrease in the temperature of an emulsion system, required for the desired solidification rate of the components cannot be limited to any specific range, but naturally depends on the emulsion system, i.a. on the used compounds and the concentrations/ratios thereof, as well as on the used solvents, and is chosen accordingly. It is also evident that any techniques may be used to provide sufficient heating or cooling effect to the dispersed system to cause the desired solidification.

In one embodiment the heating or cooling effect is obtained by bringing the emulsion system with a certain temperature to an inert receiving medium with significantly different temperature, e. g. as stated above, whereby said temperature change of the emulsion system is sufficient to cause the rapid solidification of the droplets. The receiving medium can be gaseous, e. g. air, or a liquid, preferably a solvent, or a mixture of two or more solvents, wherein the catalyst component (s) is (are) immiscible and which is inert in relation to the catalyst component (s). For instance, the receiving medium comprises the same immiscible solvent used as the continuous phase in the first emulsion formation step.

Said solvents can be used alone or as a mixture with other solvents, such as aliphatic

or aromatic hydrocarbons, such as alkanes. Preferably a fluorinated solvent as the receiving medium is used, which may be the same as the continuous phase in the emulsion formation, e. g. perfluorinated hydrocarbon.

Alternatively, the temperature difference may be effected by gradual heating of the emulsion system, e. g. up to 10°C per minute, preferably 0.5 to 6°C per minute and more preferably in 1 to 5°C per minute.

In case a melt of e. g. a hydrocarbon solvent is used for forming the dispersed phase, the solidification of the droplets may be effected by cooling the system using the temperature difference stated above.

Preferably, the "one phase" change as usable for forming an emulsion can also be utilised for solidifying the catalytically active contents within the droplets of an emulsion system by, again, effecting a temperature change in the dispersed system, whereby the solvent used in the droplets becomes miscible with the continuous phase, preferably a fluorous continuous phase as defined above, so that the droplets become impoverished of the solvent and the solidifying components remaining in the "droplets" start to solidify. Thus the immiscibility can be adjusted with respect to the solvents and conditions (temperature) to control the solidification step.

The miscibility of e.g. organic solvents with fluorous solvents can be found from the literature and be chosen accordingly by a skilled person. Also the critical temperatures needed for the phase change are available from the literature or can be determined using methods known in the art, e. g. the Hildebrand-Scatchard-Theorie.

Thus according to the invention, the entire or only part of the droplet may be converted to a solid form. The size of the "solidified" droplet may be approximately the same or smaller than that of the original droplet. The solid catalyst particles recovered can be used, after an optional washing step, in a polymerisation process of an olefin. Alternatively, the separated and optionally washed solid particles can be dried to remove any solvent present in the particles before use in the polymerisation step. The separation and optional washing steps can be effected in a known manner, e. g. by filtration and subsequent washing of the solids with a suitable solvent.

The droplet shape of the particles may be substantially maintained. The formed particles may have an average size range of 1 to 500 µm, e.g. 5 to 500 µm, advantageously 5 to 200 µm or 10 to 150 µm. Even an average size range of 5 to 60 µm is possible. The size may be chosen depending on the polymerisation the catalyst is used for. Advantageously, the particles are essentially spherical in shape, they have a low porosity and a low surface area.

The formation of solution can be effected at a temperature of 0-100°C, e.g. at 20-80°C. The dispersion step may be effected at -20 °C-100°C, e.g. at about -10-70°C, such as at -5 to 30°C, e.g. around 0 °C.

To the obtained dispersion an emulsifying agent as defined above, may be added to improve/stabilise the droplet formation. The solidification of the catalyst component in the droplets is preferably effected by raising the temperature of the mixture, e.g. from 0 °C temperature up to 100°C, e.g. up to 60-90°C, gradually. E.g. in 1 to 180 minutes, e.g. 1-90 or 5-30 minutes, or as a rapid heat change. Heating time is dependent on the size of the reactor.

During the solidification step, which is preferably carried out at about 60 to 100 °C, preferably at about 75 to 95 °C, (below the boiling point of the solvents) the solvents may preferably be removed and optionally the solids are washed with a wash solution, which can be any solvent or mixture of solvents such as those defined above and/or used in the art, preferably a hydrocarbon, such as pentane, hexane or heptane, suitably heptane. The washed catalyst can be dried or it can be slurried into an oil and used as a catalyst-oil slurry in polymerisation process.

All or part of the preparation steps can be done in a continuous manner. Reference is made to WO2006/069733 describing principles of such a continuous or semicontinuous preparation methods of the solid catalyst types, prepared via emulsion/solidification method.

The formed catalyst preferably has good stability/kinetics in terms of longevity of reaction, high activity and the catalysts enable low ash contents.

Activities in gas phase of more than 12 kg polymer per g catalysts/h can be achieved, preferably at least 15 kg polymer per g catalyst /h.

Catalyst kinetics are also good. Catalysts should have at least a 30 minute period without any drop off in performance, preferably at least 1 h.

Isolation of Catalyst

The resulting solid catalyst particles may be separated and recovered from the catalyst suspension by any procedure known in the art. For example, the suspension may be filtered. Other commonly known methods for isolating are decanting, centrifuging and flotation.

The catalyst may then optionally be washed and/or dried to remove any solvent residuals present in the particles. The washing and/or drying of the catalyst particles may be carried out in any manner conventional in the art.

It will be appreciated that the process of the invention can be carried out in a continuous, rather than in a batch wise manner.

Resulting Catalyst Particles

The solid particles obtained from the process of the invention may have an average size range of 1 to 500 μm , particularly 5 to 500 μm , advantageously 5 to 200 μm , e.g. 10 to 100 μm , or even 10 to 50 μm . Advantageously the size can be controlled by varying the size of the droplets of dispersed phase obtained during the emulsification step. The present method may also enable catalyst particles with high catalytic activity to be prepared. These catalyst particles have uniform morphology, they are nicely spherical in shape, they have high bulk density and high loading. And as is clearly disclosed above, they do not contain any external carrier. Further, the catalyst particles obtained have very low porosity and a low surface area, e.g. of less than 100 m^2/g , preferably less than 50 m^2/g and more preferably less than 20 m^2/g , or even below 5 m^2/g , measured by the BET-method.

The catalyst particles obtained by the process of the present invention are highly homogenous in respect of their morphological characteristics (i.e. catalyst particles obtained by the process of the invention display a high level of consistency in their characteristics), as disclosed above. Due to the replica effect the polymers produced by using the catalyst produced by the process of the invention have the same kind of uniform particle morphology.

The catalyst system of the invention can be used alone or together with an additional cocatalyst(s) in the actual polymerisation step in a manner known in the art.

The solid catalysts can, if desired, be pre-polymerised off-line before feeding to the polymerisation process, which optionally might comprise a process pre-polymerisation step. Such off-line pre-polymerisation methods are described e.g. in WO2010052263, WO2010052264 and 2010052260.

Olefin Polymerisation

The olefin to be polymerised using the catalyst system of the invention can be any olefin polymerisable in a coordination polymerisation including an α -olefin alone or as a mixture with one or more comonomers. Preferred olefins are ethylene or propene, or a mixture of ethylene or propene with one or more α -olefin(s). Preferred comonomers are C_{2-12} olefins, preferably C_{4-10} olefins, such as 1-butene, isobutene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene-1-decene, as well as diene, such as butadiene, 1,7-octadiene and 1,4-hexadiene, or cyclic olefins, such as norbornene, and any mixtures thereof.

Polyethylene and polypropylene and any copolymers thereof are particularly contemplated. Most especially, the catalyst system is used for the polymerisation of propylene, e.g. propylene homopolymers or propylene copolymers with comonomers such as ethylene and butene. In any polypropylene, propylene forms the major comonomer residue present.

Furthermore, the catalyst system of the invention can be used for the polymerisation of long chain branched α -olefins (with 4 to 40 C-atoms), alone or together with short chain branched α olefins.

Polymerisation may be effected in one or more, e.g. one, two or three polymerisation reactors, using conventional polymerisation techniques, in particular gas phase, solution phase, slurry or bulk polymerisation. Polymerisation can be a batch or continuous polymerisation process. Generally a combination of slurry (or bulk) and at least one gas phase reactor is preferred, particularly with gas phase operation coming last.

For slurry reactors, the reaction temperature will generally be in the range of 60 to 115 °C, e.g. 80-110 °C, the reactor pressure will generally be in the range 5 to 80 bar, e.g. 50-60 bar, and the residence time will generally be in the range of 0.3 to 5 hours, e.g. 0.5 to 2 hours. The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100 °C. In such reactors, polymerisation may, if desired, be effected under supercritical conditions.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 110 °C, e.g. 70 to 95 °C, the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be non-reactive gas such as nitrogen or propane together with monomer (e.g. ethylene or propylene).

Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be used.

With the method of the invention a catalyst system with a high bulk density and a good morphology is obtained and the catalyst exhibits a high catalytic activity. The bulk density and morphology correlate with product bulk density and morphology - the so-called "replica effect". Thus the catalyst leads to a polymer with a higher bulk density than obtained with homogeneous systems of the prior art, without using an external support material. Accordingly, the catalyst of the method of the invention combines the advantages of the prior art homogeneous and heterogeneous catalyst systems.

The present invention is further described by way of the following non-limiting examples.

Examples

5

The present invention is further illustrated by the following Examples, in which parts and percentages are by weight and degrees are Celsius, unless otherwise stated. It should be understood that these Examples, while indicating preferred embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, various modifications of the invention in addition to those shown and described herein will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

15

Chemicals

As Metallocene (MC) was used rac-anti-dimethylsilanediyl(2-methyl-4-(p-tert-butylphenyl)inden-1-yl)(2-methyl-4-phenyl-5-methoxy-6-tert-butyl inden-1-yl) zirconium dichloride, as described in WO 2013/007650 (Metallocene E2). MAO (Chemtura) was used as a 30 wt-% solution in toluene. Trityl tetrakis(pentafluorophenyl)borate (Boulder Chemicals) was used as purchased. Perfluoroalkylethyl Acrylate Esters (CAS number 65605-70-1) (Cytonix corporation), dried over activated molecular sieves (2 times) and degassed by argon bubbling prior to use (Reference surfactant S0). 1H,1H-Perfluoro(2-methyl-3-oxahexan-1-ol (CAS number 26537-88-2) (Apollo Scientific) degassed by argon bubbling prior to use (Surfactant S3). 3-(Nonafluoro-tert-butyl)propan-1-ol (CAS number 14115-49-2) (Apollo Scientific), degassed by argon bubbling prior to use (Surfactant S1). 3,4,4,4-Tetrafluoro-3-(trifluoromethyl)butan-1-ol (CAS number 90999-87-4) (Apollo Scientific), degassed by argon bubbling prior to use (surfactant S2). Hexadecafluoro-1,3-dimethylcyclohexane (PFC) (CAS number 335-27-3) was obtained from commercial sources and dried over activated molecular sieves (2 times) and degassed by argon bubbling prior to use. Propylene is provided by Borealis and adequately purified before use. Triethylaluminum

25

30

was purchased from Crompton and used in pure form. Hydrogen is provided by AGA and purified before use.

All the chemicals and chemical reactions were handled under an inert gas atmosphere using Schlenk and glovebox techniques, with oven-dried glassware, syringes, needles or
5 cannulas.

Measurement methods:

Al and Zr determination (ICP-method)

The elementary analysis of a catalyst was performed by taking a solid sample of mass, M, cooling over dry ice. Samples were diluted up to a known volume, V, by dissolving in nitric acid (HNO₃, 65 %, 5 % of V) and freshly deionised (DI) water (5 % of V). The solution was then added to hydrofluoric acid (HF, 40 %, 3 % of V), diluted with DI water up to the
15 final volume, V, and left to stabilise for two hours.

The analysis was run at room temperature using a Thermo Elemental iCAP 6300 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) which was calibrated using a blank (a solution of 5 % HNO₃, 3 % HF in DI water), and 6 standards of 0.5 ppm, 1 ppm, 10 ppm, 50 ppm, 100 ppm and 300 ppm of Al, with 0.5 ppm, 1 ppm, 5 ppm,
20 20 ppm, 50 ppm and 100 ppm of Hf and Zr in solutions of 5 % HNO₃, 3 % HF in DI water.

Immediately before analysis the calibration is 'resloped' using the blank and 100 ppm Al, 50 ppm Hf, Zr standard, a quality control sample (20 ppm Al, 5 ppm Hf, Zr in a solution of 5 % HNO₃, 3 % HF in DI water) is run to confirm the reslope. The QC sample is also run after every 5th sample and at the end of a scheduled analysis set.

The content of hafnium was monitored using the 282.022 nm and 339.980 nm lines and the content for zirconium using 339.198 nm line. The content of aluminium was monitored via the 167.079 nm line, when Al concentration in ICP sample was between 0-10 ppm (calibrated only to 100 ppm) and via the 396.152 nm line for Al concentrations above 10 ppm.

The reported values are an average of three successive aliquots taken from the same sample and are related back to the original catalyst by inputting the original mass of sample and the dilution volume into the software.

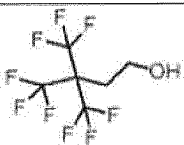
Melt Flow Rate

The melt flow rate (MFR) is determined according to ASTM D1238. The MFR is an indication of the flowability, and is inversely proportional to the viscosity. The higher the melt flow rate, the lower the viscosity. The MFR is determined at 230°C and may be determined at different temperatures.

5 (MFR₂₁).

Catalyst preparation examples

Table 1. Surfactants used in examples

S0 (Reference)	S1	S2
Perfluoroalkylethyl Acrylate Esters	 3-(Nonafluoro-tert-butyl)propan-1-ol	 3,4,4-trifluorobutyl acrylate ester

10

Comparative example CE

Inside the glovebox, 88.0 mg of metallocene MC

catalyst was left to settle up on top of the PFC and after 35 minutes the solvent was siphoned off. The remaining nice red catalyst was dried during 2 hours at 50 °C over an argon flow. 1.2 g of a red free flowing powder was obtained.

5 Inventive example IE1a

Inside the glovebox, 88.0 mg of metallocene MC was mixed with 4 ml of 30 wt.-% Chemtura MAO in a septum bottle and the solution was stirred for 60 minutes and then 105.0 mg of trityl tetrakis(pentafluorophenyl)borate was added. The mixture was left to react overnight at room temperature inside the glovebox. Then, in another septum bottle, 93.0 mg of dry and
10 degassed surfactant S1 was mixed with 2 mL of 30 wt.-% Chemtura MAO. The solutions were left under stirring overnight.

The following day, 1 mL of the surfactant-MAO solution to 4 mL of the MAO-MC-borate solution was added and left to react for 30 minutes. Then, 5 ml of

15 MAO/Borate/MC/surfactant solution was added into a 50mL emulsification glass reactor containing 40mL of PFC at -10 °C and equipped with an overhead stirrer (stirring speed = 600 rpm). A red emulsion formed immediately and stirred during 15 minutes at -10 °C / 600rpm. Then the emulsion was transferred via a 2/4 Teflon tube to 100 mL of hot PFC at 90 °C and stirred at 600rpm until the transfer is completed. Then the speed was reduced to 300
20 rpm. After 15 minutes stirring, the oil bath was removed and the stirrer turned off. The catalyst was left to settle up on top of the PFC and after 35 minutes the solvent was siphoned off. The remaining nice red catalyst was dried during 2 hours at 50 °C over an argon flow. 0.8 g of a red free flowing powder was obtained.

25 Inventive example IE1b

Catalyst of Inventive example IE1b was prepared according to the same procedure as in Inventive example IE1a, but 48.2 mg of dry and degassed surfactant S1 was mixed with 2 mL of 30 wt.-% Chemtura MAO. 0.7 g of a red free flowing powder was obtained.

30 Inventive example IE2

Catalyst of Inventive example IE2 was prepared according to the same procedure as in Inventive example IE1a, but 79.6 mg of dry and degassed surfactant S2 was mixed with 2 mL of 30 wt.-% Chemtura MAO. 0.7 g of a red free flowing powder was obtained.

Inventive example IE3a

Catalyst of Inventive example IE3a was prepared according to the same procedure as in Inventive example IE1a, but 62.0 mg of dry and degassed surfactant S3 was mixed with 2 mL of 30 wt.-% Chemtura MAO. 0.75 g of a red free flowing powder was obtained.

5

Inventive example IE3b

Catalyst of Inventive example IE3b was prepared according to the same procedure as in Inventive example IE1a, but 60.0 mg of dry and degassed surfactant S3 was mixed with 2 mL of 30 wt.-% Chemtura MAO. 0.77 g of a red free flowing powder was obtained.

10

Table 2. Summary of catalyst preparations

Catalyst	Surfactant	Surfactant amount /mg	Al/Surfactant ratio/ mol/mol
CE1	S0	43,3	250
IE1a	S1	48.0	125
IE1b	S1	24,1	250
IE2	S2	39,8	125
IE3a	S3	31,0	250
IE3b	S3	30,0	250

Table 3. Catalyst elemental analysis.

Catalyst	ICP analysis		
	Al- wt%	Zr- wt%	Al/Zr mol/mol
CE1	27,5	0,45	206
IE1a	30,5	0,53	194
IE1b	30,9	0.55	190

IE2	31,3	0,51	207
IE3a	31,8	0,50	215
IE3b	31,5	0,55	193

Polymerisation

All the catalysts in the series were tested in the 5 L polymerisation reactor. 250 μ l of triethylaluminum was fed as a scavenger in 5 mL of dry and degassed pentane. Then 6 mmol of hydrogen was loaded (measured in mmol) and 1400 g of liquid propylene (purified via columns filled with copper-catalyst, molecular sieves and Selexsorb COS) was fed into the reactor. The temperature was set to 20 °C. The desired amount of catalyst (5 to 10 mg) in 5mL of PFC is flushed into the reactor with a nitrogen overpressure. After 5 minutes (prepolymerisation) the temperature is raised to 70 °C over a period of 15 minutes. The polymerisation is stopped after 60 minutes by venting the reactor and flushing with nitrogen before the polymer is collected.

The catalyst activity was calculated on the basis of the 60 minutes period according to the following formula:

$$\text{Catalyst Activity (kg/(g(cat)*h))} = \frac{\text{amount of polymer produced (kg)}}{\text{catalyst loading (g)} \times \text{polymerisation time (h)}}$$

Table 4. Propylene homopolymerisation (H₂=6 mmol) results using comparative and inventive catalysts.

	Yield (g)	Activity (kg- PP/g- Cat/h)	MFR ₂₁ (g/10min)
CE1	424,9	59,8	27,20
IE1a	561,5	56,7	31,5
IE1b	528,0	57,4	21,90
IE2	475,2	55,9	27,30
IE3a	581,9	71,0	22,60
IE3b	524,5	61,7	32,70

Claims

1. A process for producing an olefin polymerisation catalyst comprising an organometallic compound of a transition metal of Group 3 to 10 of the Periodic Table (IUPAC), or of an actinide or lanthanide and a cocatalyst in the form of solid particles, said organometallic compound having the formula (I):



wherein

“M” is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007) or of an actinide or lanthanide,

each “X” is independently a monoanionic ligand, such as a σ -ligand,

each “L” is independently an organic ligand which coordinates to the transition metal

“M”,

“R” is a bridging group linking said organic ligands (L),

“m” is 1, 2 or 3, preferably 2

“n” is 0, 1 or 2, preferably 1,

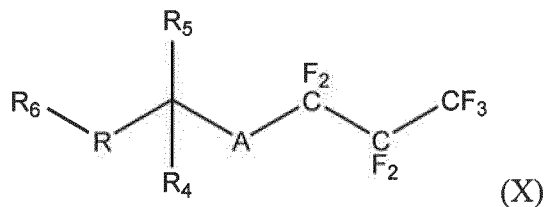
“q” is 1, 2 or 3, preferably 2 and

m+q is equal to the valency of the transition metal (M);

said process comprising the steps of:

- a) preparing a homogenous solution of one or more catalyst components including said organometallic compound of formula (I);
- b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;
- c) solidifying said dispersed phase to convert said droplets to solid particles, and
- d) optionally recovering said particles to obtain said catalyst;

characterised in that an emulsifying agent is present during the formation of said emulsion system and said emulsifying agent comprises a compound of formula (X):



wherein

R₆ is HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C-, or CF₃(O)C-

A is -O-, a covalent bond or CF₂;

5 R₄ is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

R₅ is -H, -F, -CF₃, -Me, -CF₂CF₃, or ethyl;

R is -CF₂-, (-CH₂)_n-, -CF₂CF₂-, or a covalent bond

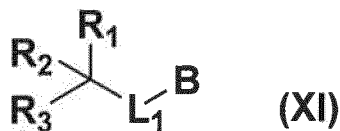
n is 1 to 2;

with the proviso that compound (X) is not a perfluoroalcohol or perfluorocarboxylic

10 acid;

or a salt thereof, e.g. a NH₄⁺, Na⁺, or K⁺ salt;

or a compound of formula (XI)



15

wherein

R₁, R₂, and R₃ are independently selected from any one of F, -CF₃ or CF₃CF₂-
provided at least one R group is -CF₃;

20 L₁ is a linear or branched C₁₋₆ alkyl group wherein each C atom is substituted with 0, 1, 2 or 3 F atoms, and optionally said alkyl group contains an ether linkage;

B is selected from HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C- or CF₃(O)C-;
or a salt thereof.

25 2. A process for producing an olefin polymerisation catalyst comprising an organometallic compound of a transition metal of Group 3 to 10 of the Periodic Table (IUPAC), having the formula (I):



wherein

“M” is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007) or an actinide or lanthanide,

each “X” is independently a monoanionic ligand, such as a σ -ligand,

each “L” is independently an organic ligand which coordinates to the transition metal “M”,

“R” is a bridging group linking said organic ligands (L),

“m” is 1, 2 or 3, preferably 2

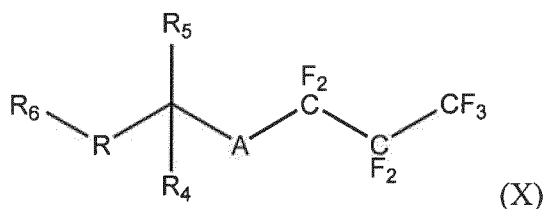
“n” is 0, 1 or 2, preferably 1,

“q” is 1, 2 or 3, preferably 2 and

m+q is equal to the valency of the transition metal (M); in the form of solid particles, comprising the steps of:

- a) preparing a homogenous solution of one or more catalyst components including said organometallic compound of formula (I);
- b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;
- c) solidifying said dispersed phase to convert said droplets to solid particles, and
- d) optionally recovering said particles to obtain said catalyst;

characterised in that an emulsifying agent is present during the formation of said emulsion system and said emulsifying agent comprises the reaction product of (i) a compound of formula (X):



wherein

R₆ is HO-, HO(O)C-, H(O)C-, F(O)C-, CH₃(O)C-, or CF₃(O)C-

A is -O-, a covalent bond or CF₂;

R₄ is -H, -F, -CF₃, -Me, CF₂CF₃, or ethyl;

R₅ is -H, -F, -CF₃, -Me, CF₂CF₃, or ethyl;

R is -CF₂, (-CH₂)_n, -CF₂CF₂- or a covalent bond

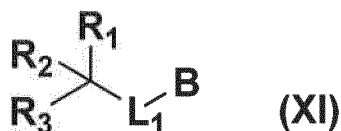
n is 1 to 2;

with the proviso that compound (X) is not a perfluoroalcohol or perfluorocarboxylic acid;

or a salt thereof, e.g. a NH_4^+ , Na^+ , K^+ salt

5

or a compound of formula (XI)



10

wherein

R_1 , R_2 , and R_3 are independently selected from any one of F, $-\text{CF}_3$ or CF_3CF_2- provided at least one R group is $-\text{CF}_3$;

L_1 is a linear or branched C_{1-6} alkyl group wherein each C atom is substituted with 0, 1, 2 or 3 F atoms, and optionally said alkyl group contains an ether linkage;

15

B is selected from $\text{HO}-$, $\text{HO}(\text{O})\text{C}-$, $\text{H}(\text{O})\text{C}-$, $\text{F}(\text{O})\text{C}-$, $\text{CH}_3(\text{O})\text{C}-$ or $\text{CF}_3(\text{O})\text{C}-$; or a salt thereof; and

(ii) a cocatalyst.

20

3. A process according to claim 1 to 2 wherein the homogeneous solution of one or more catalyst components comprises a solvent selected from a linear, branched or cyclic alkane or alkene, an aromatic hydrocarbon and/or a halogen-containing hydrocarbon or a mixture thereof.

25

4. A process according to any preceding claim wherein the emulsifying agent is added to the catalyst solution which forms the dispersed phase of the emulsion.

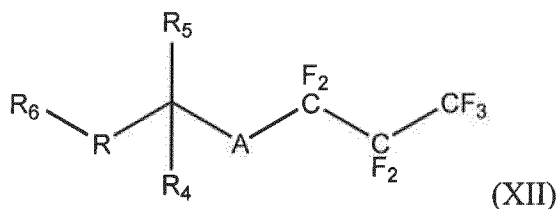
5. A process according to claim 1 to 4 wherein the homogeneous solution of one or more catalyst components comprises an A1 or B cocatalyst.

30

6. A process according to any preceding claim wherein said immiscible solvent comprises a semi, highly or perfluorinated hydrocarbon or mixture thereof.

7. A process according to claim 6 wherein said immiscible solvent comprises a perfluorohydrocarbon, preferably C3-C30 perfluoroalkanes, -alkenes or -cycloalkanes, more preferred C4-C10 perfluoroalkanes, -alkenes or -cycloalkanes, particularly preferred perfluorohexane, perfluoroheptane, perfluorooctane or perfluoro(methylcyclohexane) or a mixture thereof.

8. A process according to any preceding claim wherein said emulsifying agent is a surfactant of formula (XII) or a reaction product of the surfactant of formula (XII) with a cocatalyst;



wherein R_6 is HO- , HO(O)C- , or F(O)C- ;

A is $-\text{O-}$;

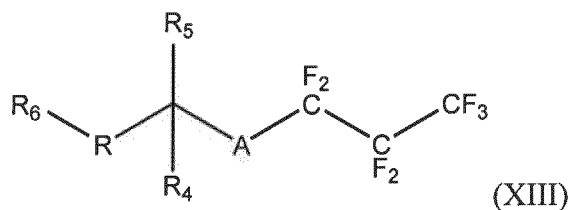
R_4 is $-\text{F}$, or $-\text{CF}_3$;

R_5 is $-\text{F}$ or $-\text{CF}_3$;

R is $-\text{CH}_2-$ or a covalent bond

or a salt thereof.

9. A process according to claim 1 to 7 wherein the emulsifying agent is a surfactant of formula (XIII) or a reaction product of the surfactant of formula (XIII) with a cocatalyst



wherein

R_6 is HO- , HO(O)C- , or F(O)C- ;

A is a covalent bond or $-\text{CF}_2-$;

R_4 is $-\text{H}$, or $-\text{F}$;

R_5 is -H, or -F;

R is $(-CH_2)_n$ or a covalent bond

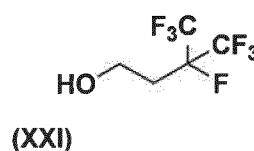
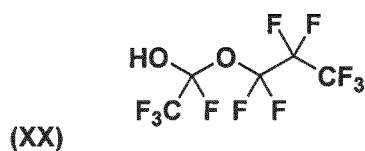
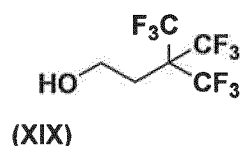
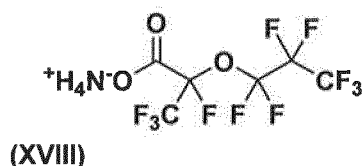
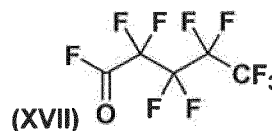
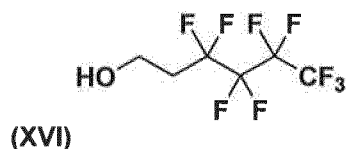
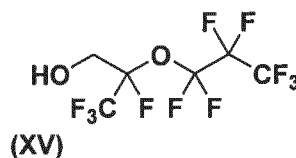
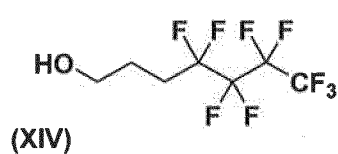
n is 1 to 2;

or a salt thereof; with the proviso that compound (XIII) is not a perfluoroalcohol or

5 perfluorocarboxylic acid.

10. A process according to any preceding claim wherein B is OH; and the L_1 group is free of F atoms.

10 11. A process according to any preceding claim wherein the surfactant is selected from compounds of formulas (XIV) to (XXI)



15 12. A process according to claim 2 wherein said emulsifying agent is prepared by reacting said surfactant with a cocatalyst compound, preferably aluminoxane.

13. A process as claimed in claims 12 wherein the reaction product of said surfactant and aluminoxane is added to the homogenous solution of one or more catalyst components.

14. A process as claimed in claim 12 or 13 wherein the molar ratio of the Al:surfactant is in the range of 10:1 to 5000:1, preferably in the range of 50:1 to 2000:1, more preferably in the range of 100:1 to 1000:1, especially in the range of 100:1 to 500:1.

5 15. A process according to any preceding claim wherein the molar ratio in the catalyst of cocatalyst Al or B, to metal M is Al/M is 1:1 to 10,000:1, preferably 5:1 to 8000:1, 10:1 to 500:1, such as 100:1 to 300:1 or B/M 5:1 to 1:5.

10 16. A process according to any preceding claim wherein the solidification is effected by a temperature change treatment.

17. A process according to any preceding claim wherein the transition metal compound is a compound of formula (III)

15 $(Cp)_mR_nMX_q$ (III)

wherein

each Cp independently is substituted or unsubstituted cyclopentadienyl or a bi- or multicyclic derivative of a cyclopentadienyl which optionally bear further substituents; d;

20 R is a divalent bridge selected from $-R'_2C-$, $-R'_2Si-$, wherein each R' is independently a hydrogen atom, C_1 to C_{20} alkyl, C_2 to C_{10} cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} arylalkyl and C_7 - C_{20} -alkylaryl;

M is a transition metal of Group 4 to 6, such as Group 4, e.g. Ti, Zr or Hf,

each X is independently a sigma-ligand,

25 n is 0, or 1, e.g. 1;

m is 1, 2 or 3, e.g. 1 or 2, preferably 2;

q is 1, 2 or 3, e.g. 2 or 3, preferably 2;

wherein $m+q$ is equal to the valency of M.

30 18. A process for (co) polymerising an olefin in the presence of a catalyst produced by the process of claim 1 to 17.

19. Use of a compound of formula (X) or (XI) as claimed in claim 1 or the reaction product of a compound of formula (X) or (XI) and a cocatalyst as an emulsifying agent in a process comprising

- 5 a) preparing a homogenous solution of one or more catalyst components and a cocatalyst;
- b) dispersing said solution in a solvent immiscible therewith to form a liquid/liquid emulsion system in which said one or more catalyst components are present in the droplets of the dispersed phase;
- c) solidifying said dispersed phase to convert said droplets to solid particles, and
- 10 d) optionally recovering said particles to obtain said catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/079592

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F4/6592 C08F110/06 C08F4/659 B01J31/02 B01J37/03
B01J31/04 B01J31/14 B01J31/16 B01J31/22

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/051934 A2 (BOREALIS TECH OY [FI]; DENIFL PETER [AT]; VAN PRAET ERIK [SE]; BARTKE) 26 June 2003 (2003-06-26) cited in the application	1-7,12, 13,15-19
Y	page 32 - page 33; example 1 page 33, line 21 - page 34, line 8 page 3, line 28 - page 4, line 3 ----- -/--	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Luka, Martin

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/079592

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	US 2009/137773 A1 (JACKSON ANDREW [US] ET AL) 28 May 2009 (2009-05-28) page 7, scheme 1 -----	1-19
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