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(54) Title: PROCESS FOR THE POLYMERIZATION OF OLEFINS

(57) Abstract: The present invention relates to processes for the polymerization of olefins that reduces the concentration of impurities present in olefin-containing hydrocarbon feedstock and/or diluent, by passing said feedstock and/or said diluent, over a sorbent material comprising a compound deposited on silica, wherein said compound is selected from dialkyl or trialkyl aluminoxane, dialkyl or trialkyl aluminoxane halide.



PROCESS FOR THE POLYMERIZATION OF OLEFINS

Field of the invention

The present invention relates to a process for the polymerization of olefins. More in particular the present invention relates to a process for the polymerization of ethylene or propylene.

Background of the invention

Polyolefins, such as polyethylene (PE), are synthesized by polymerizing monomers, such as ethylene ($\text{CH}_2=\text{CH}_2$). Because they are cheap, safe, stable to most environments and easy to be processed polyolefins are useful in many applications. Polyethylene can be classified into several types, such as but not limited to LDPE (Low Density Polyethylene), LLDPE (Linear Low Density Polyethylene), and HDPE (High Density Polyethylene) as well as High Molecular Weight (HMW), Medium Molecular Weight (MMW) and Low Molecular Weight (LMW). Each type of polyethylene has different properties and characteristics.

Olefin polymerization processes are usually carried out in a reactor using olefin monomer, optionally one or more co-monomer(s), a catalyst, optionally diluent, and optionally hydrogen.

Various types of catalysts can be used for the polymerization process, being metallocene catalysts increasingly prevalent in the industry due to their improved product qualities.

Unfortunately most catalytic systems are expensive and very sensitive to impurities. Their activities can be severely limited by impurities –or poisons– present in the monomer, diluent or hydrogen feed.

The amounts of impurities can fluctuate from olefin source to olefin source, thereby causing catalyst activities to fluctuate as well, resulting in non-controlled polymerization processes. Needless to say, precise control over functional product structure is an essential requirement for designing and synthesizing polyolefins because the structure of the resultant macromolecule is intimately linked to its material properties, which ultimately determines the potential applications of the polymeric material.

Accordingly, there is a need for alternative and improved polymerization processes with reduced poisoning of the catalysts.

Summary of the invention

It is an object of the present invention to purify an olefin-containing hydrocarbon feed and/or a diluent feed.

According to a first aspect, the invention relates to a process for the polymerization of olefins comprising the following steps in this order:

(a1) passing at least one diluent over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound deposited on silica; wherein
5 said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b1) feeding said diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the
10 presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

According to a second aspect, the invention relates to a process for the polymerization of olefins comprising the following steps in this order:

(a2) passing at least one olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound
15 deposited on silica, or modified silica containing any other metal oxide or metal, wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b2) feeding said at least one olefin-containing hydrocarbon feedstock, and a diluent into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the
20 presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

With the processes according to the invention, it has been unexpectedly found that the compound as described herein supported on silica, acts as sorbent material reacting
25 with impurities present in an olefin-containing feedstock or diluent. By substantially removing impurities, the catalyst activity during the polymerization process can remain constant. Hence, polymerization conditions no longer need to be continuously adjusted and the polymer product melt flow indices are stabilized.

The processes of the present invention are capable of improving productivities and
30 activities of catalysts such as metallocene catalysts by reducing the concentration of impurities present in the diluent and/or in the olefin-containing hydrocarbon feed. The original concentration of impurities may be as high as 1000 ppm or higher depending on the process used to produce the original feedstock or diluent. In some embodiments, it

can be advantageous to carry out in advance known purification processes such as distillation or the use of molecular sieves prior to the process of the present invention.

Brief description of the figures

5 Figure 1 schematically illustrates a set up according to an embodiment of the present invention.

Figure 2 schematically illustrates a set up according to another embodiment of the present invention.

Description of the invention

10 The independent and dependent claims set out particular and preferred features of the invention. Features from the dependent claims may be combined with features of the independent or other dependent claims as appropriate.

15 In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

20 Before the present method and products of the invention are described, it is to be understood that this invention is not limited to particular methods, components, products or combinations described, as such methods, components, products and combinations may, of course, vary. It is also to be understood that the terminology used herein is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

As used herein, the singular forms "a", "an", and "the" include both singular and plural referents unless the context clearly dictates otherwise.

25 The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. It will be appreciated that the terms "comprising", "comprises" and "comprised of" as used herein comprise the terms "consisting of", "consists" and "consists of".

30 The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within the respective ranges, as well as the recited endpoints.

The term “about” or “approximately” as used herein when referring to a measurable value such as a parameter, an amount, a temporal duration, and the like, is meant to encompass variations of +/-10% or less, preferably +/-5% or less, more preferably +/-1% or less, and still more preferably +/-0.1% or less of and from the specified value, insofar
5 such variations are appropriate to perform in the disclosed invention. It is to be understood that the value to which the modifier “about” refers is itself also specifically, and preferably, disclosed.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in
10 the art to which this invention belongs. By means of further guidance, definitions for the terms used in the description are included to better appreciate the teaching of the present invention.

Reference throughout this specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with the
15 embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this
20 disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the claims, any of the claimed embodiments can be used in any
25 combination.

All documents cited in the present specification are hereby incorporated by reference in their entirety.

According to the first aspect of the invention, a diluent is first passed over a sorbent zone comprising a sorbent material prior to being introduced into a polymerization reactor.

30 In an embodiment, the process comprises the following steps in this order:

(a1) passing at least one diluent over a sorbent zone comprising a sorbent material trapped therein, wherein said sorbent material comprises a compound deposited on silica; wherein said compound is selected from dialkyl aluminoxane, trialkyl

aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide; said sorbent material remaining in said sorbent zone, at the end of step (a1);

(b1) feeding said diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

- 5 (c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin.

Step (a1) of the process comprises passing at least one diluent over a sorbent zone comprising a sorbent material trapped within said sorbent zone, wherein the sorbent material comprises i) a compound deposited on silica, wherein said compound is selected
10 from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide, trityl borate, fluorinated borane, and anilinium borate, more preferably dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide. Step (a1) comprises purifying the diluent over a bed of sorbent material comprising a compound deposited on silica. The diluent at the end of step (a1) is
15 free of sorbent material.

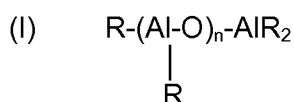
As used herein, the term "diluent" refers to diluents in a liquid or gas state, liquid or gas at room temperature or preferably liquid under pressure conditions.

Diluents which are suitable for being used in accordance with the present invention may comprise but are not limited to hydrocarbon diluents such as aliphatic, cycloaliphatic and
20 aromatic hydrocarbon solvents, or halogenated versions of such solvents. The preferred solvents are C12 or lower, straight chain or branched chain, saturated hydrocarbons, C5 to C9 saturated alicyclic or aromatic hydrocarbons or C2 to C6 halogenated hydrocarbons. Non-limiting illustrative examples of solvents are butane, isobutane, pentane, hexane, isohexane, heptane, cyclopentane, cyclohexane, cycloheptane, methyl
25 cyclopentane, methyl cyclohexane, isooctane, benzene, toluene, xylene, chloroform, chlorobenzenes, tetrachloroethylene, dichloroethane and trichloroethane. Suitable diluents which can be used for gas phase polymerization include nitrogen gas. Preferably the diluent is selected from the group comprising isobutane, nitrogen, hexane, isohexane, pentane, heptane. Preferably, the diluent is isobutane or nitrogen. In a more preferred
30 embodiment, said diluent is isobutane. However, it should be clear from the present invention that other diluents may as well be applied according to the present invention.

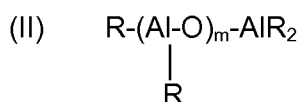
Suitable compounds deposited on silica may be selected from methylaluminoxane, ethylaluminoxane, n-butylaluminoxane, and isobutylaluminoxane. Examples of boron-containing compounds which can be deposited on silica include, among other, trityl

borate, fluorinated borane, and anilinium borate. Suitable boron-containing compounds may also be selected from a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP 0427696, or those of the general formula $[L'-H] + [B \text{ Ar1 Ar2 X3 X4}]^-$ as described in EP 0277004 (page 6, line 30 to page 7, line 7).

The alumoxanes (also referred as aluminoxanes) that may be used in the process of the present invention are well known by the person skilled in the art and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (I) or (II):



for oligomeric, linear alumoxanes and



for oligomeric, cyclic alumoxane,

wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_{1-8} alkyl group and preferably methyl.

Generally, in the preparation of alumoxanes, for example, methylalumoxane (MAO), a mixture of linear and cyclic compounds can be obtained. Preferred alumoxanes are MethylAluminOxane (MAO), and modified MAO.

In one embodiment, the aluminoxane is methylaluminoxane, ethylaluminoxane, *n*-butylaluminoxane, or isobutylaluminoxane.

Preferably, the sorbent material is immobilized within the sorbent zone, and preferably provided as a sorbent bed.

Suitable sorbent material comprising a compound deposited on silica can be commercially available from for instance Albermarle Corp. Alternatively, the material may be prepared according to the procedure described in US2003/0236365, in Journal of Molecular Catalysis, 260(1-2), pp 21 5-220 (2006), or in Journal of Applied Polymer Science, Vol. 80, pp 454-466 (2001), each of which are herein incorporated by reference. For example the compound can be deposited on the silica support by dissolving the compound in a suitable solvent, mixing the solution with the silica support and precipitating the compound, and subsequently washing and drying the precipitate.

As used herein the term "silica" encompasses silicon based oxide such as silicon oxide per se without precluding the presence of additional metals or metal oxides. In a preferred embodiment the silica is silicon oxide of stoichiometry equal to or close to SiO_2 . In some embodiment, the silica is silicon oxide of stoichiometry equal to or close to SiO_2 with a
5 purity greater than 90%.

The total weight of compound may represent from 10 wt. % up to 80 wt. % based on the total weight of the sorbent material. Accordingly, the sorbent material may include 20 to 90 wt.% of silica.

The specific surface area of the sorbent material can be between 100 and 900 m^2/g , for
10 example from 100 to 600 m^2/g . In an embodiment, the silica has a pore volume between 0.5 and 4 ml/g.

The silica onto which the compound is deposited may be amorphous or crystalline and of any grade usually used in polymerization reactions. In one embodiment, the silica has an average particle size D50 of 3 to 100 μm , preferably of 5 to 50 μm .

15 The D50, also expressed as $d(v0.5)$, is defined as the particle size value for which fifty percent by volume of the distribution of the particles has a size below this value. The D50 is measured by laser diffraction analysis on a Malvern type analyzer after having put the material to be measured in suspension, for instance in cyclohexane. Suitable Malvern systems include the Malvern 2000, Malvern 2600 and Malvern 3600 series. The Malvern
20 MasterSizer may also be useful as it can more accurately measure the D50 towards the lower end of the range e.g. for average particle sizes of less 8 μm , by applying the theory of Mie, using appropriate optical means.

The sorbent material can be prepared ex situ and stored either under a convenient saturated liquid hydrocarbon, like cyclohexane or dodecane, or under a non-oxidizing
25 atmosphere like nitrogen gas (N_2).

In one embodiment, the sorbent material further comprises a metal selected from nickel, chromium, iron, cobalt, copper, ruthenium, palladium, silver, and platinum, or a metal oxide selected from nickel oxide, copper oxide, zinc oxide, zirconium oxide, and manganese oxide. The metal or metal oxide is preferably dispersed on the silica support
30 in a range of from 0.01 to about 10 wt. % (i.e. 10% by weight) based on the total weight of the sorbent material.

Optionally, additional sorbents may be used in combination with the sorbent material. These can act as guard beds and as a result, the sorbent material's overall lifetime is

increased. The additional sorbents can be any sorbent known to a person skilled in the art. Examples of possible additional sorbents are metal oxides such as copper oxide, zinc oxide, zirconium oxide or manganese oxide, palladium, platinum, and molecular sieves such as 3A, 4A, 5A or 13X, as well as copper/copper oxide sorbents.

- 5 In one embodiment, the at least one diluent is also passed over one or more of the following molecular sieves, such as 3A and/or 13X molecular sieves.

In a preferred embodiment, the at least one diluent is passed first over 3A molecular sieves, and then over a sorbent material as described herein above.

- 10 In one embodiment, the at least one diluent is passed first over 13X molecular sieves, and then over a sorbent material as described herein above. In a preferred embodiment, the at least one diluent is passed first over 3X molecular sieves, and then over a sorbent material as described herein above.

In a preferred embodiment, the at least one diluent is passed first over 3A molecular sieves, then through the 13X and then through a sorbent material as described above.

- 15 The present invention therefore encompasses also processes comprising the following steps in this order:

(i) optionally passing at least one diluent over 3A molecular sieves;

(ii) optionally passing said diluent over 13X molecular sieves;

- 20 (a1) passing said diluent over a zone comprising a sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

(b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

- 25 (c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

The present invention therefore encompasses also processes comprising the following steps in this order:

(i) optionally passing at least one diluent over 3A molecular sieves;

- 30 (ii) optionally passing said diluent over 13X molecular sieves;

(a1) passing said diluent over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

5 (b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

Preferably, said process comprises

(i) passing at least one diluent over 3A molecular sieves;

10 (ii) optionally passing said diluent over 13X molecular sieves;

(a1) passing said diluent over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

15 (b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

More preferably, said process comprises successively:

(i) passing at least one diluent over 3A molecular sieves;

20 (ii) passing said diluent over 13X molecular sieves;

(a1) passing said diluent over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

25 (b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

In one embodiment, the sorbent material is provided as a sorbent bed in the sorbent zone.

30 In an embodiment, the sorbent material is provided in an elongated cylindrical vertical structure, preferably as a sorbent bed. Preferably this elongated cylindrical vertical structure has a length to diameter (L/D) ratio of at least 2.

The flow rate of the diluent over the sorbent zone, i.e. the liquid or gas hourly space velocity (LHSV or GHSV, respectively) can vary from 1 to 150 l/l.h. The size of the sorbent bed can be adjusted according to the LHSV and the GHSV.

5 As used herein the term "gas hourly space velocity or "GHSV" refers to the numerical ratio of the rate at which a fluid as gas is charged to a sorbent zone in liters per hour at standard condition of temperature and pressure (for example at about 40bar, and at room temperature) divided by the liters of sorbent material contained in such zone to which the fluid is charged.

10 As used herein the term "liquid hourly space velocity or "LHSV" refers to the numerical ratio of the rate at which a liquid is charged to a sorbent zone in liters per hour at standard condition of temperature and pressure (for example at about 40 bar, and at room temperature) divided by the liters of sorbent material contained in such zone to which the fluid is charged.

In an embodiment, the sorbent material can be regenerated at the end of step (a1).

15 Step (a1) of passing at least one diluent over a sorbent zone can be performed at room temperature.

In an embodiment, the diluent such as isobutane can be passed over the sorbent zone at a liquid hourly space velocity (LHSV) of from 1 to 120 l/l.h, more preferably of from 5 to 20 l/l.h, preferably at room temperature. Preferably, the diluent is isobutane and is passed
20 over the sorbent zone at a liquid hourly space velocity (LHSV) of from 5 to 20 l/l.h.

In an embodiment, said sorbent material further comprises a single site metallocene catalyst or an iron complex catalyst, also deposited on the silica. In this embodiment, the sorbent material can be discarded or regenerated at the end of step (a1). In an embodiment, the sorbent material is used to clean the diluent and is then is discarded.

25 The terms "single site metallocene catalyst" or "metallocene catalyst" refer to compounds of Group IV transition metals of the Periodic Table such as titanium, zirconium, hafnium, etc., and have a coordinated structure with a metal compound and ligands composed of one or two groups of cyclo-pentadienyl, indenyl, fluorenyl or their derivatives.

30 The term "iron complex catalyst" refers to a non-single site iron complex catalyst. Non-limiting examples of suitable complex catalysts include ferrocene-substituted bis(imino) pyridine iron and cobalt complexes disclosed by Gibson et al. in Gibson V.C., Long N.J., Oxford, P.J. , White A.J. P., and Williams D.J., in Organometallics ASAP article DOI: 10.1021/om0509589 or the ferrocene-substituted bis(imino) nickel and palladium

complexes disclosed by Gibson et al. in J. Chem. Soc. Dalton Trans 2003, 918-926, or the iron complexes disclosed in WO2010/034461 such as iron complex comprising tridentate ligand.

In an embodiment, the metallocene catalyst has a general formula (III) or (IV):

5 $(Ar)_2MQ_2$ (III); or

$R^1(Ar)_2MQ_2$ (IV)

wherein the metallocenes according to formula (III) are non-bridged metallocenes and the metallocenes according to formula (IV) are bridged metallocenes;

10 wherein said metallocene according to formula (III) or (IV) has two Ar bound to M which can be the same or different from each other;

 wherein Ar is an aromatic ring, group or moiety and wherein each Ar is independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, wherein each of said groups may be optionally substituted with one or more substituents each independently selected from the group consisting of halogen, a hydrosilyl, a SiR^2_3 group wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl and P;

 wherein M is a transition metal M selected from the group consisting of titanium, zirconium, hafnium and vanadium; and preferably is zirconium;

20 wherein each Q is independently selected from the group consisting of halogen; a hydrocarboxy having 1 to 20 carbon atoms; and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl and P; and

 wherein R^1 is a divalent group or moiety bridging the two Ar groups and selected from the group consisting of a C_1 - C_{20} alkylene, a germanium, a silicon, a siloxane, an alkylphosphine and an amine, and wherein said R^1 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, a hydrosilyl, a SiR^3_3 group wherein R^3 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl and P.

The term "hydrocarbyl having 1 to 20 carbon atoms" as used herein is intended to refer to a moiety selected from the group comprising a linear or branched C_1 - C_{20} alkyl; C_3 - C_{20}

cycloalkyl; C₆-C₂₀ aryl; C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl, or any combinations thereof. Exemplary hydrocarbonyl groups are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, and phenyl. Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, fluorine and chlorine are preferred.

As used herein, the term "alkyl", by itself or as part of another substituent, refers to straight or branched saturated hydrocarbon group joined by single carbon-carbon bonds having 1 or more carbon atom, for example 1 to 12 carbon atoms, for example 1 to 6 carbon atoms, for example 1 to 4 carbon atoms. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Thus, for example, C₁₋₁₂alkyl means an alkyl of 1 to 12 carbon atoms. Examples of alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl, 2-methylbutyl, pentyl and its chain isomers, hexyl and its chain isomers, heptyl and its chain isomers, octyl and its chain isomers, nonyl and its chain isomers, decyl and its chain isomers, undecyl and its chain isomers, dodecyl and its chain isomers. Alkyl groups have the general formula C_nH_{2n+1}.

As used herein, the term "cycloalkyl", by itself or as part of another substituent, refers to a saturated or partially saturated cyclic alkyl radical. Cycloalkyl groups have the general formula C_nH_{2n-1}. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Thus, examples of C₃₋₆cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, or cyclohexyl.

As used herein, the term "aryl", by itself or as part of another substituent, refers to a radical derived from an aromatic ring, such as phenyl, naphthyl, indanyl, or 1,2,3,4-tetrahydro-naphthyl. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain.

As used herein, the term "alkylaryl", by itself or as part of another substituent, refers to an aryl group as defined herein, wherein a hydrogen atom is replaced by an alkyl as defined herein. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group or subgroup may contain.

As used herein, the term "arylalkyl", by itself or as part of another substituent, refers to an alkyl group as defined herein, wherein a hydrogen atom is replaced by an aryl as defined herein. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Examples of C₆-

₁₀arylC₁₋₆alkyl radicals include benzyl, phenethyl, dibenzylmethyl, methylphenylmethyl, 3-(2-naphthyl)-butyl, and the like.

As used herein, the term “alkylene”, by itself or as part of another substituent, refers to alkyl groups that are divalent, i.e., with two single bonds for attachment to two other groups. Alkylene groups may be linear or branched and may be substituted as indicated herein. Non-limiting examples of alkylene groups include methylene (-CH₂-), ethylene (-CH₂-CH₂-), methylmethylene (-CH(CH₃)-), 1-methyl-ethylene (-CH(CH₃)-CH₂-), n-propylene (-CH₂-CH₂-CH₂-), 2-methylpropylene (-CH₂-CH(CH₃)-CH₂-), 3-methylpropylene (-CH₂-CH₂-CH(CH₃)-), n-butylene (-CH₂-CH₂-CH₂-CH₂-), 2-methylbutylene (-CH₂-CH(CH₃)-CH₂-CH₂-), 4-methylbutylene (-CH₂-CH₂-CH₂-CH(CH₃)-), pentylene and its chain isomers, hexylene and its chain isomers, heptylene and its chain isomers, octylene and its chain isomers, nonylene and its chain isomers, decylene and its chain isomers, undecylene and its chain isomers, dodecylene and its chain isomers. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. For example, C₁-C₂₀ alkylene refers to an alkylene having between 1 and 20 carbon atoms.

Suitable examples of metallocene catalysts comprise but are not limited to bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂), bis(cyclopentadienyl) titanium dichloride (Cp₂TiCl₂), bis(cyclopentadienyl) hafnium dichloride (Cp₂HfCl₂); bis(tetrahydroindenyl) zirconium dichloride, bis(indenyl) zirconium dichloride, and bis(n-butyl-cyclopentadienyl) zirconium dichloride; ethylenebis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride, ethylenebis(1-indenyl) zirconium dichloride, dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride, diphenylmethylene (cyclopentadienyl)(fluoren-9-yl) zirconium dichloride, and dimethylmethylene [1-(4-tert-butyl-2-methyl-cyclopentadienyl)](fluoren-9-yl) zirconium dichloride.

Preferably, bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂) is used as metallocene catalyst.

Preferably, said process comprises the following steps in this order:

- (i) optionally passing at least one diluent over 3A molecular sieves;
- (ii) optionally passing said diluent over 13X molecular sieves;
- (a1) passing said diluent over a sorbent bed, comprising a sorbent material, said sorbent material comprising a compound and a single site metallocene catalyst, both compound and catalyst being deposited on silica; wherein said compound is selected

from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

(b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

- 5 (c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

Preferably, said process comprises the following steps in this order:

(i) passing at least one diluent over 3A molecular sieves;

(ii) optionally passing said diluent over 13X molecular sieves;

- 10 (a1) passing said diluent over a sorbent bed comprising a sorbent material, said sorbent material comprising a compound and a single site metallocene catalyst, both compound and catalyst being deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

- 15 (b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

Preferably, said process comprises the following steps in this order:

- 20 (i) passing at least isobutane over 3A molecular sieves;

(ii) optionally passing said isobutane over 13X molecular sieves;

- (a1) passing said isobutane over a sorbent bed comprising a sorbent material, said sorbent material comprising a compound and a single site metallocene catalyst, both compound and catalyst being deposited on silica; wherein said compound is selected
25 from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

(b1) after step (a1) feeding said diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

- (c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the
30 presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

The sorbent material as used herein is particularly useful in reducing catalysts poisoning. The sorbent material as used herein is particularly useful in purifying diluent. The sorbent material as used herein is particularly useful in reducing the water content of the diluent feed. The sorbent material as used herein is particularly useful in reducing the low oxygenated compound content of the diluent feed. By substantially removing impurities from the diluent, the catalyst activity during the polymerization process can remain constant. Hence, polymerization conditions no longer need to be continuously adjusted, leading to a reduction of costs and better productivity.

Step (b1) of the present process comprises feeding an olefin-containing hydrocarbon feedstock and the diluent treated in step (a1) into a polymerization reactor.

As used herein the terms "olefin-containing hydrocarbon feed" or "olefin-containing hydrocarbon feedstock" refer to any charge stock which contains greater than about 75, 80, 85, or 90 weight percent monomer and optionally co-monomer.

As used herein, the term "monomer" refers to an alpha-olefin compound that is to be polymerized. This alpha-olefin monomer may be selected from ethylene, propylene, butene, pentene, hexene, octene, and any combination thereof. Preferred examples of alpha-olefin monomers are ethylene and propylene.

As used herein, the term "co-monomer" refers to olefin co-monomers which are suitable for being polymerized with ethylene or propylene monomers. Co-monomers may comprise but are not limited to aliphatic C3-C20 alpha-olefins. Examples of suitable aliphatic C3-C20 alpha-olefins include propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene.

Preferably, the olefin-containing hydrocarbon feedstock comprises a monomer and optionally a co-monomer, each independently selected from ethylene, propylene, butene, pentene, hexene, octene, and any combination thereof. Preferably, the feedstock comprises ethylene or propylene and optionally one or more co-monomers.

In an embodiment, the feedstock comprises more than 80% of ethylene, preferably from 90 to 99.99 wt.%.

In another embodiment, the feedstock comprises more than 80% of propylene, preferably from 90 to 99.99 wt.%.

The polymerization can be carried out in slurry or in gas phase conditions.

The polymerization reactor can be a loop reactor or a gas phase reactor. In an embodiment, the polymerization reactor comprises at least two loop reactors connected in series. The reactors can be connected in series by one or more settling legs of the first reactor connected for discharge of slurry from the first reactor to said second reactor.

5 Alternatively they can be connected via a transfer line.

In a slurry loop reactor, the monomer (e.g. ethylene) polymerizes in a liquid diluent (e.g. isobutane), in the presence of a catalyst, optionally in the presence of a co-monomer (e.g. hexene), optionally hydrogen. The slurry can be maintained in circulation by an axial pump. The polymerization heat can be extracted by water cooling jackets.

10 Step (c1) comprises converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

The at least one catalyst used in step (c1), can be any suitable catalyst as known in the art. As used herein, the term "catalyst" refers to a substance that causes a change in the rate of a polymerization reaction. In the present invention, it is especially applicable to catalysts suitable for the polymerization of alpha-olefins to polyolefins. Examples of suitable catalysts include metallocene catalysts, chromium catalysts, and Ziegler-Natta catalysts.

15 Preferably, the step of converting at least part of the olefins contained in a hydrocarbon feedstock into a polyolefin is performed in the presence of a metallocene catalyst. Any metallocene catalyst known in the art can be used.

In an embodiment, the metallocene catalyst has a general formula (III) or (IV) as described herein above.

25 Illustrative examples of metallocene catalysts comprise but are not limited to bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2), bis(cyclopentadienyl) titanium dichloride (Cp_2TiCl_2), bis(cyclopentadienyl) hafnium dichloride (Cp_2HfCl_2); bis(tetrahydroindenyl) zirconium dichloride, bis(indenyl) zirconium dichloride, and bis(n-butyl-cyclopentadienyl) zirconium dichloride; ethylenebis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride, ethylenebis(1-indenyl) zirconium dichloride, dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride, diphenylmethylen
30 (cyclopentadienyl)(fluoren-9-yl) zirconium dichloride, and dimethylmethylen [1-(4-tert-butyl-2-methyl-cyclopentadienyl)](fluoren-9-yl) zirconium dichloride.

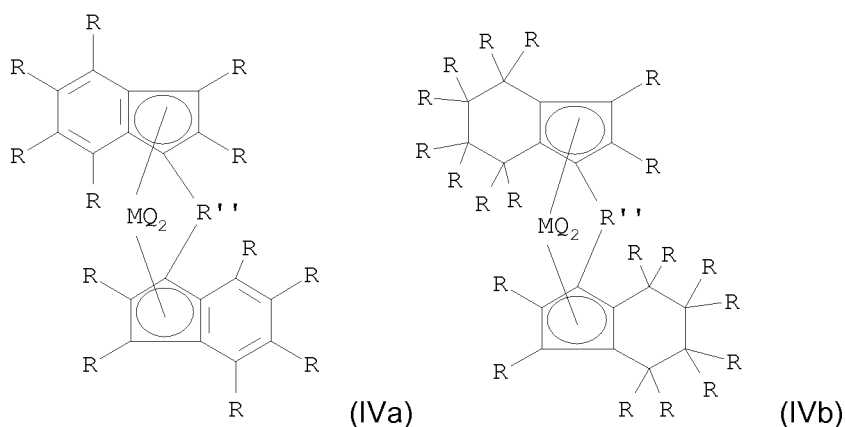
The metallocene catalysts are preferably provided on a solid support. The support can be an inert solid, organic or inorganic, which is chemically unreactive with any of the components of the conventional metallocene catalyst. Suitable support materials for the supported catalyst include solid inorganic oxides, such as silica, alumina, magnesium oxide, titanium oxide, thorium oxide, as well as mixed oxides of silica and one or more Group 2 or 13 metal oxides, such as silica-magnesia and silica-alumina mixed oxides. Silica, alumina, and mixed oxides of silica and one or more Group 2 or 13 metal oxides are preferred support materials. Preferred examples of such mixed oxides are the silica-aluminas. Most preferred is silica. The silica may be in granular, agglomerated, fumed or other form. The support is preferably a silica compound. In a preferred embodiment, the metallocene catalyst is provided on a solid support, preferably a silica support. Preferably, the support is silica having a surface area between 200 and 900 m²/g and a pore volume between 0.5 and 4 ml/g. In an embodiment, the catalyst for use in the present process is a supported metallocene-alumoxane catalyst comprising a metallocene and an alumoxane which are bound on a porous silica support.

The term "chromium catalysts" refers to catalysts obtained by deposition of chromium oxide on a support, e.g. a silica or aluminium support. Illustrative examples of chromium catalysts comprise but are not limited to CrSiO₂ or CrAl₂O₃.

The term "Ziegler-Natta catalyst" or "ZN catalyst" refers to catalysts having a general formula M¹X¹_v, wherein M¹ is a transition metal compound selected from group IV to VII, wherein X¹ is a halogen, and wherein v is the valence of the metal. Preferably, M¹ is a group IV, group V or group VI metal, more preferably titanium, chromium or vanadium and most preferably titanium. Preferably, X¹ is chlorine or bromine, and most preferably, chlorine. Illustrative examples of the transition metal compounds comprise but are not limited to TiCl₃, TiCl₄. Suitable ZN catalysts for use in the invention are described in US6930071 and US6864207, which are incorporated herein by reference.

Preferably step (c1) is performed in the presence of a metallocene catalyst.

Preferably, step (c1) is carried out in the presence of a metallocene comprising a bridged bis-indenyl and/or a bridged bis-tetrahydrogenated indenyl catalyst component. The metallocene can be selected from one of the following formula (IVa) or (IVb):



wherein each R in formula (IVa) or (IVb) is the same or different and is selected independently from hydrogen or XR'^v in which X is chosen from Group 14 of the Periodic Table (preferably carbon), oxygen or nitrogen and each R' is the same or different and is chosen from hydrogen or a hydrocarbonyl of from 1 to 20 carbon atoms and $v+1$ is the valence of X, preferably R is a hydrogen, methyl, ethyl, n-propyl, iso-propyl, n-butyl, tert-butyl group; R'' is a structural bridge between the two indenyl or tetrahydrogenated indenyls to impart stereorigidity that comprises a $\text{C}_1\text{-C}_4$ alkylene radical, a dialkyl germanium, silicon or siloxane, or an alkyl phosphine or amine radical; Q is a hydrocarbonyl radical having from 1 to 20 carbon atoms or a halogen, preferably Q is F, Cl or Br; and M is a transition metal Group 4 of the Periodic Table or vanadium.

Each indenyl or tetrahydro indenyl component may be substituted with R in the same way or differently from one another at one or more positions of either of the fused rings. Each substituent is independently chosen.

If the cyclopentadienyl ring is substituted, its substituent groups must not be so bulky so as to affect coordination of the olefin monomer to the metal M. Any substituents XR'^v on the cyclopentadienyl ring are preferably methyl. More preferably, at least one and most preferably both cyclopentadienyl rings are unsubstituted.

In a particularly preferred embodiment, the metallocene comprises a bridged unsubstituted bis-indenyl and/or bis-tetrahydrogenated indenyl i.e. all R are hydrogens.

More preferably, the metallocene comprises a bridged unsubstituted bis-tetrahydrogenated indenyl. Most preferably the metallocene is ethylene-bis(tetrahydroindenyl)zirconium dichloride or ethylene-bis(tetrahydroindenyl) zirconium difluoride .

Preferably, the supported metallocene catalyst is activated. The cocatalyst, which activates the metallocene catalyst component, can be any cocatalyst known for this

purpose such as an aluminium-containing cocatalyst, a boron-containing cocatalyst or a fluorinated catalyst. The aluminium-containing cocatalyst may comprise an alumoxane, an alkyl aluminium, a Lewis acid and/or a fluorinated catalytic support.

In an embodiment, alumoxane is used as an activating agent for the metallocene catalyst.

- 5 The alumoxane can be used in conjunction with a catalyst in order to improve the activity of the catalyst during the polymerization reaction.

The alumoxanes that can be used preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (I) or (II) as described herein above. Preferred alumoxanes are MethylAluminOxane (MAO), and modified MAO.

- 10 When alumoxane is not used as the co-catalyst, one or more aluminiumalkyl represented by the formula AlR^a_x can be used wherein each R^a is the same or different and is selected from halogens or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Non-limiting examples are Tri-Ethyl Aluminum (TEAL), Tri-Iso-Butyl Aluminum (TIBAL), Tri-Methyl Aluminum (TMA), and Methyl-Methyl-Ethyl Aluminum (MMEAL). Especially suitable are trialkylaluminums, the most preferred being triisobutylaluminium (TIBAL) and triethylaluminum (TEAL).
- 15

- In an embodiment, when the feedstock comprises more than 80% of ethylene, preferably from 90 to 99.99 wt.%, the metallocene catalyst is selected from ethylene bis(tetrahydroindenyl) zirconium dichloride, ethylene bis(indenyl) zirconium dichloride, bis(n-butylcyclopentadienyl) zirconium dichloride, and a mixture thereof.
- 20

- In another embodiment, when the feedstock comprises more than 80% of propylene, preferably from 90 to 99.99 wt.%, the metallocene catalyst is selected from dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride, dimethylsilylbis(2-methylindenyl)zirconium dichloride, dimethylsilylbis(2-methyl-4,5-benzoidindenyl)zirconium dichloride, isopropylidene-(cyclopentadienyl)(fluorenyl)zirconium dichloride, isopropylidene(2-methyl-4-tert-butyl-cyclopentadienyl)(fluorenyl)zirconium dichloride, isopropylidene(2-methyl-4-tert-butyl-cyclopentadienyl)(ditertbutyl-fluorenyl)zirconium dichloride, and a mixture thereof.
- 25

Polyolefins are preferably prepared in a reactor either in slurry or in gas phase conditions.

- 30 As used herein, the term "polymerization slurry" or "polymer slurry" or "slurry" means substantially a multi-phase composition including at least polymer solids and a liquid phase and allows for a third phase (gas) to be at least locally present in the process, the liquid phase being the continuous phase. The solids include catalyst and a polymerized

olefin, such as polyethylene or polypropylene. The liquids include an inert diluent, such as isobutane, dissolved monomer such as ethylene or propylene, co-monomer, molecular weight control agents, such as hydrogen, antistatic agents, antifouling agents, scavengers, and other process additives.

- 5 Where the reaction is performed in a slurry using, for example, isobutane, a reaction temperature in the range of 70°C to 110°C may be used. The reaction can also be carried out in a bulk process i.e. where the diluent and monomer are the same. Where the reaction is performed in solution, by selection of a suitable solvent a reaction temperature in the range 150°C to 300°C may be used. Alternatively, the reaction may also be
10 performed in the gas phase using a suitably supported catalyst.

The product (e.g. polyethylene or propylene) can be taken out of the reactor with some diluent through settling legs and discontinuous discharge valves. A small fraction of the total circulating flow can be withdrawn. It can be moved to a polymer degassing section in which the solid content is increased.

- 15 A non-limiting example of a set up according to one embodiment of the present invention is for instance illustrated in figure 1.

Figure 1 schematically illustrates a set up according to an embodiment of the present invention. In figure 1, a diluent feed **1** is directed via line **11** to the sorbent zone **100**, wherein the diluent feed is passed over one 3A sorbent bed **2**, then one 13X sorbent bed
20 **3** and over the sorbent material as defined herein above **4**. The thus purified diluent feed is then conveyed through lines **13**, **14** and **16**, and with the help of pump **5**, into slurry loop reactor **8**. An olefin-containing hydrocarbon feedstock **6**, is directed through lines **15** and **17**, and with the aid of pump **7**, also into the slurry loop reactor **8**, wherein polymerization takes place in the presence of at least one catalyst. Reactor **8** can be provided with one or
25 more settling leg (not shown) for discharging the product to a product recovery zone (not shown), wherein the polyolefin product is further recovered.

The recovered polyolefin product can then be directed through line **18** to extruder **9**, wherein extrusion of the polyolefin product is performed. The resulting pellets can then be conveyed via line **19**, into a storage or process zone **10**.

- 30 Preferably, the process comprises the following steps in this order:

- (i) optionally passing at least one diluent over 3A molecular sieves;
- (ii) optionally passing said diluent over 13X molecular sieves;

(a1) passing said diluent over a sorbent bed, comprising a sorbent material, said sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

5 (b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

Preferably, the process comprises the following steps in this order:

10 (i) optionally passing at least one diluent over 3A molecular sieves;

(ii) optionally passing said diluent over 13X molecular sieves;

(a1) passing said diluent over a sorbent bed, comprising a sorbent material, said sorbent material comprising a compound and a single site metallocene catalyst, both compound and catalyst being deposited on silica; wherein said compound is selected
15 from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b1) after step (a1) feeding said at least one diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in the
20 presence of at least one metallocene catalyst, into a polyolefin and recovering the polyolefin product.

According to the second aspect of the invention, at least one olefin-containing hydrocarbon feedstock is first passed over a sorbent zone comprising a sorbent material prior to being introduced into a polymerization reactor.

25 In an embodiment, the process comprises the following steps in this order:

(a2) passing at least one olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material trapped therein, wherein said sorbent material comprises a compound deposited on silica; wherein said compound is selected from
30 dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide; said sorbent material remaining in said sorbent zone, at the end of step (a1);

(b2) feeding a diluent and said at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin.

- 5 Step (a2) of the process comprises passing at least one olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material trapped within said sorbent zone, wherein the sorbent material comprises i) a compound deposited on silica, wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide, trityl borate, fluorinated borane, and
- 10 anilinium borate, more preferably dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide. Step (a2) comprises purifying the olefin-containing hydrocarbon feedstock over a bed of sorbent material comprising a compound deposited on silica. The olefin-containing hydrocarbon feedstock at the end of step (a2) is free of sorbent material.
- 15 Suitable compounds deposited on silica have been described herein above in respect of step (a1) of the process according to the first aspect. The embodiments therein for said compounds, apply mutatis mutandis to suitable deposited compounds described in step (a2) of the process according to the second aspect of the invention. Suitable alumoxanes comprise alumoxanes represented by the formula (I) or (II), as described above. In one
- 20 embodiment, the aluminoxane is methylaluminoxane (MAO), ethylaluminoxane, n-butylaluminoxane, or isobutylaluminoxane. Preferred alumoxanes are MethylAluminOxane (MAO).

Preferably, the sorbent material is immobilized within the sorbent zone, and preferably provided as a sorbent bed.

- 25 Suitable sorbent material has been described herein above for step (a1). The embodiments therein for said sorbent material, apply mutatis mutandis to sorbent material described in step (a2) of the process according to the second aspect of the invention. In a preferred embodiment, the sorbent material may include 20 to 90 wt.% of silica. In one embodiment, the silica has an average particle size D50 of 3 to 100 μm , preferably of 5 to
- 30 50 μm . In a preferred embodiment the silica is silicon oxide of stoichiometry equal to or close to SiO_2 . In some embodiment, the silica is silicon oxide of stoichiometry equal to or close to SiO_2 with a purity greater than 90%.

In one embodiment, the at least one olefin-containing hydrocarbon feedstock is also passed over one or more of the following molecular sieves, such as 3A and/or 13X molecular sieves.

5 In a preferred embodiment, the at least one olefin-containing hydrocarbon feedstock is passed first over 3A molecular sieves, and then over a sorbent material as described herein above.

In one embodiment, the at least one olefin-containing hydrocarbon feedstock is passed first over 13X molecular sieves, and then over a sorbent material as described herein above. In a preferred embodiment, the at least one olefin-containing hydrocarbon
10 feedstock is passed first over 3X molecular sieves, and then over a sorbent material as described herein above.

In a preferred embodiment, the at least one olefin-containing hydrocarbon feedstock is passed first over 3A molecular sieves, then through the 13X and then through a sorbent material as described above.

15 The present invention therefore encompasses also processes comprising the following steps in this order:

(i) optionally passing at least one olefin-containing hydrocarbon feedstock over 3A molecular sieves;

(ii) optionally passing said olefin-containing hydrocarbon feedstock over 13X molecular
20 sieves;

(a2) passing said olefin-containing hydrocarbon feedstock over a zone comprising a sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminosilane, trialkyl aluminosilane, dialkyl aluminosilane halide, or trialkyl aluminosilane halide;

25 (b2) after step (a2) feeding diluent and said at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

The present invention therefore encompasses also processes comprising the following
30 steps in this order:

(i) optionally passing at least one olefin-containing hydrocarbon feedstock over 3A molecular sieves;

(ii) optionally passing said olefin-containing hydrocarbon feedstock over 13X molecular sieves;

(a2) passing said olefin-containing hydrocarbon feedstock over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b2) after step (a2) feeding at least one diluent and said at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

Preferably, said process comprises

(i) passing at least one olefin-containing hydrocarbon feedstock over 3A molecular sieves;

(ii) optionally passing said olefin-containing hydrocarbon feedstock over 13X molecular sieves;

(a2) passing said olefin-containing hydrocarbon feedstock over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b2) after step (a2) feeding at least one diluent and said at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

More preferably, said process comprises successively:

(i) passing at least one olefin-containing hydrocarbon feedstock over 3A molecular sieves;

(ii) passing said olefin-containing hydrocarbon feedstock over 13X molecular sieves;

(a2) passing said olefin-containing hydrocarbon feedstock over a zone comprising sorbent material comprising a compound deposited on silica; wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;

(b2) after step (a2) feeding at least one diluent and said at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and

(c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product

Olefin-containing hydrocarbon feedstock has been described herein above for step (b1). The embodiments described therein for said feedstock, apply mutatis mutandis to feedstock described in step (a2) of the process according to the second aspect of the invention.

Preferably, the olefin-containing hydrocarbon feedstock comprises a monomer and optionally a co-monomer, each independently selected from ethylene, propylene, butene, pentene, hexene, octene, and any combination thereof. Preferably, the feedstock comprises ethylene or propylene and optionally one or more co-monomers.

Step (a2) of passing at least one olefin-containing hydrocarbon feedstock, over a sorbent zone, can be performed at room temperature.

In an embodiment, the olefin ethylene and it is passed over the sorbent zone at a gas hourly space velocity (GHSV) of from 5 to 150 l/l.h, preferably of from 5 to 100 l/l.h, more preferably of from 10 to 20 l/l.h, preferably at room temperature.

In another embodiment, the olefin is propylene and/or the diluent is isobutane, each independently is passed over the sorbent zone at a liquid hourly space velocity (LHSV) of from 1 to 120 l/l.h, more preferably from of 5 to 20 l/l.h, preferably at room temperature.

Step (b2) comprises feeding the olefin-containing hydrocarbon feedstock obtained after step (a2) and a diluent into a polymerization reactor.

In an embodiment, the diluent used in step (b2) is first (b2a) passed over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound deposited on silica, or modified silica containing any other metal oxide or metal, wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide. The embodiments described for diluent, and sorbent material and compounds under step (a1) apply mutatis mutandis to diluent and sorbent material and compounds used in step (b2a) of the process according to the second aspect of the invention. Preferably the diluent is selected from the group comprising isobutane, nitrogen, hexane, isohexane, pentane, heptane. Preferably, the diluent is isobutane or nitrogen. In a more preferred embodiment, said diluent is isobutane.

The sorbent material as used herein is particularly useful in reducing the low oxygenated compound content of the olefin-containing hydrocarbon feedstock. By substantially

removing impurities from the olefin-containing hydrocarbon feedstock, the catalyst activity during the polymerization process can remain constant. Hence, polymerization conditions no longer need to be continuously adjusted, leading to a reduction of costs and better productivity.

- 5 Step (b2) comprises feeding the olefin-containing hydrocarbon feedstock and diluent into a polymerization reactor. The polymerization can be carried out in slurry or in gas phase conditions, as described herein before for step (b1).

Step (c2) comprises converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the
10 polyolefin product.

Step (c2) can be carried out in the presence of any suitable catalyst as known in the art. Suitable catalysts have been described herein above in respect of step (c1) of the process according to the first aspect. The embodiments therein for said catalysts, apply mutatis mutandis to catalyst used in step (c2) of the process according to the second aspect of
15 the invention.

Preferably step (c2) is performed in the presence of a metallocene catalyst. Suitable metallocene catalysts have been described herein above in respect of step (c1) of the process according to the first aspect. The embodiments therein for said metallocene catalysts, apply mutatis mutandis to suitable metallocene catalysts used in step (c2) of the
20 process according to the second aspect of the invention.

Preferably, step (c2) is carried out in the presence of a metallocene comprising a bridged bis-indenyl and/or a bridged bis-tetrahydrogenated indenyl catalyst component. The metallocene can be selected from one of the following formula (IVa) or (IVb), as described herein above for step (c1). Most preferably the metallocene is ethylene-
25 bis(tetrahydroindenyl)zirconium dichloride or ethylene-bis(tetrahydroindenyl) zirconium difluoride.

A non-limiting example of a set up according to one embodiment of the present invention is for instance illustrated in figure 2.

Figure 2 schematically illustrates a set up according to another embodiment of the present
30 invention. In figure 2, an olefin-containing hydrocarbon feedstock **1a** is directed via line **11a** to the sorbent zone **100a**, wherein the olefin-containing hydrocarbon feedstock is contacted with 3A sorbent bed **2a**, then 13X sorbent bed **3a** and then over the sorbent material as defined herein above in step (a2) **4a**. The thus purified olefin-containing

hydrocarbon feedstock is then conveyed through lines **13a**, **14a** and **16a**, and with the help of pump **5a**, into slurry loop reactor **8a**, wherein polymerization takes place in the presence of at least one catalyst. Reactor **8a** can be provided with one or more settling leg (not shown) for discharging the product to a product recovery zone (not shown),
5 wherein the polyolefin product is further recovered.

The recovered polyolefin product can then be directed through line **18a** to extruder **9a**, wherein extrusion of the polyolefin product is performed. The resulting pellets can then be conveyed via line **19a**, into a storage or process zone **10a**.

In a preferred embodiment, the process comprises the following steps in this order:

- 10 (a2) passing at least one olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material comprising methylalumoxane deposited on silica;
- (b2) feeding said olefin-containing hydrocarbon feedstock and a diluent into a polymerization reactor; and
- (c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the
15 presence of at least one catalyst, and recovering the polyolefin product.

Preferably, the process comprises the following steps in this order:

- (a2) passing at least one alpha-olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material comprising methylalumoxane deposited on silica;
- (b2) feeding said alpha-olefin-containing hydrocarbon feedstock and a diluent into a
20 polymerization reactor; and
- (c2) converting at least part of the alpha-olefins contained in said hydrocarbon feedstock, in the presence of a metallocene catalyst, into a polyolefin, and recovering the polyolefin product.

The present invention also encompasses a process for the polymerization of olefins
25 comprising the following steps in this order:

- (a3) feeding at least one olefin-containing hydrocarbon feedstock into a loop reactor;
- (b3) prior to or simultaneously with the addition of a supported catalyst, feeding into the reactor a sorbent material comprising a co-catalyst deposited on silica, or modified silica containing any other metal oxide or metal; wherein said co-catalyst is selected from dialkyl
30 or trialkyl aluminoxane, dialkyl or trialkyl aluminoxane halide, trityl borate, fluorinated borane, and anilinium borate;

(c3) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst; into a polyolefin and recovering the polyolefin product.

According to this process, either alone or in combination with the first and second aspects of the present invention, it has been unexpectedly found that a co-catalyst supported on silica, acts as sorbent material reacting with impurities present in an olefin-containing feedstock. By substantially removing impurities from the hydrocarbon feedstock, the catalyst activity during the polymerization process can remain constant. Hence, polymerization conditions no longer need to be continuously adjusted.

The processes of the present invention are capable of improving productivities and activities of catalysts such as metallocene catalysts by reducing the concentration of impurities present in the olefin-containing hydrocarbon feed. The original concentration of impurities may be as high as 1000 ppm or higher depending on the process used to produce the original feedstock. In some embodiments, it can be advantageous to carry out in advance known purification processes such as distillation or the use of molecular sieves prior to the process of the present invention.

Step (a3) of the present process comprises feeding at least one olefin-containing hydrocarbon feedstock into a loop reactor.

Olefin-containing hydrocarbon feedstock has been described herein above for step (b1) and (b2). The embodiments described therein for said feedstock, apply mutatis mutandis to feedstock described in step (a3) of the above described process. Preferably, the olefin-containing hydrocarbon feedstock comprises a monomer and optionally a co-monomer, each independently selected from ethylene, propylene, butene, pentene, hexene, octene, and any combination thereof. Preferably, the feedstock comprises ethylene or propylene and optionally one or more co-monomers.

The polymerization can be carried out in slurry conditions. The polymerization reactor can be single loop reactor. In an embodiment, the polymerization reactor comprises at least two loop reactors connected in series.

The reactors can be connected in series by one or more settling legs of the first reactor connected for discharge of slurry from the first reactor to said second reactor. Alternatively they can be connected via a transfer line.

Step (b3) comprises feeding into the reactor a sorbent material comprising a compound co-catalyst deposited on silica, wherein said compound co-catalyst is selected from dialkyl or trialkyl aluminoxane, dialkyl or trialkyl aluminoxane halide, trityl borate, fluorinated

borane, and anilinium borate; and this prior to or simultaneously with the addition of a supported catalyst.

The embodiments described for compound co-catalyst, and sorbent material and under step (a2) apply mutatis mutandis to diluent and sorbent material and compounds used in
5 step (b3) of the process as described herein. In one embodiment, the aluminoxane is methylaluminoxane, ethylaluminoxane, n-butylaluminoxane, or isobutylaluminoxane, preferably MAO.

This silica supported co-catalyst, when added to the reactor further improves the activity of the catalyst during the polymerization reaction by reducing catalyst poisoning.

10 Suitable sorbent material has been described herein above for step (a1). The embodiments therein for said sorbent material, apply mutatis mutandis to sorbent material described in step (a3) of the present process. In a preferred embodiment, the sorbent material may include 20 to 90 wt.% of silica. In one embodiment, the silica has an average particle size D50 of 3 to 100 μm , preferably of 5 to 50 μm . In a preferred embodiment the
15 silica is silicon oxide of stoichiometry equal to or close to SiO_2 . In some embodiment, the silica is silicon oxide of stoichiometry equal to or close to SiO_2 with a purity greater than 90%. The total weight of compound may represent from 10 wt. % up to 80 wt. % based on the total weight of the sorbent material. Accordingly, the sorbent material may include 20 to 90 wt.% of silica.

20 In one embodiment, the supported catalyst and the sorbent material are fed into said polymerization reactor through the same or separate pipe line(s).

In one embodiment, the sorbent material is fed into said polymerization reactor in dry form or in suspension in a suitable diluent.

In one embodiment, the sorbent material is fed into the polymerization reactor in an
25 amount of at least 1 wt.% relative to the content of the supported catalyst. In one embodiment, the sorbent material is fed into the polymerization reactor in an at least 5 wt.% relative to the content of the supported catalyst. In one embodiment, the sorbent material is fed into the polymerization reactor in an amount of at most 10 wt.% relative to the content of the supported catalyst.

30 The supported catalyst and the sorbent material can be introduced in the reactor with a diluent. The embodiments described for diluent, under step (a1) apply mutatis mutandis to diluent used herein. Preferably, the diluent is selected from the group comprising

isobutane, nitrogen, hexane, isohexane, pentane, heptane. Preferably, the diluent is isobutane or nitrogen. In a more preferred embodiment, said diluent is isobutane.

Steps (b3) and (c3) can be carried out in the presence of any suitable supported catalyst as known in the art, as described above in steps (b1) and (c1).

- 5 Preferably, step (c3) is performed in the presence of a metallocene catalyst. Any metallocene catalyst known in the art can be used, preferably, the metallocene catalysts described above for step (c1). The embodiments therein for said catalysts, apply mutatis mutandis to catalyst used in step (b3) and (c3).

Preferably step (c3) is performed in the presence of a supported metallocene catalyst.

- 10 Preferably, step (c3) is carried out in the presence of a metallocene comprising a bridged bis-indenyl and/or a bridged bis-tetrahydrogenated indenyl catalyst component. The metallocene can be selected from one of the following formula (IVa) or (IVb), as described herein above for step (c1). Most preferably the metallocene is ethylene-bis(tetrahydroindenyl)zirconium dichloride or ethylene-bis(tetrahydroindenyl) zirconium difluoride.
- 15

- In one embodiment, in the process for the polymerization of olefins, any one of steps (a3) feeding at least one olefin-containing hydrocarbon feedstock into a loop reactor, or (b3) prior to or simultaneously with the addition of a supported catalyst, feeding a sorbent material comprising a compound deposited on silica, or modified silica containing any
- 20 other metal oxide or metal; into said loop reactor, thus any one of steps (a3) and (b3) is carried out at room temperature.

The sorbent material is particularly useful in reducing catalysts poisoning.

Preferably, the process comprises following steps in this order

- (a3) feeding at least one olefin-containing hydrocarbon feedstock into a loop reactor;
- 25 (b3) prior to or simultaneously with the addition of a supported metallocene catalyst, feeding into the reactor a sorbent material comprising an alumoxane deposited on silica;
- (3c) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst; into a polyolefin and recovering the polyolefin product.

Preferably, the process comprises the following steps in this order:

- 30 (a3) feeding at least one alpha-olefin-containing hydrocarbon feedstock into a loop reactor;

(b3) prior to or simultaneously with the addition of a supported metallocene catalyst, feeding into the reactor a sorbent material comprising methyl alumoxane deposited on silica;

- 5 (c3) converting at least part of the alpha-olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst; into a polyolefin and recovering the polyolefin product.

Preferably, the process comprises the following steps in this order:

(a3) feeding at least one alpha-olefin monomer, optionally one or more co-monomers into a slurry loop reactor;

- 10 (b3) prior to or simultaneously with the addition of a supported metallocene catalyst, feeding into the reactor a sorbent material comprising methyl alumoxane deposited on silica; and

(c3) converting at least part of the alpha-olefins, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.

- 15 The product (e.g. polyethylene or propylene) can be taken out of the reactor with some diluent through settling legs and discontinuous discharge valves. A small fraction of the total circulating flow can be withdrawn. It can be moved to a polymer degassing section in which the solid content is increased.

Further combinations or preferred embodiments are disclosed in the patent claims.

- 20 The following examples are given though by way of illustration only, to show preferred processes of the present invention. These examples should not, however, be constructed as limiting the scope of the claimed invention, as there are many variations which may be made thereon, as those skilled in the art will recognize.

Examples

- 25 **Example 1** Examples E1 and E2, purification of isobutane in a setting as illustrated in figure 1

In example E2 according to an embodiment of the invention, the isobutane feed **1**, is directed through line **11** to a dryer zone **100**, comprising three sorbent zones connected in series, with the first sorbent zone **2** having a volume of 5m³ and containing 3A molecular
30 sieve, with the second sorbent zone **3** having a volume of 5m³ containing 13X molecular sieve, and with the third sorbent zone **4** having a volume of 5m³ and containing methyl alumoxane deposited on silica. The thus purified diluent feed is then directed through lines

13, **14** and **16**, and with the aid of pump **5**, into the slurry loop reactor **8**. Reactor **8** is further fed with ethylene via lines **15** and **17**, and polymerization is performed in the presence of a metallocene catalyst.

In comparative example E1, the isobutane feed **1**, is directed through line **11** to the dryer zone **100**, but the feed does not pass through sorbent zone 4 and is directed to the reactor without passing the MAO deposited on silica. The diluent feed is fed into the slurry loop reactor **8**. Reactor **8** is further charged with ethylene via lines **15** and **17**, and polymerization is performed in the presence of a metallocene catalyst.

The activity of the metallocene catalyst is measured for both examples and the results are presented in table 1.

Table 1.

example	<u>Catalyst activity (g/g.h)</u>
Comparative E1	5100
E2	8500

Example 2 Examples E3 and E4, purification of propylene in a setting as illustrated in figure 2.

In example E4 according to an embodiment of the invention, the propylene feed **1a**, is directed through line **11a** to a dryer zone **100a**, comprising three sorbent zones connected in series, with the first sorbent zone **2a** having a volume of 25m³ and containing 3A molecular sieve, with the second sorbent zone **3a** having a volume of 25m³ containing 13X molecular sieve, and with the third sorbent zone **4a** having a volume of 2.5m³ and containing methyl alumoxane deposited on silica. The thus purified propylene feed is then directed through lines **13a**, **14a** and **16a**, and with the aid of pump **5a**, into the slurry loop reactor **8a** wherein polymerization is performed in the presence of a metallocene catalyst.

In comparative example E3, the propylene feed **1a**, is directed through line **11a** to the dryer zone **100a**, but the feed does not pass through sorbent zone **4a** and is directed to the reactor without passing the MAO deposited on silica. The propylene feed is fed into the slurry loop reactor **8** and polymerization is performed in the presence of a metallocene catalyst.

The activity of the metallocene catalyst is measured for both comparative examples and presented in table 2.

Table 2.

<u>example</u>	<u>Catalyst activity (g/g.h)</u>
Comparative E3	11300
E4	18500

Claims

1. A process for the polymerization of olefins comprising the following steps in this order:
 - (a1) passing at least one diluent over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound deposited on silica;
5 wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;
 - (b1) feeding said diluent and at least one olefin-containing hydrocarbon feedstock into a polymerization reactor; and
 - (c1) converting at least part of the olefins contained in said hydrocarbon feedstock, in
10 the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.
2. The process according to claim 1, wherein said sorbent material further comprises a single site metallocene catalyst or an iron complex catalyst.
3. A process for the polymerization of olefins comprising the following steps in this order:
 - 15 (a2) passing at least one olefin-containing hydrocarbon feedstock over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound deposited on silica, or modified silica containing any other metal oxide or metal, wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide;
 - 20 (b2) feeding said at least one olefin-containing hydrocarbon feedstock, and a diluent into a polymerization reactor; and
 - (c2) converting at least part of the olefins contained in said hydrocarbon feedstock, in the presence of at least one catalyst, into a polyolefin and recovering the polyolefin product.
- 25 4. The process according to claim 3, wherein the diluent used in step (b2) is first passed over a sorbent zone comprising a sorbent material, wherein said sorbent material comprises a compound deposited on silica, or modified silica containing any other metal oxide or metal, wherein said compound is selected from dialkyl aluminoxane, trialkyl aluminoxane, dialkyl aluminoxane halide, or trialkyl aluminoxane halide.
- 30 5. The process according to any one of claims 1 to 4, wherein the diluent is selected from the group comprising isobutane, butane, pentane, hexane, isohexane, heptane, cyclopentane, cyclohexane, cycloheptane, methyl cyclopentane, methyl cyclohexane,

isooctane, benzene, toluene, xylene, chloroform, chlorobenzenes, tetrachloroethylene, dichloroethane, nitrogen and trichloroethane; preferably diluent is selected from the group comprising isobutane, nitrogen, hexane, isohexane, pentane, heptane.

- 5 6. The process according to any one of claims 1 to 5, wherein the aluminosilicate is methylaluminosilicate, ethylaluminosilicate, n-butylaluminosilicate, or isobutylaluminosilicate.
7. The process according to any one of claims 1 to 6, wherein the sorbent material further comprises a metal selected from aluminum, nickel, chromium, iron, cobalt, copper, ruthenium, palladium, silver, and platinum, or a metal oxide selected from
10 nickel oxide, copper oxide, zinc oxide, zirconium oxide, and manganese oxide.
8. The process according to any one of claims 1 to 7, wherein the silica has an average particle size D50 between 3 and 100 μm .
9. The process according to claims 1 or 3, wherein step (a1)/ (a2) is performed at room temperature.
- 15 10. The process according to any one of claims 1 to 9, wherein the olefin-containing hydrocarbon feedstock comprises a monomer and optionally a co-monomer, each independently selected from ethylene, propylene, butene, pentene, hexene, octene, and any combination thereof.
11. The process according to any one of claims 1 to 10, wherein the polymerization is
20 carried out in slurry or in gas phase conditions.
12. The process according to any one of claims 3 to 11, wherein the olefin is ethylene and it is passed over the sorbent material at a gas hourly space velocity (GHSV) from 5 to 150 l/l.h.
13. The process according to any one of claims 3 to 11, wherein the olefin is propylene
25 and, is passed over the sorbent material zone at a liquid hourly space velocity (LHSV) from 1 to 120 l/l.h.
14. The process according to any one of claim 1, 2, 4 to 11, wherein the diluent is passed over the sorbent zone at a liquid hourly space velocity (LHSV) from 1 to 120 l/l.h.
- 30 15. The process according to any one of claims 1 to 14, wherein the catalyst is a metallocene catalyst.

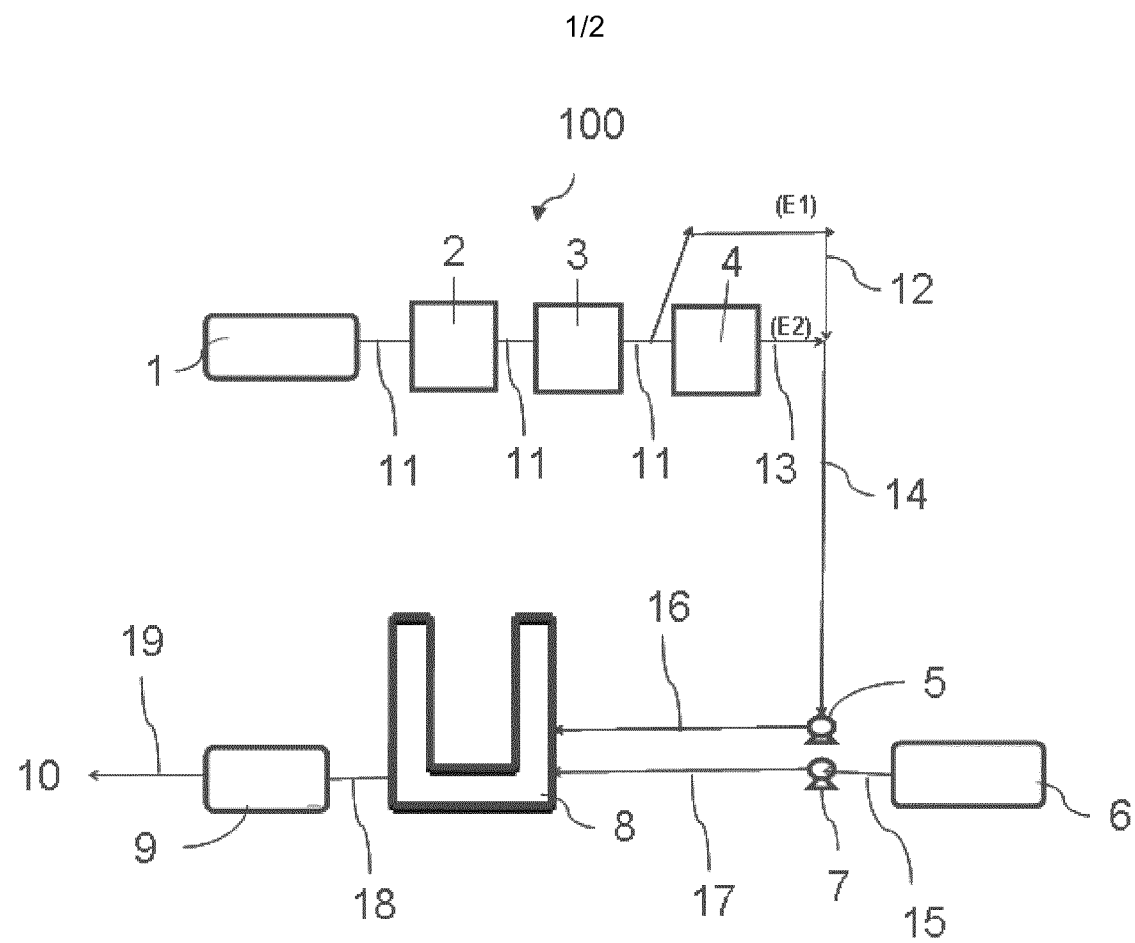


FIG. 1

2/2

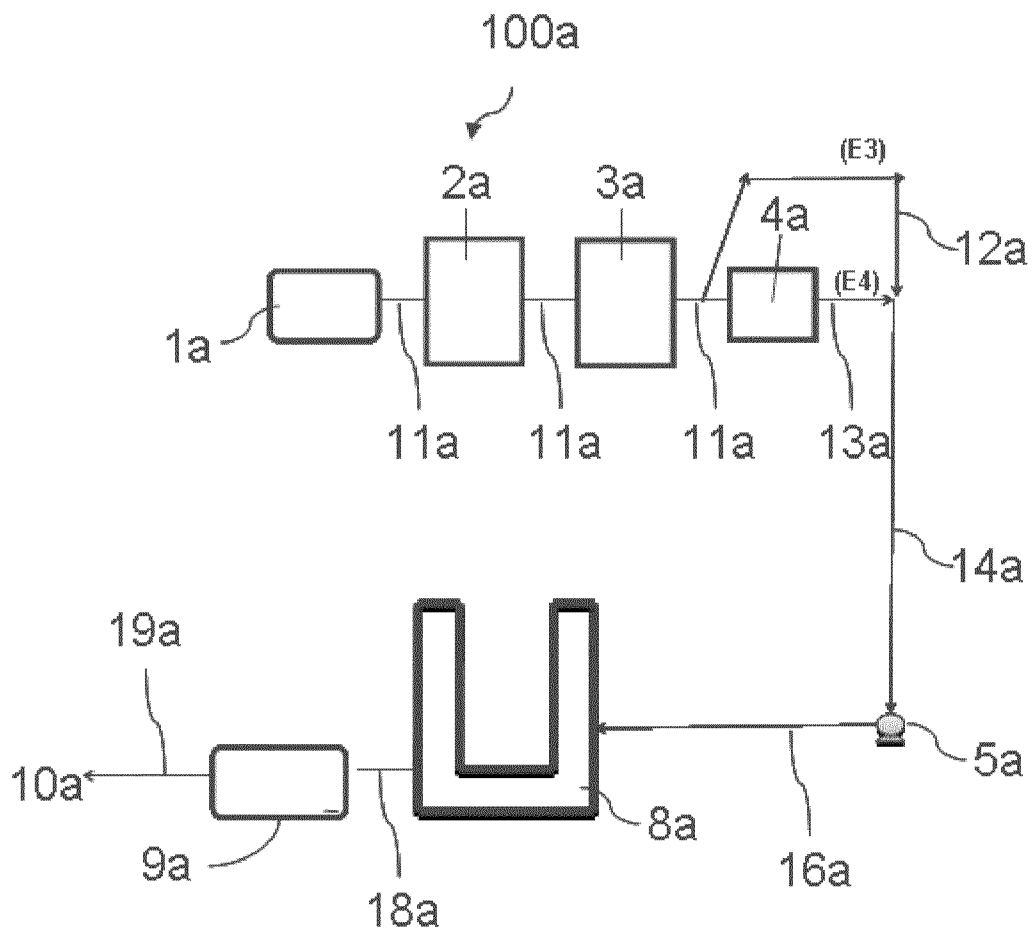


FIG. 2.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/063986

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F10/00 C08F2/00 C08F4/02 C07C7/12
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 August 2013

Date of mailing of the international search report

21/08/2013

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/063986

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