

CATALYTIC SUPPORT AND USES THEREOF

INTRODUCTION

[0001] The present invention relates to catalytic support materials and uses thereof. More particularly, the present invention relates to catalytic support materials based on solid polymethylaluminoxane, as well as the use of such materials in polymerisation of olefins.

BACKGROUND OF THE INVENTION

[0002] It is well known that ethylene (and α -olefins in general) can be readily polymerised at low or medium pressures in the presence of certain transition metal catalysts. These catalysts are generally known as Ziegler-Natta type catalysts.

[0003] A particular group of these Ziegler-Natta type catalysts, which catalyse the polymerization of ethylene (and α -olefins in general), comprise an aluminoxane activator and a metallocene transition metal catalyst. Metallocenes comprise a metal bound between two η^5 -cyclopentadienyl type ligands. Generally the η^5 -cyclopentadienyl type ligands are selected from η^5 -cyclopentadienyl, η^5 -indenyl and η^5 -fluorenyl.

[0004] Catalytic reactions involving metallocene-based Ziegler-Natta catalysts have traditionally employed the catalyst in solution phase. However, this technique has a number of drawbacks, most notably the difficulty of effectively separating the catalyst from the reaction medium and then recycling it for further use.

[0005] Given the high value that industry places on polyethylene (as well as other polyolefins), there is a need for improved solid-phase support materials capable of effectively supporting metallocene-based Ziegler-Natta catalysts.

[0006] The present invention was devised with the foregoing in mind.

SUMMARY OF THE INVENTION

[0007] According to a first aspect of the present invention there is provided a solid-phase support material suitable for supporting a metallocene catalytic compound, the solid-phase support material comprising a solid polymethylaluminoxane modified by reaction with a compound of formula (I) or (II) defined herein, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.3:1.

[0008] According to a further aspect of the present invention, there is provided a method of preparing a solid-phase support material as claimed in any preceding claim, the method comprising the steps of:

- a) providing a solid polymethylaluminoxane in a first solvent;
- b) contacting the solid polymethylaluminoxane of step a) with one or more compounds of formula (I) or (II) as defined herein; and
- c) isolating the product formed from step b);

wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.3:1.

[0009] According to a further aspect of the present invention, there is provided a solid-phase support material obtained, directly obtained or obtainable by a process defined herein.

[0010] According to a further aspect of the present invention, there is provided a use of a solid-phase support material defined herein as a solid-phase support for supporting a metallocene catalytic compound.

[0011] According to a further aspect of the present invention, there is provided a catalytic composition comprising:

- a) a compound of formula (III) defined herein; and
- b) a solid-phase support material as defined herein.

[0012] According to a further aspect of the present invention, there is provided a method for the preparation of a catalytic composition defined herein, the method comprising the steps of:

- a) providing a solid-phase support material as defined herein in a suitable solvent
- b) contacting the solid-phase support material of step a) with a compound of formula (III) defined herein; and
- c) isolating the product resulting from step b).

[0013] According to a further aspect of the present invention, there is provided a catalytic composition obtained, directly obtained or obtainable by a process defined herein.

[0014] According to a further aspect of the present invention, there is provided a use of a catalytic composition as defined herein as a polymerisation catalyst for the preparation of a polyolefin.

[0015] According to a further aspect of the present invention, there is provided a process for forming a polyolefin (e.g. a polyethylene), the process comprising the step of reacting olefin monomers in the presence of a catalytic composition defined herein.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0016] The term “alkyl” as used herein includes reference to a straight or branched chain alkyl moieties, typically having 1, 2, 3, 4, 5 or 6 carbon atoms. This term includes reference to groups such as methyl, ethyl, propyl (n-propyl or isopropyl), butyl (n-butyl, sec-butyl or tert-butyl), pentyl (including neopentyl), hexyl and the like. In particular, an alkyl may have 1, 2, 3 or 4 carbon atoms.

[0017] The term “alkenyl” as used herein include reference to straight or branched chain alkenyl moieties, typically having 2, 3, 4, 5 or 6 carbon atoms. The term includes reference to alkenyl moieties containing 1, 2 or 3 carbon-carbon double bonds (C=C). This term includes reference to groups such as ethenyl (vinyl), propenyl (allyl), butenyl, pentenyl and hexenyl, as well as both the *cis* and *trans* isomers thereof.

[0018] The term “alkynyl” as used herein include reference to straight or branched chain alkynyl moieties, typically having 2, 3, 4, 5 or 6 carbon atoms. The term includes reference to alkynyl moieties containing 1, 2 or 3 carbon-carbon triple bonds (C≡C). This term includes reference to groups such as ethynyl, propynyl, butynyl, pentynyl and hexynyl.

[0019] The term “alkoxy” as used herein include reference to -O-alkyl, wherein alkyl is straight or branched chain and comprises 1, 2, 3, 4, 5 or 6 carbon atoms. In one class of embodiments, alkoxy has 1, 2, 3 or 4 carbon atoms. This term includes reference to groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, pentoxy, hexoxy and the like.

[0020] The term “aryl” as used herein includes reference to an aromatic ring system comprising 6, 7, 8, 9 or 10 ring carbon atoms. Aryl is often phenyl but may be a polycyclic ring system, having two or more rings, at least one of which is aromatic. This term includes reference to groups such as phenyl, naphthyl and the like.

[0021] The term “carbocyclyl” as used herein includes reference to an alicyclic moiety having 3, 4, 5, 6, 7 or 8 carbon atoms. The group may be a bridged or polycyclic ring system. More often cycloalkyl groups are monocyclic. This term includes reference to groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl, bicyclo[2.2.2]octyl and the like.

[0022] The term “heterocyclyl” as used herein includes reference to a saturated (e.g. heterocycloalkyl) or unsaturated (e.g. heteroaryl) heterocyclic ring moiety having from 3, 4, 5, 6, 7, 8, 9 or 10 ring atoms, at least one of which is selected from nitrogen, oxygen, phosphorus, silicon and sulphur. In particular, heterocyclyl includes a 3- to 10-membered ring or ring system and more particularly a 5- or 6-membered ring, which may be saturated or unsaturated.

[0023] A heterocyclic moiety is, for example, selected from oxiranyl, aziriny, 1,2-oxathiolanyl, imidazolyl, thienyl, furyl, tetrahydrofuryl, pyranly, thiopyranly, thianthrenyl, isobenzofuranyl, benzofuranyl, chromenyl, 2*H*-pyrrolyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, imidazolidinyl, benzimidazolyl, pyrazolyl, pyrazinyl, pyrazolidinyl, thiazolyl, isothiazolyl, dithiazolyl, oxazolyl, isoxazolyl, pyridyl, pyrazinyl, pyrimidinyl, piperidyl, piperazinyl, pyridazinyl, morpholinyl, thiomorpholinyl, especially thiomorpholino, indoliziny, isoindolyl, 3*H*-indolyl, indolyl, benzimidazolyl, cumaryl, indazolyl, triazolyl, tetrazolyl, purinyl, 4*H*-quinoliziny, isoquinolyl, quinolyl, tetrahydroquinolyl, tetrahydroisoquinolyl, decahydroquinolyl, octahydroisoquinolyl, benzofuranyl, dibenzofuranyl, benzothiophenyl, dibenzothiophenyl, phthalazinyl, naphthyridinyl, quinoxalyl, quinazolinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, furazanyl, phenazinyl, phenothiazinyl, phenoxazinyl, chromenyl, isochromanyl, chromanyl and the like.

[0024] The term "heteroaryl" as used herein includes reference to an aromatic heterocyclic ring system having 5, 6, 7, 8, 9 or 10 ring atoms, at least one of which is selected from nitrogen, oxygen and sulphur. The group may be a polycyclic ring system, having two or more rings, at least one of which is aromatic, but is more often monocyclic. This term includes reference to groups such as pyrimidinyl, furanyl, benzo[b]thiophenyl, thiophenyl, pyrrolyl, imidazolyl, pyrrolidinyl, pyridinyl, benzo[b]furanyl, pyrazinyl, purinyl, indolyl, benzimidazolyl, quinolinyl, phenothiazinyl, triazinyl, phthalazinyl, 2*H*-chromenyl, oxazolyl, isoxazolyl, thiazolyl, isoindolyl, indazolyl, purinyl, isoquinolinyl, quinazolinyl, pteridinyl and the like.

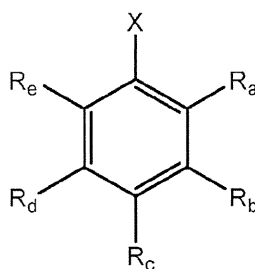
[0025] The term "halogen" or "halo" as used herein includes reference to F, Cl, Br or I. In a particular, halogen may be F or Cl, of which Cl is more common.

[0026] The term "substituted" as used herein in reference to a moiety means that one or more, especially up to 5, more especially 1, 2 or 3, of the hydrogen atoms in said moiety are replaced independently of each other by the corresponding number of the described substituents. The term "optionally substituted" as used herein means substituted or unsubstituted.

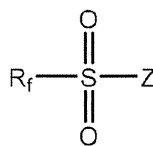
[0027] It will, of course, be understood that substituents are only at positions where they are chemically possible, the person skilled in the art being able to decide (either experimentally or theoretically) without inappropriate effort whether a particular substitution is possible. For example, amino or hydroxy groups with free hydrogen may be unstable if bound to carbon atoms with unsaturated (e.g. olefinic) bonds. Additionally, it will of course be understood that the substituents described herein may themselves be substituted by any substituent, subject to the aforementioned restriction to appropriate substitutions as recognised by the skilled person.

Solid phase support material

[0028] As discussed hereinbefore, the present invention provides a solid-phase support material suitable for supporting a metallocene catalytic compound, the solid-phase support material comprising a solid polymethylaluminoxane modified by reaction with a compound of formula (I) or (II) shown below:



(I)



(II)

wherein

X is hydroxyl or a group $B(Y)_2$ or a group $Al(Y)_2$,

wherein each Y is independently selected from hydroxyl, phenyl and naphthalenyl, any of which may be optionally substituted with one or more groups selected from halo, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trihaloalkyl;

R_a and R_b are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, or

R_a and R_b are linked, such that, when taken with the atoms to which they are attached, they form a 6-membered aromatic ring that is optionally substituted by one or more groups selected from halo, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trihaloalkyl;

R_c - R_e are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl;

Z is hydroxyl or a group $-NR_xR_y$,

wherein R_x and R_y are independently selected from hydrogen and (1-4C)alkyl;

R_f is (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, trihaloalkyl or a phenyl group that is optionally substituted with one or more groups selected from hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo and trihaloalkyl;

wherein the mole ratio of the compound of formula (I) or (II) to the solid polyaluminumoxane within the solid-phase support material ranges from 0.0001:1 to 0.3:1.

[0029] The solid-phase support materials of the invention present a number of advantages over other solid-phase support material. Perhaps most notably, when used in the preparation of supported metallocene-based Ziegler-Natta catalysts for use in the polymerisation of olefins, the solid-phase support materials of the invention give rise to a marked increase in catalytic activity.

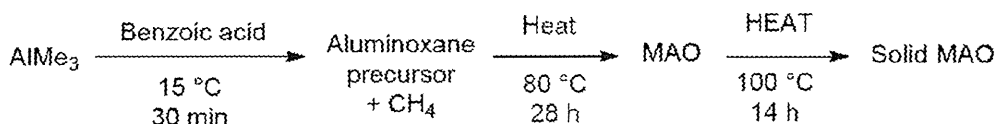
[0030] It will be understood that the term "solid polymethylaluminoxane" and "solid MAO" as used herein synonymously refer to a solid-phase material having the general formula $-(\text{Me})\text{AlO})_n-$, wherein n is an integer from 10 to 50. Any suitable solid polymethylaluminoxane may be used..

[0031] There exist numerous substantial structural and behavioural differences between solid polymethylaluminoxane and other (non-solid) methyl aluminoxanes. Perhaps most notably, solid polymethylaluminoxane is distinguished from other methyl aluminoxanes (MAOs) as it is insoluble in hydrocarbon solvents and so acts as a heterogeneous support system. The solid polymethylaluminoxanes useful in the preparation of the solid-phase support material of the invention are insoluble in toluene and hexane.

[0032] In contrast to non-solid (hydrocarbon-soluble) methyl aluminoxanes, which are traditionally used as an activator species in slurry polymerisation or to modify the surface of a separate solid support material (e.g. SiO_2), the solid polyaluminumoxanes useful as part of the present invention are themselves suitable for use as solid-phase support materials, without the need for an additional activator. Hence, the solid-phase support materials of the invention are devoid of any other species that could be considered a solid support (e.g. inorganic material such as SiO_2 , Al_2O_3 and ZrO_2). Similarly, the only inorganic solid support employed in the catalytic compositions of the invention is the solid-phase support material of the invention (i.e. no additional solid support such as SiO_2 , Al_2O_3 and ZrO_2 are necessary). Moreover, given the dual function of the solid-phase support materials of the invention (as catalytic support and activator species), the catalytic compositions of the invention contain no additional catalytic activator species.

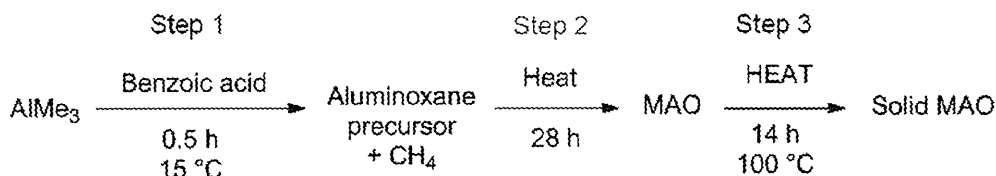
[0033] In an embodiment, the solid polymethylaluminoxane is prepared by heating a solution containing polymethylaluminoxane and a hydrocarbon solvent (e.g. toluene), so as to precipitate solid polymethylaluminoxane. The solution containing polymethylaluminoxane and a hydrocarbon solvent may be prepared by reacting trimethyl aluminium and benzoic acid in a hydrocarbon solvent (e.g. toluene), and then heating the resulting mixture.

[0034] In an embodiment, the solid polymethylaluminoxane is prepared according to the following protocol:



The properties of the solid polymethylaluminoxane can be adjusted by altering one or more of the processing variables used during its synthesis. For example, in the above-outlined protocol, the properties of the solid polymethylaluminoxane may be adjusted by varying the Al:O ratio, by fixing the amount of AlMe_3 and varying the amount of benzoic acid. Exemplary Al:O ratios are 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1 and 1.6:1. Suitably the Al:O ratio is 1.2:1 or 1.3:1. Alternatively, the properties of the solid polymethylaluminoxane may be adjusted by fixing the amount of benzoic acid and varying the amount of AlMe_3 .

[0035] In another embodiment, the solid polymethylaluminoxane is prepared according to the following protocol:



[0036] In the above protocol, steps 1 and 2 may be kept constant, with step 2 being varied. The temperature of step 2 may be 70-100°C (e.g. 70°C, 80°C, 90°C or 100°C). The duration of step 2 may be from 12 to 28 hours (e.g. 12, 20 or 28 hours). The duration of step 2 may be from 5 minutes to 24 hours. Step 3 may be conducted in a solvent such as toluene.

[0037] In an embodiment, the aluminium content of the solid polymethylaluminoxane falls within the range of 36–41 wt%.

[0038] The solid polymethylaluminoxane useful as part of the present invention is characterised by extremely low solubility in toluene and n-hexane. In an embodiment, the solubility in n-hexane at 25°C of the solid polymethylaluminoxane is 0–2 mol%. Suitably, the solubility in n-hexane at 25°C of the solid polymethylaluminoxane is 0–1 mol%. More suitably,

the solubility in n-hexane at 25°C of the solid polymethylaluminoxane is 0–0.2 mol%. Alternatively or additionally, the solubility in toluene at 25°C of the solid polymethylaluminoxane is 0–2 mol%. Suitably, the solubility in toluene at 25°C of the solid polymethylaluminoxane is 0–1 mol%. More suitably, the solubility in toluene at 25°C of the solid polymethylaluminoxane is 0–0.5 mol%. The solubility in solvents can be measured by the method described in JP-B(KOKOKU)-H07 42301.

[0039] In a particularly suitable embodiment, the solid polymethylaluminoxane is as described in US2013/0059990, WO2010/055652 or WO2013/146337, and is obtainable from Tosoh Finechem Corporation, Japan.

[0040] In an embodiment, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.2:1. Suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.1:1. More suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.07:1. Most suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.05:1.

[0041] In an embodiment, Z is hydroxyl.

[0042] In another embodiment, X is hydroxyl or a group B(Y)₂.

[0043] In another embodiment, X is hydroxyl or a group Al(Y)₂.

[0044] In another embodiment, each Y is independently selected from hydroxyl, phenyl and naphthalenyl, any of which may be optionally substituted with one or more groups selected from fluoro, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trifluoroalkyl.

[0045] In another embodiment, each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trifluoroalkyl.

[0046] Suitably, each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro, (1-4C)alkyl and trifluoromethyl.

[0047] More suitably, each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro and trifluoromethyl.

[0048] In an embodiment, R_a-R_e are each independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, or

R_a and R_b are linked, such that, when taken with the atoms to which they are attached, they form a 6-membered aromatic ring that is optionally substituted by one or more groups selected from halo and trihaloalkyl.

[0049] Suitably, R_a - R_e are each independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, or

R_a and R_b are linked, such that, when taken with the atoms to which they are attached, they form a 6-membered aromatic ring that is optionally substituted by four groups, each being independently selected from halo (e.g. fluoro) and trihaloalkyl (e.g. trifluoromethyl).

[0050] More suitably, R_a - R_e are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, fluoro or trifluoroalkyl.

[0051] Even more suitably, R_a - R_e are independently hydrogen, (1-4C)alkyl, fluoro or trifluoroalkyl.

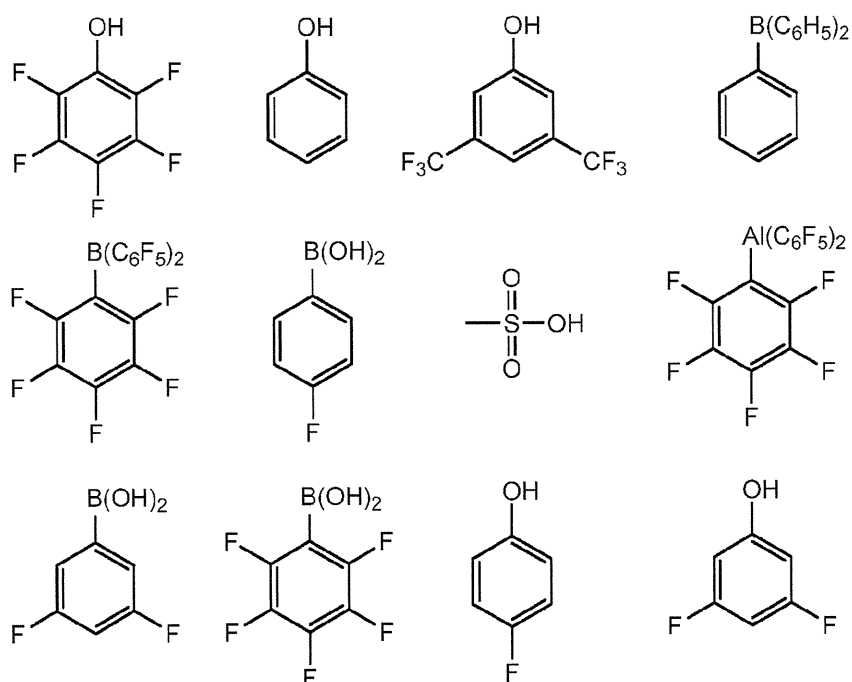
[0052] Most suitably, R_a - R_e are independently hydrogen, methyl, ethyl, tert-butyl, fluoro or trifluoromethyl.

[0053] In another embodiment, R_f is (1-4C)alkyl, trihaloalkyl or a phenyl group that is optionally substituted with one or more groups selected from hydroxyl, (1-4C)alkyl, halo and trihaloalkyl.

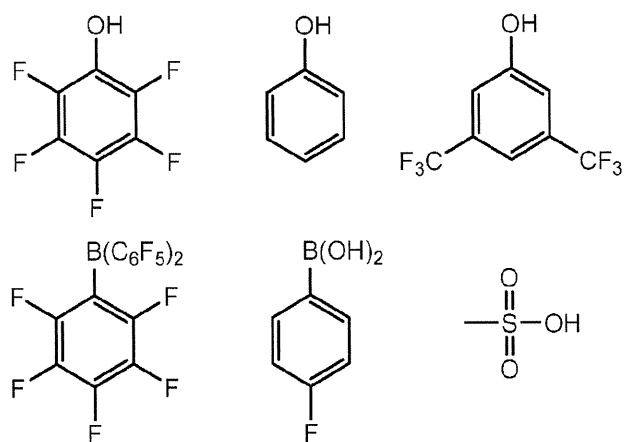
[0054] Suitably, R_f is (1-4C)alkyl, trihaloalkyl or *p*-toluenyl.

[0055] More suitably, wherein R_f is methyl, ethyl, trifluoromethyl or *p*-toluenyl.

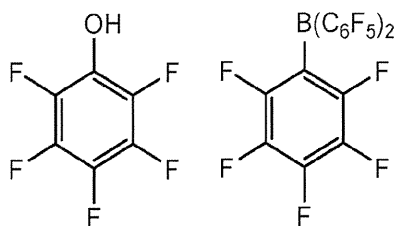
[0056] In an embodiment, the compound of formula (I) or formula (II) is selected from one or more of the following:



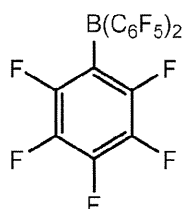
[0057] In an embodiment, the compound of formula (I) or formula (II) is selected from one or more of the following:



[0058] Suitably, the compound of formula (I) or (II) is selected from one or more of the following:



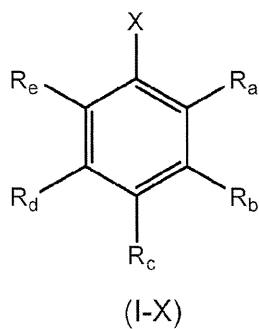
[0059] Most suitably, the compound of formula (I) or (II) is:



[0060] In an embodiment, the solid-phase support material has an aluminium content of 23 to 40 wt%. Suitably, the solid-phase support material has an aluminium content of 28 to 40 wt%. The aluminium content of the solid-phase support material can be determined, for example, by ICP-MS.

[0061] In an embodiment, the BET surface area of the solid-phase support material is 10.0 to 20.0 $\text{m}^2\text{mmol}_{\text{Al}}^{-1}$.

[0062] In another aspect, the present invention also provides a solid-phase support material suitable for supporting a metallocene catalytic compound, the solid-phase support material comprising a solid polymethylaluminoxane modified by reaction with a compound of formula (I-X) shown below:



wherein

X is hydroxyl or a group $B(Y)_2$,

wherein each Y is pentafluorophenyl; and

R_a - R_e are each fluoro.

[0063] In an embodiment, the mole ratio of the compound of formula (I-X) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 1:1.

Preparation of solid-phase support material

[0064] As described hereinbefore, the present invention also provides a method of preparing a solid-phase support material described herein, the method comprising the steps of:

- a) providing a solid polymethylaluminoxane in a first solvent;
- b) contacting the solid polymethylaluminoxane of step a) with one or more compounds of formula (I) or (II) as defined herein; and
- c) isolating the product formed from step b);

wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.3:1.

[0065] The solid-phase support materials of the invention are straightforwardly prepared using mild reaction conditions.

[0066] Step a) may comprise the steps of:

- i. precipitating a solid polymethylaluminoxane from a reaction medium,
- ii. isolating the precipitated solid polymethylaluminoxane from the reaction medium, and
- iii. dispersing the isolated solid polymethylaluminoxane in the first solvent.

[0067] In an embodiment, the one or more compounds of formula (I) or (II) used in step b) is provided in a second solvent.

[0068] The first and second solvents may be the same or different. Any suitable aromatic or aliphatic may be used, including toluene, benzene and hexane. In an embodiment, both the first and second solvent are toluene.

[0069] Step b) may be conducted at a temperature of 18-150 °C. Suitably, step b) is conducted at a temperature of 18-50 °C. More suitably, step b) is conducted at a temperature of 20-30 °C. Suitably, step b) involves mixing the solid polymethylaluminoxane of step a) with the one or more compounds of formula (I) or (II) as defined herein.

[0070] In an embodiment, step b) further comprises the step of sonicating the mixture of the solid polymethylaluminoxane and the one or more compounds of formula (I) or (II). Sonication

may be performed for a period of 0.1–24 hours or a period of 0.1–5 hours. Suitably, sonication is performed for a period of 0.5–1.5 hours. When sonication is used, step b) is suitably conducted at a temperature of 10–65°C, preferably 18–50°C. More suitably, when sonication is used, step b) is suitably conducted at a temperature of 18–35°C.

[0071] In an embodiment, step b) further comprises the step of sonicating the mixture of the solid polymethylaluminoxane and the one or more compounds of formula (I) or (II), wherein the temperature of the mixture when sonication begins is 15–25°C, and wherein the temperature of the mixture rises to 40–80°C (e.g. 40–65°C) during the course of sonication.

[0072] In an embodiment, when step b) comprises sonicating the mixture of the solid polymethylaluminoxane and the one or more compounds of formula (I) or (II), the temperature of the mixture may not rise above 85°C over the course of step b). Suitably, when step b) comprises sonicating the mixture of the solid polymethylaluminoxane and the one or more compounds of formula (I) or (II), the temperature of the mixture may not rise above 65°C over the course of step b).

[0073] Any suitable sonicating technique may be used. Suitably, when sonication is used in step b), it is conducted in a sonicating water bath. Suitably, the ultrasonic frequency used in step b) is >15 kHz.

[0074] The inventors have surprisingly found that sonicating the mixture of the solid polymethylaluminoxane and the one or more compounds of formula (I) or (II) advantageously obviates the need for conducting step b) at high temperatures, which is believed to result in degradation of the solid-phase support material.

[0075] In an embodiment, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.2:1. Suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.1:1. More suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.07:1. Most suitably, the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step b) ranges from 0.0001:1 to 0.05:1.

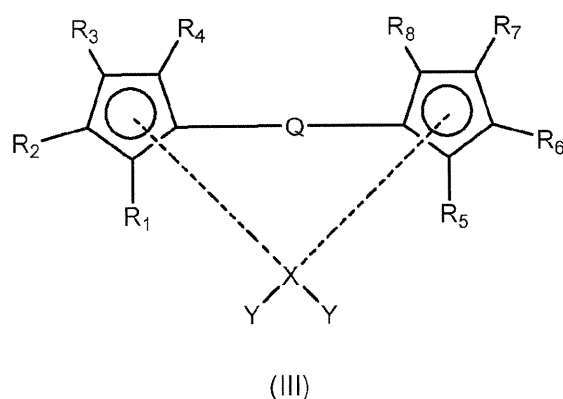
[0076] In another aspect, the present invention also provides a method of preparing a solid-phase support material described herein, the method comprising the steps of:

- a) providing a solid polymethylaluminoxane in a first solvent;
- b) contacting the solid polymethylaluminoxane of step a) with one or more compounds of formula (I-X); and
- c) isolating the product formed from step b).

Catalytic compositions

[0077] As described hereinbefore, the present invention also provides a catalytic composition comprising:

- a) a compound of formula (III) shown below; and
- b) a solid-phase support material as defined herein



wherein

R_1 and R_2 are each independently hydrogen or (1-2C)alkyl;

R_3 and R_4 are each independently hydrogen or (1-4C)alkyl, or R_3 and R_4 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

R_5 and R_6 are each independently hydrogen or (1-4C)alkyl, or R_5 and R_6 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

R_7 and R_8 are each independently hydrogen or (1-4C)alkyl, or R_3 and R_4 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

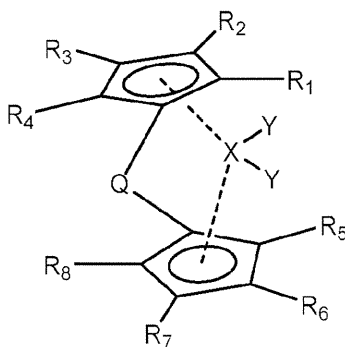
Q is absent (in which case each cyclopentadienyl ring is bound to hydrogen at this position), or is a bridging group selected from -CH₂- or -CH₂CH₂-, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and aryl, or Q is a bridging group -Si(R₉)(R₁₀)-,

wherein R₉ and R₁₀ are independently (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl or aryl;

X is zirconium or hafnium; and

each Y group is independently selected from halo, hydride, (1-6C)alkyl, (1-6C)alkoxy, aryl or aryloxy, either or which is optionally substituted with one or more groups selected from (1-6C)alkyl and halo.

[0078] It will be appreciated that the structural formula (III) presented above is intended to show the substituent groups in a clear manner. A more representative illustration of the spatial arrangement of the groups is shown in the alternative representation below:



[0079] It will also be appreciated that, depending on the identities of substituents R₁-R₈, the compounds of the present invention may be present as *meso* or *rac* isomers, and the present invention includes both such isomeric forms. A person skilled in the art will appreciate that a mixture of isomers of the compound of the present invention may be used for catalysis applications, or the isomers may be separated and used individually (using techniques well known in the art, such as, for example, fractional crystallization).

[0080] If the structure of a compound of formula (III) is such that *rac* and *meso* isomers do exist, the compound may be present in the *rac* form only, or in the *meso* form only.

[0081] The catalytic compositions of the invention exhibit superior catalytic performance when compared with current metallocene compounds/compositions used in the polymerisation of α -olefins. In particular, when compared with analogous solid MAO-supported the compositions of the invention, containing a modified solid MAO support material, exhibit significantly increased catalytic activity in the homopolymerisation and copolymerisation of α -olefins.

[0082] The compound of formula (III) may be immobilized on the solid phase support material by one or more ionic or covalent interactions.

[0083] In the compositions of the invention, the solid-phase support materials of the invention are the only inorganic solid supports used (i.e. no additional solid support such as SiO_2 , Al_2O_3 and ZrO_2 are necessary). Moreover, given the dual function of the solid-phase support materials of the invention (as catalytic support and activator species), the catalytic compositions of the invention contain no additional catalytic activator species.

[0084] In an embodiment, R_1 and R_2 are each hydrogen.

[0085] In another embodiment, R_3 and R_4 are each independently hydrogen or (1-4C)alkyl, or R_3 and R_4 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl and (1-6C)alkoxy.

[0086] Suitably, R_3 and R_4 are each independently hydrogen or (1-4C)alkyl, or R_3 and R_4 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl.

[0087] In another embodiment, R_5 and R_6 are each independently hydrogen or (1-4C)alkyl, or R_5 and R_6 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl and (1-6C)alkoxy.

[0088] Suitably, R_5 and R_6 are each independently hydrogen or (1-4C)alkyl, or R_5 and R_6 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl.

[0089] In another embodiment, R_7 and R_8 are each independently hydrogen or (1-4C)alkyl, or R_7 and R_8 are linked such that, when taken in combination with the atoms to which they are

attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl and (1-6C)alkoxy.

[0090] Suitably, R_7 and R_8 are each independently hydrogen or (1-4C)alkyl, or R_7 and R_8 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl.

[0091] In another embodiment, Q is absent, or is a bridging group selected from $-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group $-\text{Si}(\text{R}_9)(\text{R}_{10})-$,

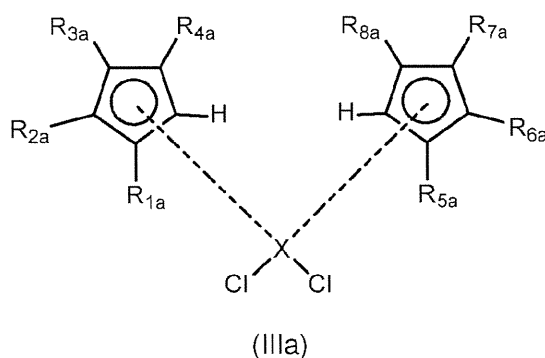
wherein R_9 and R_{10} are independently (1-4C)alkyl or aryl.

[0092] In another embodiment, X is zirconium.

[0093] In another embodiment, each Y group is independently selected from halo.

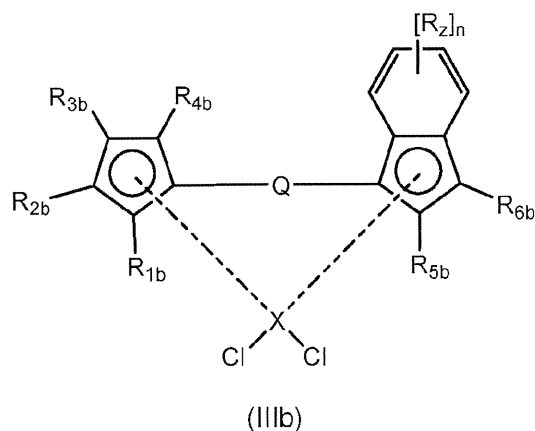
[0094] Suitably, each Y group is chloro.

[0095] In another embodiment, the compound of formula (III) has a structure according to either of formulae (IIIa) or (IIIb) shown below:



wherein

X , R_{1a} , R_{2a} , R_{3a} , R_{4a} , R_{5a} , R_{6a} , R_{7a} and R_{8a} have any of the definitions recited respectively hereinbefore for X , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8



wherein

Q, X, R_{1b}, R_{2b}, R_{3b}, R_{4b}, R_{5b} and R_{6b} have any of the definitions recited respectively hereinbefore for Q, X, R₁, R₂, R₃, R₄, R₅ and R₆;

each R_z is independently halo, (1-4C)alkyl or phenyl; and

n is 0, 1, 2, 3 or 4.

[0096] In another embodiment, the compound of formula (III) has a structure according to formula (IIIa), wherein X is Zr.

[0097] In another embodiment, the compound of formula (III) has a structure according to formula (IIIa), wherein R_{1a}, R_{2a}, R_{5a} and R_{6a} are each hydrogen.

[0098] In another embodiment, the compound of formula (III) has a structure according to formula (IIIa), wherein

R_{1a}, R_{2a}, R_{5a} and R_{6a} are each hydrogen; and

i) R_{3a} and R_{7a} are independently (1-4C)alkyl and R_{4a} and R_{8a} are hydrogen, or

ii) R_{3a} and R_{4a} are linked such that when taken with the carbon atoms to which they are attached they collectively form a 6-membered aryl group that is optionally substituted with one or more groups selected from halo, (1-4C)alkyl and phenyl, and

R_{7a} and R_{8a} are linked such that when taken with the carbon atoms to which they are attached they collectively form a 6-membered aryl group that is optionally substituted with one or more groups selected from halo, (1-4C)alkyl and phenyl.

[0099] In another embodiment, the compound of formula (III) has a structure according to formula (IIIb), wherein X is Zr.

[00100] In another embodiment, the compound of formula (III) has a structure according to formula (IIIb), wherein R_{1b} and R_{2b} are each hydrogen.

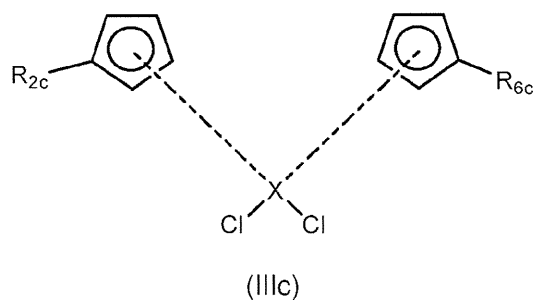
[00101] In another embodiment, the compound of formula (III) has a structure according to formula (IIIb), wherein R_{3b} and R_{4b} are each hydrogen, or R_{3b} and R_{4b} are linked such that when taken with the carbon atoms to which they are attached they collectively form a 6-membered aryl group that is optionally substituted with one or more groups selected from halo, (1-4C)alkyl and phenyl.

[00102] In another embodiment, the compound of formula (III) has a structure according to formula (IIIb), wherein R_{5b} and R_{6b} are each hydrogen, or R_{3b} and R_{4b} are linked such that when taken with the carbon atoms to which they are attached they collectively form a 6-membered aryl group that is optionally substituted with one or more groups selected from halo, (1-4C)alkyl and phenyl.

[00103] In another embodiment, the compound of formula (III) has a structure according to formula (IIIb), wherein Q is a bridging group selected from $-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-$, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group $-\text{Si}(\text{R}_9)(\text{R}_{10})-$,

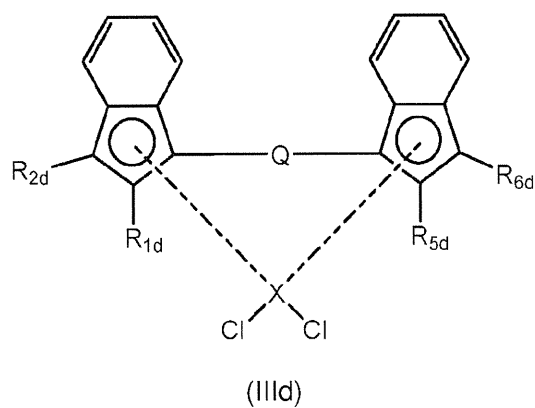
wherein R_9 and R_{10} are independently (1-4C)alkyl or phenyl.

[00104] In another embodiment, the compound of formula (III) has a structure according to any of formulae (IIIc), (IIId), (IIIe) or (IIIf) shown below:



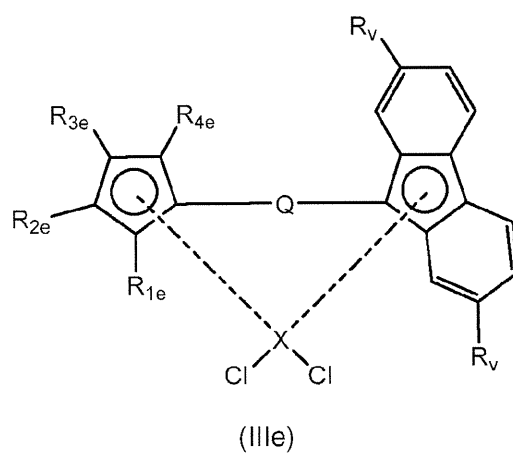
wherein

X , R_{2c} and R_{6c} have any of the definitions recited respectively hereinbefore for X , R_2 and R_6



wherein

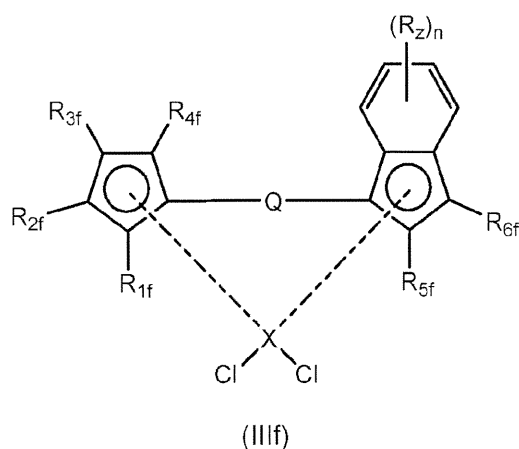
X, Q, R_{1d}, R_{2d}, R_{5d} and R_{6d} have any of the definitions recited respectively hereinbefore for X, Q, R₁, R₂, R₅ and R₆



wherein

X, Q, R_{1e}, R_{2e}, R_{3e} and R_{4e} have any of the definitions recited respectively hereinbefore for X, Q, R₁, R₂, R₃ and R₄; and

each R_v is independently (1-4C)alkyl or phenyl



wherein

R_z , n , X , Q , R_{1f} , R_{2f} , R_{3f} , R_{4f} , R_{5f} and R_{6f} have any of the definitions recited respectively hereinbefore for R_z , n , X , Q , R_1 , R_2 , R_3 , R_4 , R_5 and R_6 .

[00105] In another embodiment, the compound of formula (III) has a structure according to formula (IIIc), wherein R_{2c} and R_{6c} are each independently methyl or n-butyl.

[00106] In another embodiment, the compound of formula (III) has a structure according to formula (IIId), wherein Q is absent (in which case each cyclopentadienyl ring is bound to hydrogen at this position) or is a bridging group selected from $-CH_2-$ or $-CH_2CH_2-$, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group $-Si(R_9)(R_{10})-$,

wherein R_9 and R_{10} are independently (1-2C)alkyl or phenyl.

[00107] In another embodiment, the compound of formula (III) has a structure according to formula (IIId), wherein R_{1d} , R_{2d} , R_{5d} and R_{6d} are each independently hydrogen or (1-3C)alkyl.

[00108] In another embodiment, the compound of formula (III) has a structure according to formula (IIIe), wherein R_{1e} , R_{2e} , R_{3e} and R_{4e} each independently hydrogen or (1-3C)alkyl.

[00109] In another embodiment, the compound of formula (III) has a structure according to formula (IIIe), wherein Q is a bridging group selected from $-CH_2-$ or $-CH_2CH_2-$, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group $-Si(R_9)(R_{10})-$,

wherein R_9 and R_{10} are independently (1-2C)alkyl or phenyl.

[00110] In another embodiment, the compound of formula (III) has a structure according to formula (IIIe), wherein each R_v is independently methyl or tert-butyl

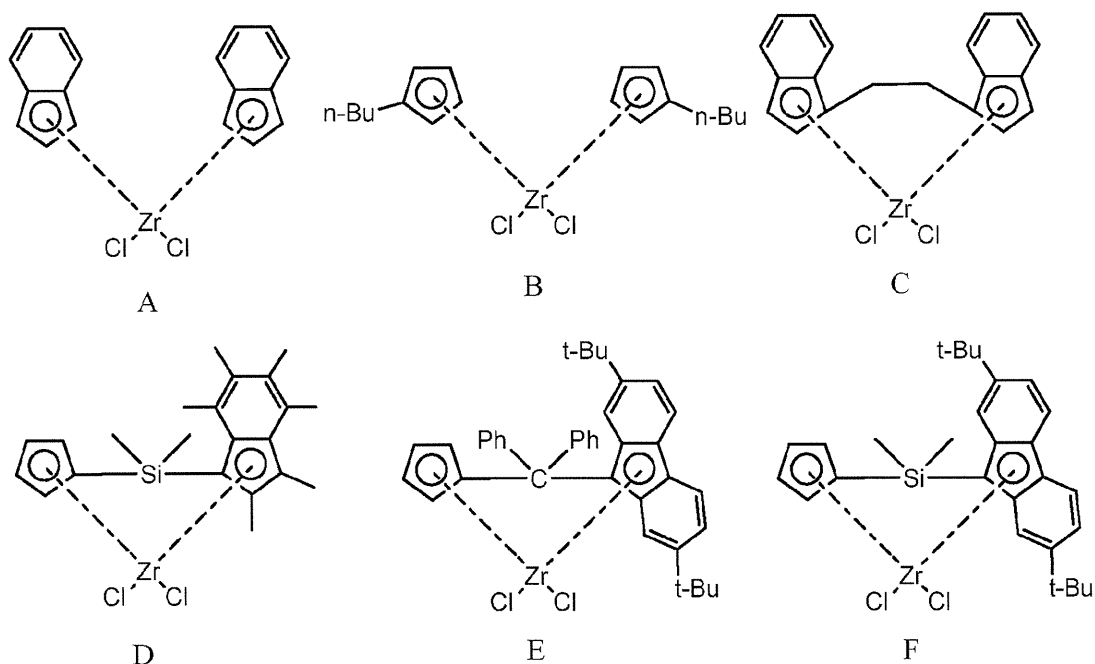
[00111] In another embodiment, the compound of formula (III) has a structure according to formula (III_f), wherein R_{1f}, R_{2f}, R_{3f}, R_{4f}, R_{5f} and R_{6f} are each independently hydrogen or (1-3C)alkyl, and

each R_z is independently (1-3C)alkyl.

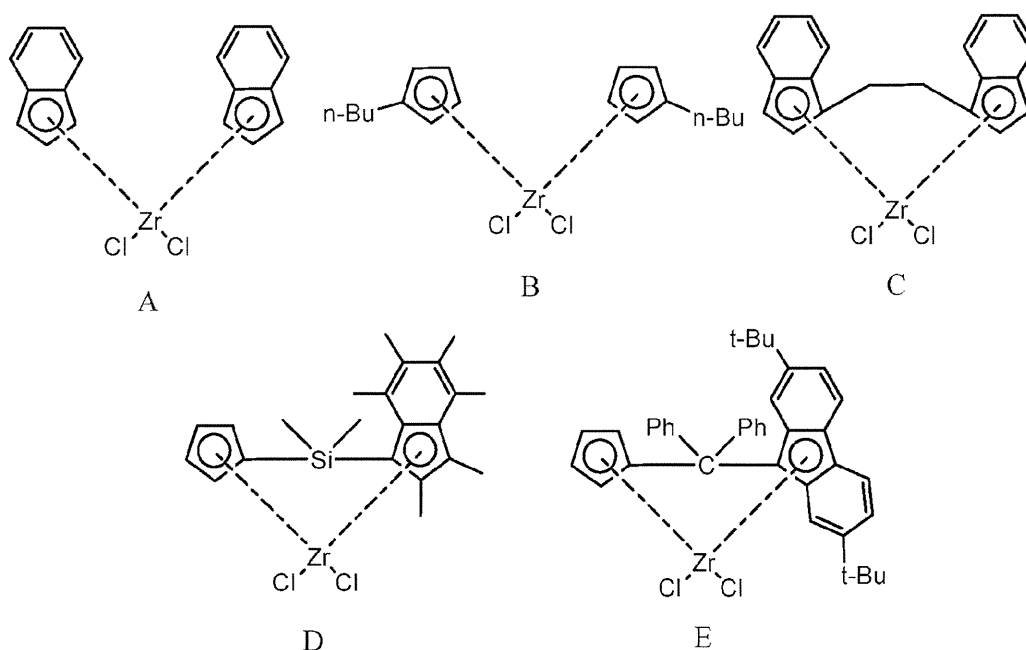
[00112] In another embodiment, the compound of formula (III) has a structure according to formula (III_f), wherein Q is a bridging group selected from -CH₂- or -CH₂CH₂-, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group -Si(R₉)(R₁₀)-,

wherein R₉ and R₁₀ are independently (1-2C)alkyl or phenyl.

[00113] In another embodiment, the compound of formula (III) has any of the structures A-F shown below:



[00114] In another embodiment, the compound of formula (III) has any of the structures A-E shown below:



[00115] Within the catalytic composition of the invention, any of the compounds according to formula (III) may be provided with any solid-phase support material defined herein.

[00116] In a particularly suitable embodiment, when Q (in formula (III)) is ethylene, R_d is selected from hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and halo.

Preparation of catalytic compositions

[00117] As described hereinbefore, the present invention also provides a method for the preparation of a catalytic composition defined herein, the method comprising the steps of:

- providing a solid-phase support material as defined herein in a suitable solvent
- contacting the solid-phase support material of step a) with a compound of formula (III) defined herein; and
- isolating the product resulting from step b).

[00118] The solid-phase support materials of the invention are straightforwardly prepared using mild reaction conditions.

[00119] Suitable solvents for use in step a) will be well known to one of ordinary skill in the art, and include toluene, *o*-xylene, mesitylene, pentane, hexane, heptane, cyclohexane and methylcyclohexane. Suitably, the solvent used in step a) is toluene.

[00120] Step b) may involve mixing the reagents for a period of 0.05–6 hours. Step b) may be conducted at a temperature of 1–3 hours.

Applications

[00121] As discussed hereinbefore, the present invention also provides a use of the solid-phase support material defined herein as a solid-phase support for supporting a metallocene catalytic compound.

[00122] The solid-phase support materials of the invention present a number of advantages over other solid-phase support material. Perhaps most notably, when used in the preparation of supported metallocene-based Ziegla-Natta catalysts for use in the polymerisation of olefins, the solid-phase support materials of the invention give rise to a marked increase in catalytic activity.

[00123] In an embodiment, the solid-phase support material is used as a solid-phase support for supporting a metallocene catalytic compound in an olefin (e.g. ethene) polymerisation reaction.

[00124] As discussed hereinbefore, the present invention also provides a use of a catalytic composition as defined herein as a polymerisation catalyst for the preparation of a polyolefin.

[00125] As discussed hereinbefore, the present invention also provides a process for forming a polyolefin (e.g. a polyethylene), the process comprising the step of reacting olefin monomers in the presence of a catalytic composition defined herein.

[00126] The catalytic compositions of the invention exhibit superior catalytic performance when compared with current metallocene compounds/compositions used in the polymerisation of α -olefins. In particular, when compared with analogous solid MAO-supported the compositions of the invention, containing a modified solid MAO support material, exhibit significantly increased catalytic activity in the homopolymerisation and copolymerisation of α -olefins.

[00127] The following paragraphs describe preferred embodiments of the above-described use and method aspects of the invention.

[00128] Since the only inorganic solid support employed in the catalytic compositions of the invention is the solid-phase support material of the invention (i.e. no additional solid support such as SiO_2 , Al_2O_3 and ZrO_2 are necessary), the compositions may be used in the absence of an inorganic support material. Moreover, given the dual function of the solid-phase support materials of the invention (as catalytic support and activator species), the catalytic compositions of the invention may be used in the absence of an additional catalytic activator species.

[00129] In an embodiment, the polyolefin is polyethylene. In such embodiments, the olefin monomers are ethene molecules.

[00130] In another embodiment, the polyolefin is a copolymer formed from ethene monomers comprising 1-10 wt%, by total weight of the monomer, of one or more (4-8C) α -olefin. Suitably, the (4-8C) α -olefin is 1-butene, 1-hexene, 1-octene, or a mixture thereof.

[00131] A person skilled in the art of olefin polymerization will be able to select suitable reaction conditions (e.g. temperature, pressures, reaction times etc.) for such a polymerization reaction. A person skilled in the art will also be able to manipulate the process parameters in order to produce a polyolefin having particular properties.

EXAMPLES

[00132] One or more non-limiting examples of the invention will now be described, for the purpose of illustration only, with reference to the accompanying figures, in which

Fig. 1: SEM images (x250 magnification) of PE samples from catalyst based on solid MAO (a) un-modified, and modified via Method A with 2 mol% loading of (b) $B(C_6F_5)_3$,

Fig. 2: SEM image (x250 magnification) of polyethylene samples from a catalyst based on solid MAO modified with 20 mol% $B(C_6F_5)_3$ via Method A.

Fig. 3: SEM images (x4000 magnification) of solid MAO samples from (a) control, and modified with (b) 10 mol% $B(C_6F_5)_3$, and (c) 40 mol% C_6F_5OH via Method B.

Fig. 4: SEM of modified solid MAO with modifier pentafluorophenol: Al ratio of a) 0.0005:1, b) 0.4:1 and c) 1.2:1.

Fig. 5: SEM of modified solid MAO with modifier 4-fluorophenol: Al ratio of a) 0.0005:1.

Fig. 6: SEM of modified solid MAO with modifier phenol: Al ratio of a) 0.0005:1.

Fig. 7: SEM of modified solid MAO with modifier 4-fluorophenylboronic acid: Al ratio of a) 0.0005:1.

Fig. 8: SEM of modified solid MAO with modifier p-toluene sulfonamide: Al ratio of a) 0.0005:1.

Fig. 9: SEM images (x250 magnification) of PE samples from catalysts based on (a)-(d) unmodified and (e)-(h) 5 mol% $B(C_6F_5)_3$ modified solid MAO with 4 zirconocene complexes.

Fig. 10: SEM images (x1000 magnification) of PE samples from catalysts based on (a)-(b) unmodified and (c)-(d) 5 mol% C_6F_5OH modified solid MAO with 2 different zirconocene complexes.

Fig. 11: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with BPh_3 at 5 mol% loading via Method B.

Fig. 12: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\text{B}(\text{C}_6\text{F}_5)_3$ at 5 mol% loading via Method B.

Fig. 13: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\text{B}(\text{C}_6\text{F}_5)_3$ at 5 mol% loading via Method B.

Fig. 14: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\text{Al}(\text{C}_6\text{F}_5)_3$ at 5 mol% loading via Method B.

Fig. 15: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\text{Al}(\text{C}_6\text{F}_5)_3$ at 5 mol% loading via Method B.

Fig. 16: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\{4\text{-F}\}\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 17: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 18: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 19: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 20: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\{4\text{-F}\}\text{C}_6\text{H}_4\text{OH}$ at 5 mol% loading via Method B.

Fig. 21: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\{4\text{-F}\}\text{C}_6\text{H}_4\text{OH}$ at 5 mol% loading via Method B.

Fig. 22: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{OH}$ at 5 mol% loading via Method B.

Fig. 23: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{OH}$ at 5 mol% loading via Method B.

Fig. 24: Selected region of the ^1H NMR spectrum in d_8 -THF of solid MAO modified with $\text{C}_6\text{F}_5\text{OH}$ at 5 mol% loading via Method B.

Fig. 25: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum in d_8 -THF of solid MAO modified with $\text{C}_6\text{F}_5\text{OH}$ at 5 mol% loading via Method B.

Fig. 26: ^{11}B DEPTH SSNMR spectrum (15 kHz spinning) of 5 mol% BPh_3 modified solid MAO via Method B.

Fig. 27: ^{19}F DEPTH SSNMR spectrum (15 kHz spinning) of 20 mol% $\text{B}(\text{C}_6\text{F}_5)_3$ modified solid MAO via Method B.

Fig. 28: ^{11}B DEPTH SSNMR spectrum (10 kHz spinning) of 20 mol% $\text{B}(\text{C}_6\text{F}_5)_3$ modified solid MAO via Method B.

Fig. 29: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\text{Al}(\text{C}_6\text{F}_5)_3$ modified solid MAO via Method B.

Fig. 30: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (10 kHz spinning) of 5 mol% $\{4\text{-F}\}\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 31: ^{11}B DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\{4\text{-F}\}\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 32: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (10 kHz spinning) of 5 mol% $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 33: $^{11}\text{B}\{^{19}\text{F}\}\{^1\text{H}\}$ DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 34: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 35: $^{11}\text{B}\{^{19}\text{F}\}\{^1\text{H}\}$ DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ modified solid MAO via Method B.

Fig. 36: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (15 kHz spinning) of 10 mol% $\{4\text{-F}\}\text{C}_6\text{H}_4\text{OH}$ modified solid MAO via Method B.

Fig. 37: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (24 kHz spinning) of 5 mol% $\{3,5\text{-F}_2\}\text{C}_6\text{H}_3\text{OH}$ modified solid MAO via Method B.

Fig. 38: $^{19}\text{F}\{^1\text{H}\}$ DEPTH SSNMR spectrum (15 kHz spinning) of 10 mol% $\text{C}_6\text{F}_5\text{OH}$ modified solid MAO via Method B.

Fig. 39: DRIFT spectrum (NaCl window) of solid MAO modified with BPh_3 at 5 mol% loading via Method B.

Fig. 40: DRIFT spectrum (NaCl window) of solid MAO modified with $\text{B}(\text{C}_6\text{F}_5)_3$ at 5 mol% loading via Method B.

Fig. 41: DRIFT spectrum (NaCl window) of solid MAO modified with $\{4\text{-F}\}\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 42: DRIFT spectrum (NaCl window) of solid MAO modified with $\{3,5\text{-F}\}_2\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

Fig. 43: DRIFT spectrum (NaCl window) of solid MAO modified with $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ at 5 mol% loading via Method B.

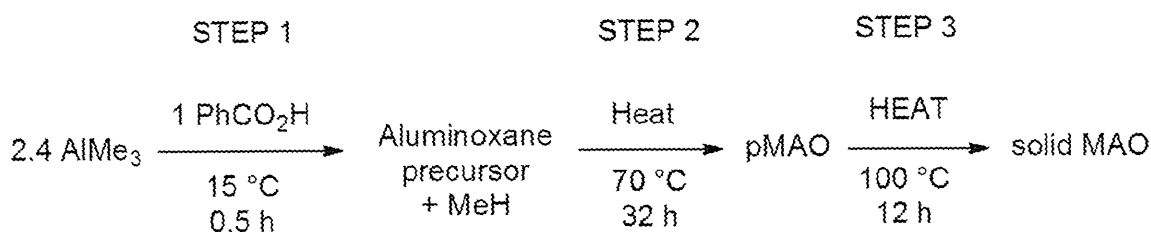
Fig. 44: DRIFT spectrum (NaCl window) of solid MAO modified with $\{4\text{-F}\}\text{C}_6\text{H}_4\text{OH}$ at 5 mol% loading via Method B.

Fig. 45: DRIFT spectrum (NaCl window) of solid MAO modified with $\{3,5\text{-F}\}_2\text{C}_6\text{H}_3\text{OH}$ at 5 mol% loading via Method B.

Fig. 46: DRIFT spectrum (NaCl window) of solid MAO modified with $\text{C}_6\text{F}_5\text{OH}$ at 5 mol% loading via Method B.

Example 1 - Preparation of solid MAO

[00133] The solid MAO useful in the preparation of the solid-phase support material of the invention may be prepared via an adaptation of the optimised procedure in Kaji *et al.* in the US 8,404,880 B2 embodiment 1 (Scheme 1). For brevity, each synthesised solid MAO is represented as solid MAO(Step 1 Al:O ratio/Step 2 temperature in °C,time in h/Step 3 temperature in °C,time in h). Hence, the synthesis conditions outlined in Scheme 1 would yield solid MAO(1.2/70,32/100,12).



Scheme 1 - Synthesis of solid MAO (1.2/70,32/100,12)

[00134] A Rotaflo ampoule containing a solution of trimethyl aluminium (2.139 g, 2.967 mmol) in toluene (8 mL) was cooled to 15 °C with rapid stirring, and benzoic acid (1.509 g, 1.239 mmol) was added under a flush of N₂ over a period of 30 min. Effervescence (presumably methane gas, MeH) was observed and the reaction mixture appeared as a white suspension, which was allowed to warm to room temperature. After 30 min the mixture appeared as a colourless solution and was heated in an oil bath at 70 °C for 32 h (a stir rate of 500 rpm was

used). The mixture obtained was a colourless solution free of gelatinous material, which was subsequently heated at 100 °C for 12 h. The reaction mixture was cooled to room temperature and hexane (40 mL) added, resulting in the precipitation of a white solid which was isolated by filtration, washed with hexane (2 x 40 mL) and dried *in vacuo* for 3 h. Total yield = 1.399 g (71% based on 40 wt% Al).

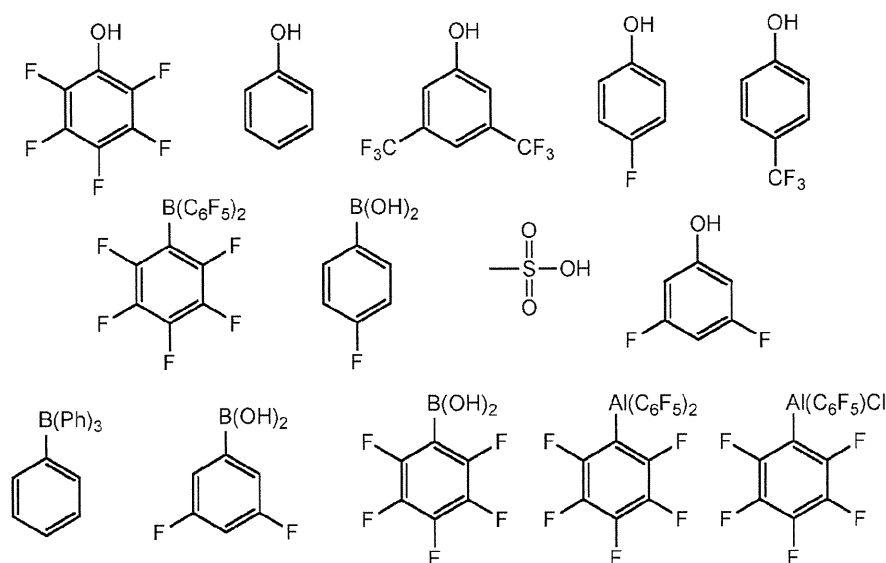
Example 2 - Preparation of solid-phase support materials

Method A

[00135] Typical experiment: To a Schlenk flask charged with solid MAO (Example 1) and the modifier was added toluene, and the resulting dispersion was heated at 80 °C for 2 h with regular swirling. The mixture was cooled to room temperature and the insoluble solids were allowed to settle. The supernatant solution was removed by decantation and the remaining slurry was washed three times with a 2:1 mixture of hexane:toluene and dried *in vacuo* overnight, to afford the modified solid MAO as a free-flowing solid.

Method B

[00136] Typical experiment: To a Schlenk flask charged with a dispersion of solid MAO (Example 1) in toluene was added a solution of the modifier in toluene and the flask was sonicated in a water bath at ambient temperature for 1 h. The resultant mixture was allowed to settle, the supernatant solution was removed by decantation and the remaining slurry was washed three times with a 2:1 mixture of hexane:toluene and dried *in vacuo* overnight, to afford the modified solid MAO as a free-flowing solid.



Modifiers

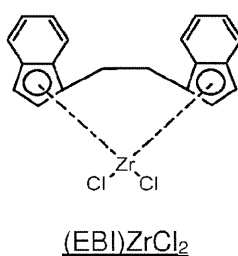
Example 3 - Characterisation of solid-phase support materials and Polymerisation studies

[00137] In order to assess the catalytic performance of the solid-phase support materials, a range of metallocene compounds were supported on a variety of the solid-phase support materials. In a typical experiment, the metallocene catalytic compound (e.g. *rac*-ethylenebis(1-indenyl) zirconium dichloride, (EBI)ZrCl₂) and the support (modified solid MAO) were loaded into a Schlenk flask and toluene (40 mL) was added. The mixture was heated at 80 °C in an oil bath and swirled regularly to ensure complete immobilisation of the metallocene complex (stirring was avoided to prevent aggregation). After 2 h the reaction was removed from the oil bath and allowed to settle, before decantation of the colourless supernatant and thorough drying *in vacuo*.

[00138] Once prepared, the ability of the supported metallocene catalysts to catalyse the polymerisation of ethylene to polyethylene was assessed. In a typical polymerisation experiment, the immobilised catalyst (10 mg), triisobutylaluminium scavenger (150 mg), and hexane (40 mL) were added to a high-pressure RotaFlo ampoule. Ethylene gas was continuously fed into the ampoule at 2 bar overpressure during polymerisation at 70 °C. After 30 min, the reaction was stopped by removing the ampoule from the oil bath, and degassing *in vacuo*. The polymer was isolated on a frit, washed with pentane (50 mL) and vacuum dried at room temperature for 1 h. Each polymerisation experiment was conducted at least twice to ensure the reproducibility of the corresponding outcome, and mean productivities are quoted in units of kg_{PE}g_{CAT}⁻¹ h⁻¹.

[00139] For large scale polymerisation studies, polymerization of ethylene was performed in a 2L stainless steel autoclave reactor as the lines of nitrogen and ethylene gases were directly connected into the reactor. First, to clear up the system, the reactor was evacuated and purged by inert nitrogen gas for 1 hour and dried n-hexane was filled. Then, triethylaluminum (TEA) was fed by pipette into the reactor following by finished catalyst, which was prepared in a glove box into the specified sampling catalyst vessel under nitrogen atmosphere. After that, 3 barg of nitrogen was replaced with ethylene for 3 times and kept within the reactor at 3 barg before starting stirrer. When the reactor was heated until temperature below the set point for 5°C, catalyst was injected into the reactor by ethylene pressure flushed with dried n-hexane. Ethylene gas was introduced via a mass flow controller to fulfill the reactor reaching to the set point of total pressure at 8 barg and the temperature was also controlled at 80°C. Polymerisation was continued for 1 hour, while feeding rate was recorded. Lastly, reaction was cut down by depressurised and cooled down temperature. Resulting mixture was poured into tray and dried at room temperature to remove solvent from polymer.

Supported (EBI)ZrCl₂ complexes



[00140] Table 1 below shows characterisation and polymerisation data for solid MAO samples modified via Method A with B(C₆F₅)₃.

Table 1. Characterisation and polymerisation data for solid MAO samples modified via Method A with B(C₆F₅)₃, Al(C₆F₅)₃ and Al(C₆F₅)₂Cl. Polymerisation conditions: 2 bar, 50 mL hexanes, TIBA.

Modifier	Ratio M:Al mole	Support % Yield	Support BET /m ² mmol _{Al} ⁻¹	Support wt% Al	Catalyst Activity /kgPEmol _{Zr} ⁻¹ h ⁻¹
Control	0	88	17.8	40.0	13686
B(C ₆ F ₅) ₃	0.02	87	15.0	32.6	13972
Al(C ₆ F ₅) ₃	0.02	83	X	30.9	12670
Al(C ₆ F ₅) ₂ Cl	0.02	80	X	32.5	11461

[00141] Although the Al-based modifiers gave rise to support materials having activities that are slightly lower than the control, it is presumed that this is attributable to the relatively high temperature employed in Method A. It is expected that such modifiers will yield improved results when the support material is prepared according to Method B, which uses softer conditions. Preliminary studies support this hypothesis.

[00142] Fig. 1 shows SEM images of polymer samples on carbon tape, which demonstrate that the PE particle size and morphology is not significantly affected by $B(C_6F_5)_3$ modified support (Fig. 1b) with respect to the control (Fig. 1a).

[00143] Table 2 below shows characterisation and polymerisation data for solid MAO samples modified via Method A with increased amounts of $B(C_6F_5)_3$ (compared with the data of Table 1).

Table 2. Characterisation and polymerisation data for solid MAO samples modified via Method A with $B(C_6F_5)_3$ at increased loadings. Polymerisation conditions: 2 bar, 50 mL hexanes, TIBA

Ratio M:Al mole	Support % Yield	Support BET /m ² mmol _{Al} ⁻¹	Support wt% Al	Catalyst Activity /kgPEmolZr ⁻¹ h ⁻¹
0	88	17.8	40.0	13686
0.01	88	14.6	35.3	10787
0.02	87	15.0	34.9	11533
0.04	58	10.6	23.0	11739
0.10	59	12.8	23.5	14028
0.20	48	9.6	19.0	14402

[00144] Although the modifier loadings of 0.01, 0.02 and 0.04 resulted in catalyst activities that are slightly lower than the control, it is expected that this is attributable to the relatively high temperature employed in Method A. It is expected that such loadings will yield improved results when the support material is prepared according to Method B, which uses softer conditions. Preliminary studies support this hypothesis. It is also noted that the results illustrated in Table 1 demonstrate that $B(C_6F_5)_3$ loadings of 0.02 may nonetheless give rise to improved activities when the support material is prepared via Method A.

[00145] SEM imaging (Fig. 2) confirmed that the PE particle size and morphology is preserved with the 20 mol% $B(C_6F_5)_3$ modified catalyst.

[00146] Table 3 below shows characterisation and polymerisation data for solid MAO samples modified via Method B with two different modifiers, $B(C_6F_5)_3$ and C_6F_5OH .

Table 3. Characterisation and polymerisation data for solid MAO samples modified via Method B with $(EBI)ZrCl_2$. Polymerisation conditions: 8 bar, 1000 mL hexanes, TEA.

Modifier	Ratio M:Al mole	Support % Yield	Support wt% Al	Catalyst Activity /kg _{PE} mol _{Zr} ⁻¹ h ⁻¹
Control	0	93.2	35.1	143608
$B(C_6F_5)_3$	0.10	72.9	24.8	211559
C_6F_5OH	0.40	98.8	18	262977

[00147] SEM images of the solid MAO samples mounted on copper tape (Fig. 3) reveal that the particle size and morphology is not significantly affected by $B(C_6F_5)_3$ and C_6F_5OH modified supports with respect to the control.

[00148] Table 4 below shows characterisation and polymerisation data for solid MAO samples modified at 10 mol% loading via Method B with two different modifiers, $B(C_6F_5)_3$ and C_6F_5OH .

Table 4. Characterisation and polymerisation data for solid MAO samples modified at 10 mol% loading via Method B with $(EBI)ZrCl_2$. Polymerisation conditions: 2 bar, 50 mL hexanes, TIBA.

Modifier	Ratio M:Al mole	Support Colour	Support % Yield	Support wt.% Al	Support BET /m ² mmol _{Al} ⁻¹	Catalyst Activity /kg _{PE} mol _{Zr} ⁻¹ h ⁻¹
Control	0	Colourless	88	39.7	15.0	12515
$B(C_6F_5)_3$	0.10	Colourless	62	24.9	18.6	16009
{4-F} C_6H_4OH	0.10	Orange	92	36.7	12.0	11366
{4-CF ₃ } C_6H_4OH	0.10	Green	87	34.8	14.9	6891
{3,5-F ₂ } C_6H_3OH	0.10	Grey	93	37.0	14.7	9178
{3,5-CF ₃ } C_6H_3OH	0.10	Dark red	95	37.9	11.9	3945
C_6F_5OH	0.10	Colourless	92	36.5	14.4	13340

[00149] Table 5 shows polyethylene polymerisation data for solid MAO modified with varying quantities of pentafluorophenol via Method B.

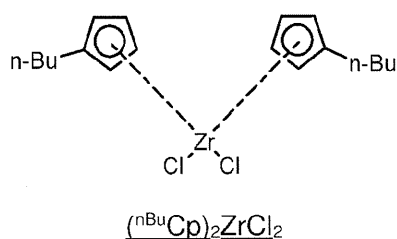
Table 5: Summary data of modified solid MAO with pentafluorophenol (Al wt%) and modified solid MAO/(EBI)ZrCl₂ (Al wt%, Zr wt%, activity, productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (Kg _{PE} /mol _{Zr} ·h)	Bulk density (ml/g)	M_w	MWD
		Al	Zr				
control	36	36	0.4	18.8	0.38	180,109	4.30
0.01	27	27	0.3	32.8	0.44	186,827	4.78
0.05	24	24	0.3	34.2	0.44	182,812	4.42
0.1	21	21	0.4	32.0	0.37	192,566	4.47
0.4	17	17	0.3	57.9	0.38	147,578	3.88
0.8	15	15	0.5	16.8	0.37	158,497	4.11
1.2	10	10	0.3	19.7	0.33	193,992	4.59

Polymerisation conditions: 25 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes

[00150] The aluminum content (wt%) of modified solid MAO decreases from 27, 24, 21 to 17 when more modifier was used. It indicates the presence of phenol compound in modified product corresponding to amount of phenol addition. At ratio of 0.4 it performs 3 folds higher catalyst activity [activity: 18.8 vs 57.9 $\times 10^4$ Kg_{PE}/mol_{Zr}·h] compared with non-modified solid MAO/(EBI)ZrCl₂. Bulk density of obtained polymer is in the range of 0.33 – 0.44 ml/g which is acceptable for polymerization.

Supported (ⁿBuCp)₂ZrCl₂ complexes



[00151] Table 6 shows polyethylene polymerisation data for solid MAO modified with varying quantities of pentafluorophenol via Method B.

Table 6: Summary data of modified solidMAO with pentafluorophenol (Al wt%) and modified solid MAO/(ⁿBuCp)₂ZrCl₂ (Al wt%, Zr wt%, activity, productivity) and polymer properties (bulk density, *M_w*, MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity ×10 ⁴ (KgPE/molZr·h)	Bulk density (ml/g)	<i>M_w</i>	MWD
		Al	Zr				
control	36	40	0.8	31.2	0.34	142,466	2.54
0.0005	40	34	0.6	38.2	0.35	138,051	2.54
0.001	35	35	0.6	34.9			
0.01	27	33	0.4	53.7	0.39	139,519	2.51
0.05	24	33	0.4	40.9			
0.1	21	37	0.5	30.7			
0.4	17	30	0.3	36.9			
0.8	15	14	0.2	53.1			
1.2	10	12	0.3	37.6			
1.6	9	12	0.2	45.9			

Polymerisation conditions: 25 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes

[00152] The increase of modifier amount (modifier: Al ratio of 0.0005 to 1.6) results in lower Al content (wt%) of modified solid MAO and Al & Zr (wt%) content in modified solid MAO/(ⁿBuCp)₂ZrCl₂. At ratio of 0.01 it shows the highest activity of 53.7 × 10⁴ KgPE/molZr·h which is higher than non-modified solid MAO/(ⁿBuCp)₂ZrCl₂ of 31.2 × 10⁴ KgPE/molZr·h. The bulk density of polymer obtained is in the range of 0.35 – 0.39 ml/g which is acceptable for slurry polymerization. The modification of solid MAO has no significant effect to polymer properties such as molecular weight and molecular weight distribution as shown in Table 6. The morphology of modified solid MAO still well controls. They have popcorn shape with particle size of 4-7 micron (Fig. 4).

[00153] Table 7 shows polyethylene polymerisation data for solid MAO modified with 4-fluorophenol via Method B.

Table 7: Summary data of modified solidMAO with 4-fluorophenol (Al wt%) and modified solidMAO/ $(^{nBu}Cp)_2ZrCl_2$ (Al wt%, Zr wt%, activity , productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)	Bulk density (ml/g)	M_w	MWD
		Al	Zr				
control	39	40	0.8	31.2	0.34	142,466	2.54
0.0005	40	-	-	-			
0.05	40	37	0.49	29.83			

Polymerisation conditions: 12.5 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00154] Table 8 shows polyethylene polymerisation data for solid MAO modified with phenol via Method B.

Table 8: Summary data of modified solid MAO with phenol (Al wt%) and modified solid MAO/ $(^{nBu}Cp)_2ZrCl_2$ (Al wt%, Zr wt%, activity , productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)	Bulk density (ml/g)	M_w	MWD
		Al	Zr				
control	39	40	0.8	31.2	0.34	142,466	2.54
0.0005	35	36	0.56	37.75			

Polymerisation conditions: 12.5 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00155] Higher amount of modifier addition (higher modifier:Al) provides lower Al and Zr content in modified solid MAO and modified solid MAO/ $(^{nBu}Cp)_2ZrCl_2$. The morphology of modified solid MAO was elucidated with SEM, (Fig. 5 and 6).

[00156] Table 9 shows polyethylene polymerisation data for solid MAO modified with methanesulfonic acid via Method B

Table 9: Summary data of modified solid MAO with methanesulfonic acid (Al wt%) and modified solid MAO/(ⁿBu Cp)₂ZrCl₂ (Al wt%, Zr wt%, activity, productivity) and polymer properties (bulk density, M_w, MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity × 10 ⁴ (Kg _{PE} /mol _{Zr} ·h)	Bulk density (ml/g)	M _w	MWD
		Al	Zr				
control	39	40	0.8	31.2	0.34	142,466	2.54
0.0045	36	36	0.48	33.8	0.35		

Polymerisation conditions: 12.5 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00157] The modifier:Al of 0.0045 shows higher activity of 33.8 × 10⁴ Kg_{PE}/mol_{Zr}·h with lower Zr content of 0.48 wt%. Bulk density is 0.35 ml/g acceptable for slurry polymerization.

[00158] Table 10 shows polyethylene polymerisation data for solid MAO modified with 4-fluorophenylboronic acid via Method B

Table 10: Summary data of modified solid MAO with 4-fluorophenylboronic acid (Al wt%) and modified solid MAO/(ⁿBu Cp)₂ZrCl₂ (Al wt%, Zr wt%, activity, productivity) and polymer properties (bulk density, M_w, MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity × 10 ⁴ (Kg _{PE} /mol _{Zr} ·h)	Bulk density (ml/g)	M _w	MWD
		Al	Zr				
control	39	40	0.8	31.2	0.34	142,466	2.54
0.0005	33	36	0.48	33.1	0.30		

Finish catalyst 0.0125 g, TEA (200 mmol/L) = 2.5 mL, T = 80°C, P = 8 Bar, solvent hexane 1 L

[00159] The modifier:Al of 0.0005 showed an increased activity of 33.1 × 10⁴ Kg_{PE}/mol_{Zr}·h. Fig. 7 shows the morphology of the modified solid MAO.

[00160] Table 11 shows polyethylene polymerisation data for solid MAO modified with 3,5-Bis(trifluoromethane)phenol via Method B

Table 11: Summary data of modified solid MAO with 3,5-Bis(trifluoromethane)phenol (Al wt%) and modified solidMAO/ $(nBuCp)_2ZrCl_2$ (Al wt%, Zr wt%, activity , productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)	Bulk density (ml/g)	M_w	MWD
control 0.0006	39	Al	Zr	31.2	0.34	142,466	2.54
	34	40	0.8	31.2			
		38	0.51	34.6			

Polymerisation conditions: 12.5 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00161] Table 12 shows polyethylene polymerisation data for solid MAO modified with p-toluene sulfonamide via Method B.

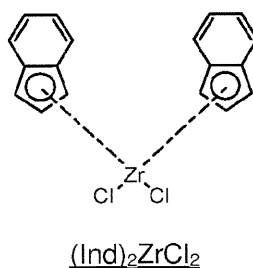
Table 12: Summary data of modified solidMAO with p-toluene sulfonamide (Al wt%) and modified solidMAO/ $(nBuCp)_2ZrCl_2$ (Al wt%, Zr wt%, activity , productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)	Bulk density (ml/g)	M_w	MWD
control 0.0005	39	Al	Zr	31.2	0.34	142,466	2.54
	32	40	0.8	31.2			
		36	0.58	28.40			

Polymerisation conditions: 12.5 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00162] Fig. 8 shows the morphology of the p-toluene sulfonamide-modified solid MAO at 0.0005 mol ratio.

Supported (Ind) $_2$ ZrCl $_2$ complexes



[00163] Table 13 shows polyethylene polymerisation data for solid MAO modified with pentafluorophenol via Method B.

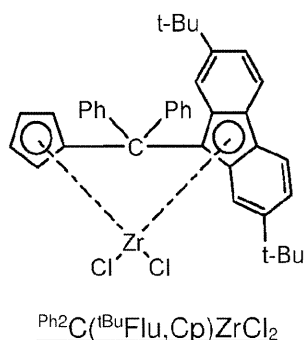
Table 13: Summary data of modified solid MAO with pentafluorophenol (Al wt%) and modified solidMAO/(Ind)₂ZrCl₂ (Al wt%, Zr wt%, activity , productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)	Bulk density (ml/g)	M_w	MWD
		Al	Zr				
control	36	41	0.78	18.47	0.34	142,466	2.54
0.0005	40				0.32		
0.4	17	19	0.44	28.4			

Polymerisation conditions: 25 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes.

[00164] The modification of solid MAO with pentafluorophenol with modifier:Al ratio of 0.4 used as solid activator for (Ind)₂ZrCl₂ is able to enhance in catalyst activity of 28.4 KgPE/gCat·h.

Supported $\text{Ph}_2\text{C}(\text{tBuFlu,Cp})\text{ZrCl}_2$ complexes



[00165] Table 14 shows polyethylene polymerisation data for solid MAO modified with varying quantities pf pentafluorophenol via Method B.

Table 14: Summary data of modified solid MAO with pentafluorophenol (Al wt%) and modified solid MAO/ $^{Ph_2}C(^{tBu}Flu,Cp)ZrCl_2$ (Al wt%, Zr wt%, activity, productivity) and polymer properties (bulk density, M_w , MWD).

Ratio M:Al (mole)	Al (wt%) - ICP Modified solidMAO	Finish catalyst ICP (wt%)		Activity $\times 10^4$ (KgPE/molZr·h)
		Al	Zr	
control	36	38	0.58	5.3
0.0005	40	36	0.6	6.2
0.001	35	38	0.67	5.5
0.01	27	37	0.67	5.4
0.05	24	30	0.34	11.6
0.1	21	29	0.29	15.9
0.4	17	16	0.36	9.2
0.8	15	12	0.40	7.7
1.2	10	11	0.13	3.2
1.6	9	11	0.08	1.0

Polymerisation conditions: 25 mg Catalyst, 2.5 mL TEA, 80 °C, 8 bar. 1 L hexanes

Further studies

[00166] Table 15 shows characterisation and polymerisation data for solid MAO samples modified with $B(C_6F_5)_3$ via Method B at different loadings, and polymerisation activities with 2 different zirconocene precatalysts.

Table 15. Characterisation data for solid MAO samples modified with $B(C_6F_5)_3$ via Method B at different loadings, and polymerisation activities with 2 different zirconocene precatalysts.

Ratio M : Al (mol)	Support Yield (%)	Support ICP-MS (wt% Al)	Support BET (m ² mmol _{Al} ⁻¹)	Activity (kgPEmolZr ⁻¹ h ⁻¹)	
				(EBI)ZrCl ₂	(ⁿ BuCp) ₂ ZrCl ₂
0.00	94	38.5	16.6	12692	11900
0.01	89	38.1	14.2	15662	10827
0.05	78	36.4	15.2	16718	9690
0.10	62	32.5	16.8	16106	9346
0.20	44	25.3	11.6	17834	9088

[00167] Table 15 shows the polymerisation activities using (EBI)ZrCl₂ and (ⁿBuCp)₂ZrCl₂ when $B(C_6F_5)_3$ was used as modifier at different molar ratios. This demonstrates an increase with the former but a decrease with the latter.

[00168] Table 16 shows characterisation and polymerisation data for solid MAO samples modified with C_6F_5OH via Method B at different loadings, and polymerisation activities with 2 different zirconocene precatalysts.

Table 16. Characterisation data for solid MAO samples modified with C_6F_5OH via Method B at different loadings, and polymerisation activities with 2 different zirconocene precatalysts.

Ratio M : Al (mol)	Support Yield (%)	Support ICP-MS (wt% Al)	Support BET ($m^2mmol_{Al}^{-1}$)	Activity ($kg_{PE}mol_{Zr}^{-1}h^{-1}$)	
				(EBI) $ZrCl_2$	($nBuCp$) $_2ZrCl_2$
0.00	94	38.5	16.6	12692	11900
0.01	93	37.5	15.6	12500	8119
0.05	83	36.8	14.8	13330	9099
0.10	91	34.4	14.4	13023	7655
0.20	93	25.4	11.9	14392	5153

[00169] Table 16 shows the polymerisation activities using (EBI) $ZrCl_2$ and ($nBuCp$) $_2ZrCl_2$ when C_6F_5OH was used as modifier at different molar ratios. This demonstrates an increase with the former but a decrease with the latter.

[00170] Tables 17 to 19 shows the molecular weights of the polyethylene using various modifiers on solid MAO and various complexes.

Table 17. Polymerisation Activities and GPC data for unmodified solid MAO (control) with 5 different zirconocene precatalysts.

Precatalyst	Activity ($kg_{PE}mol_{Zr}^{-1}h^{-1}$)	M_w (kg/mol)	PDI
(EBI) $ZrCl_2$	12692	99.0	3.5
($nBuCp$) $_2ZrCl_2$	11900	254.8	2.7
$Me_2SB(PhBu_2Flu, I^*)ZrCl_2$	5849	585.6	2.8
$Me_2SB(Cp, I^*)ZrCl_2$	9468	178.2	2.7

Table 18. *Polymerisation Activities and GPC data for $B(C_6F_5)_3$ modified solid MAO at 5 mol% loading via Method B with 5 different zirconocene precatalysts.*

Precatalyst	Activity ($\text{kgPEmolZr}^{-1}\text{h}^{-1}$)	M_w (kg/mol)	PDI
(EBI)ZrCl ₂	17512	101.6	4.0
(ⁿ BuCp) ₂ ZrCl ₂	9690	289.9	2.6
Me ₂ SB(^t Bu ₂ Flu, I*)ZrCl ₂	6319	633.6	3.0
Me ₂ SB(Cp, I*)ZrCl ₂	7020	252.1	2.5

Table 19. *Polymerisation activities and GPC data for C_6F_5OH modified solid MAO at 5 mol% loading via Method B with 5 different zirconocene precatalysts.*

Precatalyst	Activity ($\text{kgPEmolZr}^{-1}\text{h}^{-1}$)	M_w (kg/mol)	PDI
(EBI)ZrCl ₂	13330	132.9	3.7
(ⁿ BuCp) ₂ ZrCl ₂	9090	290.6	2.7
Me ₂ SB(^t Bu ₂ Flu, I*)ZrCl ₂	8016	662.2	3.3
Me ₂ SB(Cp, I*)ZrCl ₂	7671	185.5	3.2

[00171] The results presented in Tables 17-19 show that the modification of the support has no direct effect on the molecular weight of the resulting polyethylene.

[00172] Table 20 shows characterisation data for solid MAO samples modified with various modifiers at 5 mol% loading via Method B, and polymerisation data with 3 different zirconocene precatalysts.

Table 20. Characterisation data for solid MAO samples modified at 5 mol% loading via Method B, and polymerisation activities with 3 different zirconocene precatalysts.

Modifier	Yield (%)	ICP-MS Al (wt%)	BET (m ² g ⁻¹)	Activity (kgPEmolZr ⁻¹ h ⁻¹)		
				(EBI)ZrCl ₂	(ⁿ BuCp) ₂ ZrCl ₂	^{Me} 2SB(Cp,I*)ZrCl ₂
Control	94	38.5	16.6	12692	11900	9468
BPh ₃	59	36.5	15.2	10898	6204	5753
B(C ₆ F ₅) ₃	89	36.4	14.3	15662	10827	7020
Al(C ₆ F ₅) ₃	76	33.3	12.9	5449	8047	9530
{4-F}C ₆ H ₄ B(OH) ₂	87	38.4	15.0	4052	5414	5718
{3,5-F} ₂ C ₆ H ₃ B(OH) ₂	86	30.3	13.5	8036	4694	3930
C ₆ F ₅ B(OH) ₂	86	33.7	15.2	3243	3617	7956
{4-F}C ₆ H ₄ OH	90	38.0	15.2	6203	7988	4674
{3,5-F} ₂ C ₆ H ₃ OH	91	35.5	15.0	4158	9629	8066
C ₆ F ₅ OH	90	36.8	14.8	13330	9090	7671

[00173] Table 21 shows spectroscopic data for the different modified solid polymethylaluminoxane and complexes.

Table 21. Spectroscopic data for solid MAO samples modified at 5 mol% loading via Method B.

Modifier	NMR in THF- <i>d</i> ₈		SSNMR			DRIFT	
	¹ H δ _H (ppm) Me ^B	¹⁹ F{ ¹ H} δ _F (ppm)	¹ H δ _{iso} (ppm)	¹⁹ F δ _{iso} (ppm)	¹¹ B δ _{iso} (ppm)	FWHH (Hz)	ν(cm ⁻¹)
Control	-0.60	n/a	-	-	-	-	#
BPh ₃	-0.81	n/a	-	-	32	5604	#
B(C ₆ F ₅) ₃	-0.64	-123.2, -158.3, -164.2	-	-166 (s), -157 (w)	84	674	2315, 1641
Al(C ₆ F ₅) ₃	-0.63	-123.2, -158.3, -164.1	-1.18	-165, -124	-	-	-
{4-F}C ₆ H ₄ B(OH) ₂	-0.71	[§]	-0.82	-111	18 (w)	8231	#
{3,5-F} ₂ C ₆ H ₃ B(OH) ₂	-0.70	-112.2 -114.2,	-1.23, 6.55 (w)	-123	16 (w)	9346	#
C ₆ F ₅ B(OH) ₂	-0.64	[§]	-1.31, 6.29 (w)	-166, -135	7.3 (m)	3183	1647
{4-F}C ₆ H ₄ OH	-0.68	-130.0	-	-121	n/a	n/a	#
{3,5-F} ₂ C ₆ H ₃ OH	-0.80	-113.5	-1.45, 5.68 (w)	-110	n/a	n/a	2468, 2115
C ₆ F ₅ OH	-0.83	-164.8, -169.0, -177.4	-	-166, -157	n/a	n/a	2473, 1654

[§]Spectrum not fully resolved due to poor solubility.

[#]Spectrum shows no change from the control (ν = 3550, 2951, 2632, 2391, 1593, 1531, 1441, 1252, 1211 cm⁻¹).

[00174] Figures 9 and 10 shows the microscopic images for various polyethylene using various modifiers and zirconocene complexes demonstrating that the shape of the polyethylene remains the same

[00175] Figures 11 to 25 show the solution NMR spectra of various modified solid polymethylaluminoxane demonstrating the incorporation of the modifier into the product.

[00176] Figures 26 to 38 show the solid state NMR spectra of various modified solid polymethylaluminoxane demonstrating the incorporation of the modifier into the product.

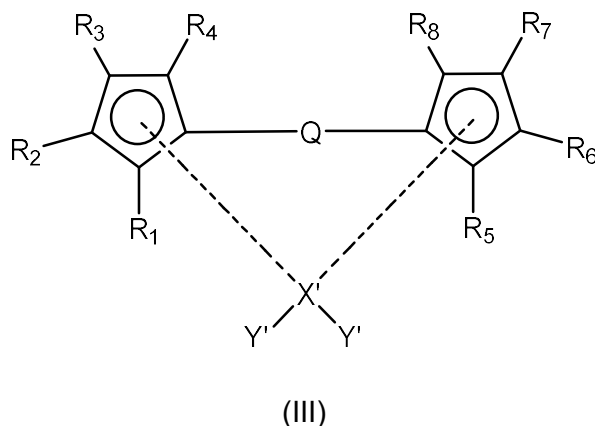
[00177] Figures 39 to 46 show the DRIFT spectra of various modified solid polymethylaluminoxane demonstrating the incorporation of the modifier into the product.

[00178] While specific embodiments of the invention have been described herein for the purpose of reference and illustration, various modifications will be apparent to a person skilled in the art without departing from the scope of the invention as defined by the appended claims.

CLAIMS

1. A catalytic composition comprising:

A) a compound of formula (III):



wherein

R_1 and R_2 are each independently hydrogen or (1-2C)alkyl;

R_3 and R_4 are each independently hydrogen or (1-4C)alkyl, or R_3 and R_4 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

R_5 and R_6 are each independently hydrogen or (1-4C)alkyl, or R_5 and R_6 are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

R_7 and R_8 are each independently hydrogen or (1-4C)alkyl, or R_7 and R_8 are linked such that, when taken in combination with the atoms to which they are

attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, aryl, heteroaryl, carbocyclic and heterocyclic, wherein each aryl, heteroaryl, carbocyclic and heterocyclic group is optionally substituted with one or more groups selected from (1-6C)alkyl, (2-6C)alkenyl, (2-6C)alkynyl, (1-6C)alkoxy, halo, amino, nitro, cyano, (1-6C)alkylamino, [(1-6C)alkyl]₂amino and -S(O)₂(1-6C)alkyl;

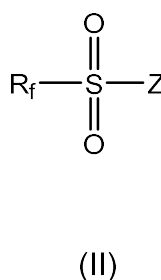
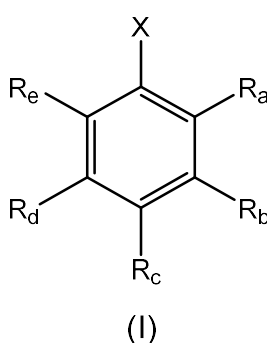
Q is absent, or is a bridging group selected from -CH₂- or -CH₂CH₂-, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and aryl, or Q is a bridging group -Si(R₉)(R₁₀)-, wherein R₉ and R₁₀ are independently (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl or aryl;

X' is zirconium or hafnium; and

each Y' group is independently selected from halo, hydride, (1-6C)alkyl, (1-6C)alkoxy, aryl or aryloxy, either or which is optionally substituted with one or more groups selected from (1-6C)alkyl and halo;

and

B) a solid-phase support material, the solid-phase support material comprising a solid polymethylaluminoxane that has been modified by reaction with a compound of formula (I) or (II):



wherein

X is hydroxyl or a group B(Y)₂ or a group Al(Y)₂,

wherein each Y is independently selected from hydroxyl, phenyl and naphthalenyl, any of which may be optionally substituted with one or

more groups selected from halo, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trihaloalkyl;

R_a and R_b are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, or

R_a and R_b are linked, such that, when taken with the atoms to which they are attached, they form a 6-membered aromatic ring that is optionally substituted by one or more groups selected from halo, 1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trihaloalkyl;

R_c - R_e are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl;

Z is hydroxyl or a group $-NR_xR_y$,

wherein R_x and R_y are independently selected from hydrogen and (1-4C)alkyl;

R_f is (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, trihaloalkyl or a phenyl group that is optionally substituted with one or more groups selected from hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo and trihaloalkyl;

wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.3:1 and

wherein the solid-phase support material has an aluminium content of 23 to 40 wt%; and

wherein the compound of formula (III) is supported on the solid polymethylaluminoxane that has been modified by reaction with the compound of formula (I) or (II).

2. The catalytic composition of claim 1, wherein Z is hydroxyl.

3. The catalytic composition of claim 1 or 2, wherein when X is hydroxyl

i) R_a - R_e are each independently halo; or

ii) R_a and R_b are linked, such that, when taken with the atoms to which they are attached, they form a 6-membered aromatic ring that is optionally substituted by one or more groups selected from halo, 1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trihaloalkyl, and

R_c - R_e are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl; or

iii) R_a , R_b and R_e are each independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, and

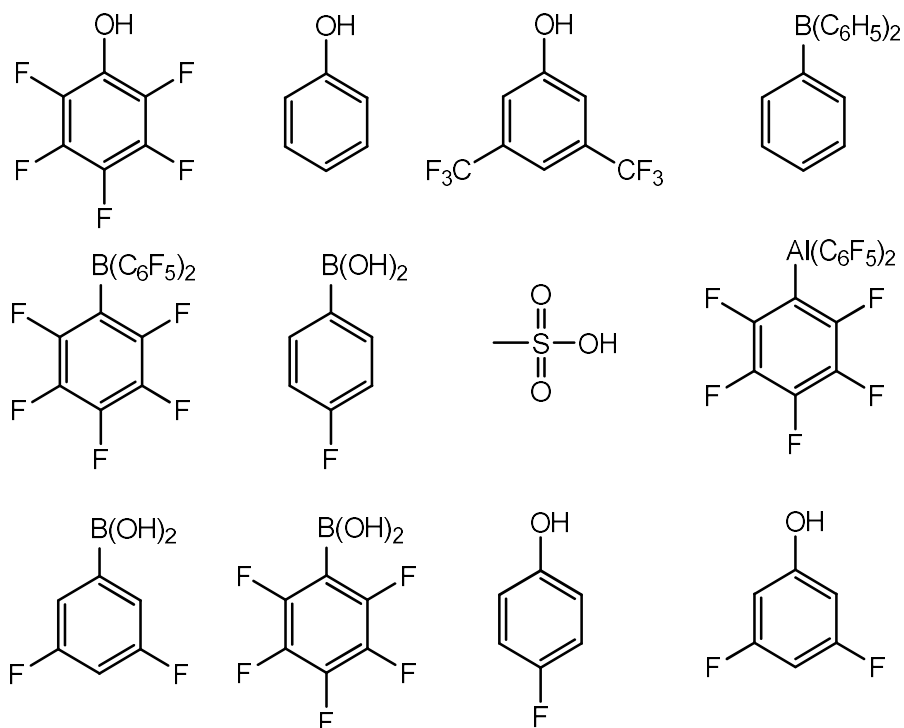
R_d and R_e are each independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl or trihaloalkyl; or

iv) R_a , R_b , R_d and R_e are each independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, halo or trihaloalkyl, and

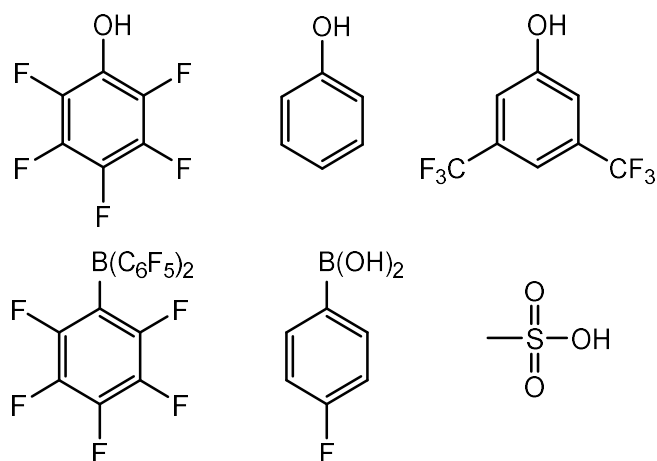
R_c is hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl or halo.

4. The catalytic composition of claim 1, 2 or 3, wherein each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl and trifluoroalkyl.
5. The catalytic composition of any preceding claim, wherein each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro, (1-4C)alkyl and trifluoromethyl.
6. The catalytic composition of any preceding claim, wherein each Y is independently selected from hydroxyl or a phenyl group that is optionally substituted with one or more groups selected from fluoro and trifluoromethyl.
7. The catalytic composition of any preceding claim, wherein R_a - R_e are independently hydrogen, hydroxyl, (1-4C)alkyl, (2-4C)alkenyl, (2-4C)alkynyl, fluoro or trifluoroalkyl.
8. The catalytic composition of any preceding claim, wherein R_a - R_e are independently hydrogen, (1-4C)alkyl, fluoro or trifluoroalkyl.

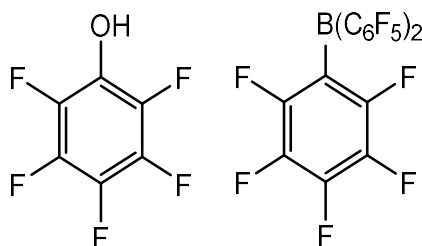
9. The catalytic composition of any preceding claim, wherein R_a - R_e are independently hydrogen, methyl, ethyl, tert-butyl, fluoro or trifluoromethyl.
10. The catalytic composition of any preceding claim, wherein R_f is (1-4C)alkyl, trihaloalkyl or a phenyl group that is optionally substituted with one or more groups selected from hydroxyl, (1-4C)alkyl, halo and trihaloalkyl.
11. The catalytic composition of any preceding claim, wherein R_f is (1-4C)alkyl, trihaloalkyl or *p*-toluenyl.
12. The catalytic composition of any preceding claim, wherein R_f is methyl, ethyl, trifluoromethyl or *p*-toluenyl.
13. The catalytic composition of any preceding claim, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.1:1.
14. The catalytic composition of any preceding claim, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.075:1.
15. The catalytic composition of any preceding claim, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane within the solid-phase support material ranges from 0.0001:1 to 0.05:1.
16. The catalytic composition of any preceding claim, wherein the compound of formula (I) or (II) is selected from one or more of the following:



17. The catalytic composition of any preceding claim, wherein the compound of formula (I) or (II) is selected from one or more of the following:



18. The catalytic composition of any preceding claim, wherein the compound of formula (I) or (II) is selected from one or more of the following:



19. The catalytic composition of any preceding claim, wherein the solid-phase support material has an aluminium content of 23 to 40 wt%.
20. The catalytic composition of any preceding claim, wherein the BET surface area of the solid-phase support material is 10.0 to 20.0 m²mmol_{Al}⁻¹.
21. The catalytic composition of any preceding claim, wherein
- R₃ and R₄ are each independently hydrogen or (1-4C)alkyl, or R₃ and R₄ are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl;
- R₅ and R₆ are each independently hydrogen or (1-4C)alkyl, or R₅ and R₆ are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl; and
- R₇ and R₈ are each independently hydrogen or (1-4C)alkyl, or R₇ and R₈ are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl.
22. The catalytic composition of any preceding claim, wherein
- R₃ and R₄ are each independently hydrogen or (1-4C)alkyl, or R₃ and R₄ are linked such that, when taken in combination with the atoms to which they are attached, they

form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl;

R₅ and R₆ are each independently hydrogen or (1-4C)alkyl, or R₅ and R₆ are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl; and

R₇ and R₈ are each independently hydrogen or (1-4C)alkyl, or R₇ and R₈ are linked such that, when taken in combination with the atoms to which they are attached, they form a 6-membered fused aromatic ring optionally substituted with one or more groups selected from methyl, ethyl and tert-butyl.

23. The catalytic composition of any preceding claim, wherein Q is absent, or is a bridging group selected from -CH₂- or -CH₂CH₂-, either or which may be optionally substituted with one or more groups selected from (1-4C)alkyl and phenyl, or Q is a bridging group -Si(R₉)(R₁₀)-,

wherein R₉ and R₁₀ are independently (1-4C)alkyl or aryl.

24. The catalytic composition of any preceding claim, wherein X' is zirconium.

25. The catalytic composition of any preceding claim, wherein each Y' group is independently selected from halo, hydride and (1-6C)alkyl.

26. The catalytic composition of any preceding claim, wherein the compound of formula (III) is supported on the solid polymethylaluminoxane that has been modified by reaction with the compound of formula (I) or (II), and the solid-phase support material is devoid of any additional species that is capable of supporting the compound of formula (III).

27. The catalytic composition of any preceding claim, wherein the solubility in n-hexane at 25°C of the solid polymethylaluminoxane used in the reaction with the compound of

formula (I) or (II) is 0-2 mol%, and the solubility in toluene at 25°C of the solid polymethylaluminoxane used in the reaction with the compound of formula (I) or (II) is 0-2 mol%.

28. A method of preparing a catalytic composition as claimed in any preceding claim, the method comprising the steps of:

- a) providing a solid-phase support material as defined in any one of claims 1 to 27;
- b) contacting the solid-phase support material of step a) with a compound of formula (III) as defined in any one of claims 1 to 27; and
- c) isolating the catalytic composition resulting from step b).

29. The method as claimed in claim 28, wherein step a) comprises:

- i) providing a solid polymethylaluminoxane in a first solvent;
- ii) contacting the solid polymethylaluminoxane of step i) with a compounds of formula (I) or (II) as defined in any preceding claim; and
- iii) isolating the solid-phase support material formed from step b);

wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step ii) ranges from 0.0001:1 to 0.3:1.

30. The method of claim 29, wherein the compound of formula (I) or (II) used in step b) is provided in a second solvent.

31. The method of claim 29 or 30, wherein step ii) is conducted at a temperature of 18-150°C.

32. The method of any of claims 29, 30 or 31, wherein step ii) is conducted at a temperature of 10-65°C.

33. The method of any of claims 29 to 32, wherein step ii) is conducted at a temperature of 18-50°C.
34. The method of any of claims 29 to 33, wherein step ii) is conducted at a temperature of 18-35°C.
35. The method of any of claims 29 to 34, wherein step ii) further comprises the step of sonicating the mixture of the solid polymethylaluminoxane and the compound of formula (I) or (II).
36. The method of claim 35, wherein the ultrasonic frequency is > 15 kHz.
37. The method of any of claims 29 to 36, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step ii) ranges from 0.0001:1 to 0.1:1.
38. The method of any of claims 29 to 37, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step ii) ranges from 0.0001:1 to 0.075:1.
39. The method of any of claims 29 to 38, wherein the mole ratio of the compound of formula (I) or (II) to the solid polymethylaluminoxane used in step ii) ranges from 0.0001:1 to 0.05:1.
40. The method of any of claims 29 to 39, wherein step i) comprises the steps:
- precipitating a solid polymethylaluminoxane from a reaction medium,
 - isolating the precipitated solid polymethylaluminoxane from the reaction medium, and
 - dispersing the isolated solid polymethylaluminoxane in the first solvent.

41. A use of a catalytic composition as claimed in any of claims 1 to 27 as a polymerisation catalyst for the preparation of a polyolefin.
42. The use according to claim 41, wherein the polyolefin is polyethylene.
43. The use according to claim 41, wherein the polyolefin is a copolymer formed from ethene monomers comprising 1-10 wt%, by total weight of the monomer, of one or more (4-8C) α -olefin.