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(54) Title: CATALYST COMPOSITION, METHODS FOR ITS PRODUCTION AND USE THEREOF

(57) Abstract: Provided is a method for preparing a pre-catalyst composition comprising (i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate; (iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition. Also, provided is a pre-catalyst and catalyst composition prepared by the claimed method and its use in a method for providing a composition comprising carbon monoxide.

CATALYST COMPOSITION, METHODS FOR ITS PRODUCTION AND USE THEREOF

INTRODUCTION

[001] A method is provided for the preparation of a pre-catalyst composition and catalyst composition. These compositions have uniform dispersion and stable nano-structure and demonstrate high carbon dioxide conversion without considerable methanation in a reverse water gas shift reaction. Also provided is a pre-catalyst and/or catalyst composition and their use in the conversion of carbon dioxide to carbon monoxide.

BACKGROUND OF THE INVENTION

[002] Continuously increasing greenhouse gas emissions is causing a climate crisis. A key challenge in reducing greenhouse gas is the reduction in carbon dioxide emissions. The International Energy Agency reported in 2018 that global energy-related carbon dioxide emissions grew to reach a historic high of 33.1 gigatonnes of carbon dioxide, and only a small amount of this (approximately 230 megatonnes per year globally) is currently recycled or mitigated.

[003] Using low carbon technologies, intense efforts are being made to develop carbon capture for storage (CCS) or utilisation (CCU) technologies. While CCS mainly deals with carbon dioxide capture to avoid carbon dioxide emissions into the atmosphere, CCU technologies are designed to transform carbon dioxide into a number of value-added products, e.g. olefins, formic acid, dimethylether (DME), urea, dimethylcarbonate (DMC), acetic acid, methanol or synthetic natural gas (syngas).

[004] An important reaction in the conversion of carbon dioxide to value-added products is the reverse water gas shift reaction (rWGS). In the rWGS, catalysts are often used to convert carbon dioxide to carbon monoxide by hydrogenation. Carbon monoxide is an important starting material in a number of commercially importance processes for the preparation of useful materials, such as the manufacture of hydrocarbons via the Fischer-Tropsch process.

[005] The rWGS has been studied with a variety of different catalysts, which include precious/noble metals such as Pt, Pd, Ru and Au. As reported in González-Castaño *et al.* (React. Chem. Eng., 2021, 6, 954), the catalytic activity and selectivity toward carbon monoxide has recently been analysed for Pd, Cu, Ni, Fe and Pt catalysts. Pt catalysts exhibited the highest carbon dioxide conversions, but lower selectivity toward CO than Fe and Cu. Ni presented the highest methanation rates.

[006] Bimetallic catalyst compositions have also been employed in order to enhance

catalytic performance in the rWGS. In particular, Cu-ZnO systems have been employed where the ZnO promotion has been related to higher Cu dispersions, and Pt-Co catalysts have demonstrated improved carbon monoxide selectivity relative to monometallic systems.

[007] Alkali metal doping has been reported to lead to improvements in carbon monoxide selectivity and higher carbon dioxide conversion. For Pt and Au catalysts, the catalytic promotion obtained through the addition of alkali metal is attributed to a metal-O(OH)-alkali interface which stabilizes the metal particles and promotes carbon dioxide dissociation and favours carbon monoxide desorption.

[008] Deactivation of catalysts can occur for a number of reasons, primarily metal sintering, carbon deposits and sulphur poisoning. Susceptibility to sintering depends on the nature of the metal and its interaction with any support material. The high stability displayed by Pt supported on zeolite catalysts has been attributed to the encapsulation of the metal particles.

[009] Despite the higher reaction rates exhibited by noble metal catalysts, their high prices and limited availability hinder their implementation at larger scales. The present invention aims to provide a pre-catalyst and/or catalyst composition which can be manufactured cheaply enough to be employed at scale and has good stability whilst demonstrating good catalytic performance in the rWGS. Suitably, the pre-catalyst and catalyst composition advantageously provide one or more of high carbon dioxide conversion, high carbon monoxide selectivity and low methanation rate.

SUMMARY OF THE INVENTION

[0010] Provided herein is a pre-catalyst composition, catalyst composition and a method for their production which is in general inexpensive, safe and uses abundant materials. The pre-catalyst and/or catalyst composition can be used in a reverse water gas shift reaction, providing high selectivity for carbon monoxide with little methane by-product and high carbon dioxide conversion rates.

[0011] In a first aspect, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof;

optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.

[0012] In a second aspect, the present invention provides a pre-catalyst composition obtained or obtainable according to the method of the first aspect.

[0013] In a third aspect, the present invention provides a method for preparing a catalyst composition comprising:

- (a) providing a pre-catalyst composition according to the second aspect;
- (b) optionally subjecting said pre-catalyst composition to calcination; and
- (c) activating said pre-catalyst composition to obtain a catalyst composition.

[0014] In a fourth aspect, the present invention provides a catalyst composition obtained or obtainable by the method of the third aspect.

[0015] In a fifth aspect, the present invention provides a shaped composition comprising a pre-catalyst composition according to the second aspect, or a catalyst composition according to the fourth aspect.

[0016] In a sixth aspect, the present invention provides a method for producing a composition comprising carbon monoxide, wherein said method comprises contacting a feed gas composition comprising carbon dioxide and hydrogen with a pre-catalyst composition according to the second aspect, or a catalyst composition according to the fourth aspect, at a temperature of at least 400°C.

[0017] In a seventh aspect, the present invention provides a reactor comprising a pre-catalyst composition according to the second aspect, or a catalyst composition according to the fourth aspect.

[0018] Preferred, suitable, and optional features of any one particular aspect of the present invention are also preferred, suitable, and optional features of any other aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Figure 1 shows XRD spectra of pre-catalyst compositions 01, 09, 16, 17, 32, 15 and 20 of Table A herein.

[0020] Figure 2 shows **a** XPS survey spectrum of pre-catalyst 17 (Fe–Cr-Zn-Zr–K); **b** High-resolution XPS spectra in the region of the Fe 2p peak on the pre-catalyst 17; **c** XPS spectra of the Cr 2p on the pre-catalyst 17; **d** XPS spectra of the Zr 3d on pre-catalyst 17; **e** XPS spectra of the Zn 2p on pre-catalyst 17; **f** XPS spectra of the K 2p on pre-catalyst 17; **g** XPS spectra of the C 1s on pre-catalyst 17; **h** XPS spectra of the O 1s on pre-catalyst 17.

[0021] Figure 3 shows TEM images of pre-catalyst composition 17 (Fe–Cr-Zn-Zr–K).

[0022] Figure 4 shows **a** SEM image, EDX mapping and elemental analysis, including Fe, Cr, Zn, C, O (left to right) elemental analysis of pre-catalyst composition 17 (Fe–Cr-Zn-Zr–K).

DETAILED DESCRIPTION OF THE INVENTION**Definitions**

[0023] As used herein, the term “pre-catalyst” refers to a precursor of the catalytically active species. Typically, the pre-catalyst will require conversion to the catalytically active species, for instance by oxidation, reduction and/or heat treatment, or a combination thereof. Suitably, activation is via reduction. The pre-catalyst may be converted to the catalytically active species (i.e. “activated”) in-situ (i.e. under the reaction conditions) or the pre-catalyst may also be converted to the catalytically active species prior to use in the reaction, for instance as a preliminary step.

[0024] As used herein the term “solid” unless otherwise specified refers to a solid physical form at standard ambient temperature and pressure (SATP), i.e. at a temperature of 298.15 K (25 °C) and at 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm).

[0025] As used herein the term “gaseous” or “gas” refers unless otherwise specified refers to gaseous physical form at standard ambient temperature and pressure (SATP), i.e. at a temperature of 298.15 K (25 °C) and at 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm).

[0026] As used herein “metal species” is any compound comprising a metal. As such, a metal species, unless otherwise provided, includes the elemental metal, metal oxides and other compounds comprising a metal, i.e. metal salts, alloys, hydroxides, carbides and hydrides. When a specific example of a metal species is stated, said term includes all compounds

comprising that metal, e.g. iron species, unless provided otherwise, includes elemental iron, iron oxides, iron salts, iron alloys, iron hydroxides, iron carbides and iron hydrides for instance.

[0027] As used herein, the term “elemental metal” or specific examples such as “elemental Pd”, for example, refers to the metal only when in an oxidation state of zero.

[0028] Unless stated to the contrary, reference to elements by use of standard notation refers to said element in any available oxidation state. Similarly, wherein the term “metal” is used without further restriction no limitation to oxidation state is intended other than to those available.

[0029] As used herein, the term “transition metal” refers to an element of one of the three series of elements arising from the filling of the 3d, 4d and 5d shells. Unless stated to the contrary, reference to transition metals in general or by use of standard notation of specific transition metals refers to said element in any available oxidation state.

[0030] As used herein, the term “alkali metal” refers to an element of Group 1 of the periodic table.

[0031] As used herein, the term “alkaline earth metal” refers to an element of Group 2 of the periodic table.

[0032] As used herein, the term “rare earth metal” refers to an element selected from scandium, yttrium, lanthanum and the lanthanide series of the periodic table.

[0033] As used herein “syngas” (also known as synthesis gas), is a fuel gas mixture essentially consisting of hydrogen and carbon monoxide. However, minor quantities of carbon dioxide and hydrocarbons may be present.

Method for preparing pre-catalyst composition

[0034] In a first aspect, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a

hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof;

optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.

[0035] In one embodiment, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.

[0036] In another embodiment, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a

hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and

- (ii) subjecting the product of (i) to calcination to provide a pre-catalyst composition.

[0037] In one embodiment, in step (i) the iron species, the chromium salt or hydrate thereof, the organic compound and the optional one or more transitions species are combined in solid form.

[0038] In one embodiment, the iron species, the chromium salt or hydrate thereof, the organic compound and the optional one or more transitions species are combined with water to yield an aqueous solution or mixture. In one embodiment, the aqueous solution or mixture is then dried to remove water and the resulting dried material subjected to calcination.

[0039] Accordingly, in one embodiment, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i)(a) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and

water

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the dried material of (i)(b) to calcination to provide a pre-catalyst composition.

[0040] In one embodiment, the present invention relates to a method for preparing a pre-catalyst composition comprising:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

optionally (ii) combining a solution of an iron salt or a hydrate thereof, and an aqueous basic solution, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.

[0041] In one embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof, and an aqueous basic solution, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate; and

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[0042] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof; and

(ii) subjecting the product of (i) to calcination to provide a pre-catalyst composition.

[0043] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of:

(i)(a) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a zinc salt or hydrate thereof, and a copper salt or a hydrate thereof; and

water;

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[0044] Suitably, in step (i)(b) of any of the above embodiments the aqueous product is dried at a temperature of about 70°C to about 100°C, more suitably about 80°C to about 100°C, in order to remove water. Suitably, the dried material is obtained as a powder or a paste.

Step (i)

[0045] In one embodiment, the iron species is an iron salt or hydrate thereof.

[0046] In one embodiment, the proportion of iron salt or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 100:1 to about 5:4. Suitably, the atomic ratio of iron to chromium is about 100:1 to about 2:1, suitably about 100:1 to about 10:3.

[0047] In another embodiment, the proportion of iron salt or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 50:1 to about 5:1. Suitably, the atomic ratio of iron to chromium is about 25:1 to about 5:1, suitably about 20:1 to about 5:1, suitably about 15:1 to about 5:1, suitably about 10:1 to about 5:1, suitably 10:1 to about 7:1, suitably about 10:1 to about 8:1.

[0048] In another embodiment, the proportion of iron salt or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 20:1 to about 5:4. Suitably, the atomic ratio of iron to chromium is about 20:1 to about 2:1, suitably about 20:1 to about 10:3.

[0049] In another embodiment, the proportion of iron salt or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 10:1 to about

5:4. Suitably, the atomic ratio of iron to chromium is about 10:1 to about 2:1, suitably about 10:1 to about 10:3. In another embodiment, the proportion of iron salt or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 10:1.

[0050] In one embodiment, in step (i) the iron salt or hydrate thereof is an iron (II) or iron (III) salt, or hydrate thereof. For example, suitable non-limiting examples of iron (II) salts or a hydrate thereof are FeCl_2 , Fe(OAc)_2 , FeSO_4 , and $\text{Fe(NO}_3)_2$ or a hydrate thereof. Suitable, non-limiting examples of iron (III) salts or a hydrate thereof are $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ or a hydrate thereof.

[0051] In one embodiment, the iron salt or hydrate thereof of step (i) is selected from one or more of the group consisting of FeCl_2 , Fe(OAc)_2 , FeSO_4 , $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, or a hydrate thereof.

[0052] In another embodiment, the iron salt or hydrate thereof of step (i) is selected from one or more of the group consisting of FeCl_2 , $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, or a hydrate thereof. In another embodiment, the iron salt or hydrate thereof of step (i) is selected from one or more of the group consisting of $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, or a hydrate thereof. In another embodiment, the iron salt or hydrate thereof of step (i) is selected from one or more of $\text{Fe(NO}_3)_2$ and $\text{Fe(NO}_3)_3$, or a hydrate thereof.

[0053] In another embodiment, the iron species is an iron oxide or hydrate thereof. Suitably the iron oxide is Fe_3O_4 .

[0054] In one embodiment, the proportion of iron oxide or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 100:1 to about 5:4. Suitably, the atomic ratio of iron to chromium is about 100:1 to about 2:1, suitably about 100:1 to about 10:3.

[0055] In another embodiment, the proportion of iron oxide or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 20:1 to about 5:4. Suitably, the atomic ratio of iron to chromium is about 20:1 to about 2:1, suitably about 20:1 to about 10:3.

[0056] In another embodiment, the proportion of iron oxide or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 50:1 to about 5:1. Suitably, the atomic ratio of iron to chromium is about 25:1 to about 5:1, suitably about

20:1 to about 5:1, suitably about 15:1 to about 5:1, suitably about 10:1 to about 5:1, suitably 10:1 to about 7:1, suitably about 10:1 to about 8:1.

[0057] In another embodiment, the proportion of iron oxide or hydrate thereof and chromium salt or hydrate thereof is such that the atomic ratio of iron to chromium is about 10:1 to about 5:4. Suitably, the atomic ratio of iron to chromium is about 10:1 to about 2:1, suitably about 10:1 to about 10:3, suitably about 10:1.

[0058] In one embodiment, in step (i) the chromium salt or hydrate thereof is a chromium (III) salt or a hydrate thereof. Suitably, the chromium salt or hydrate thereof of step (i) is not a chromium (VI) salt or hydrate thereof. In one embodiment, the method for preparing the pre-catalyst composition does not comprise addition of a chromium (VI) salt or hydrate thereof.

[0059] In one embodiment, the chromium salt or hydrate thereof of step (i) is selected from one or more of the group consisting of $\text{Cr}(\text{NO}_3)_3$, CrCl_3 , $\text{Cr}(\text{Ac})_3$ and $\text{Cr}(\text{OH})_3$, or a hydrate thereof. Suitably, the chromium salt or hydrate thereof of step (i) is $\text{Cr}(\text{NO}_3)_3$ or a hydrate thereof.

[0060] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof; a chromium (III) salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof.

[0061] In another embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof; a chromium (III) salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof.

[0062] In each of the above mentioned embodiments, suitably the iron species and chromium salt or hydrate thereof are combined with a further transition metal species. Suitably, one, two or three further transition metal species. Suitably, one or two further transition metal species.

[0063] Suitably, the transition metal species is selected from one or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0064] In another embodiment, the transition metal species is selected from two or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof.

[0065] In another embodiment, the transition metal species is selected from two or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0066] In another embodiment, the transition metal species is selected from two of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof.

[0067] In another embodiment, the transition metal species is selected from two of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, and a zinc salt or hydrate thereof.

[0068] In another embodiment, the transition metal species is selected from one or more of a manganese salt or hydrate thereof or a zirconium salt or a hydrate thereof; and one or more of a copper salt or a hydrate thereof or a zinc salt or hydrate thereof.

[0069] In another embodiment, the transition metal species is selected from:

- (i) a copper salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (ii) a zinc salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (iii) a copper salt or hydrate thereof and a zirconium salt or hydrate thereof; or
- (iv) a zinc salt or hydrate thereof and a zirconium salt or hydrate thereof.

[0070] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[0071] In another embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional

groups selected from a carboxyl, hydroxyl, amido and amino group, and optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[0072] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[0073] In another embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, and optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[0074] In one embodiment, step (i) comprises combining a manganese salt or a hydrate thereof with the iron and chromium salt or hydrate thereof. In one embodiment, in step (i) the manganese salt or hydrate thereof is a manganese (II) or (III) salt or a hydrate thereof, suitably a manganese (II) salt or a hydrate thereof. For example, suitable non-limiting examples of manganese salts or a hydrate thereof are $Mn(NO_3)_2$, $MnSO_4$, $MnCl_2$, $Mn(OAc)_2$, and manganese citrate or a hydrate thereof. Suitably, the manganese salt or hydrate thereof is $Mn(NO_3)_2$ or a hydrate thereof.

[0075] In one embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 250:1 to about 50:1.

[0076] In one embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 100:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 100:1 to about 40:1. Suitably, the atomic ratio of iron to manganese is about 80:1 to about 40:1. Suitably, the atomic ratio of iron to manganese is about 60:1 to about 40:1.

[0077] In another embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 150:1 to about 50:1.

[0078] In another embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 100:1 to about 50:1.

[0079] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally, one or more of a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0080] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally, one or more of a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0081] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[0082] In one embodiment, step (i) comprises combining an iron (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese (II) salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[0083] In one embodiment, step (i) comprises combining a zirconium salt or a hydrate thereof with the iron and chromium salt or hydrate thereof. In one embodiment, in step (i) the zirconium salt or hydrate thereof is an zirconium (III) or (IV) salt or a hydrate thereof, suitably a zirconium (IV) salt or a hydrate thereof. For example, suitable non-limiting examples of zirconium salts or hydrate thereof are $Zr(NO_3)_4$, $ZrO(NO_3)_2$, $ZrOCl_2$, zirconium acetate or a hydrate thereof. Suitably, the zirconium salt or hydrate thereof is $ZrO(NO_3)_2$ or a hydrate thereof.

[0084] In one embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to zirconium is about 250:1 to about 50:1.

[0085] In another embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to zirconium is about 150:1 to about 50:1.

[0086] In another embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 100:1 to about 50:1. Suitably, the atomic ratio of iron to zirconium is about 100:1 to about 80:1. Suitably, the atomic ratio of iron to zirconium is about 100:1.

[0087] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium salt or a hydrate thereof and, optionally, one or more of a manganese salt or a hydrate thereof, a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0088] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium salt or a hydrate thereof and, optionally, one or more of a copper salt or a hydrate thereof and a zinc salt or hydrate thereof.

[0089] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[0090] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[0091] In one embodiment, step (i) comprises combining a copper salt or a hydrate thereof with the iron and chromium salt or hydrate thereof. In one embodiment, in step (i) the copper salt is a copper (I) or (II) salt or a hydrate thereof, suitably a copper (II) salt or a hydrate thereof. For example, suitable non-limiting examples of copper salts or hydrate thereof are Cu(NO₃)₂, Cu(OAc)₂, CuCl₂, CuSO₄, Cu₂CO₃(OH)₂, CuCl, Cu₂SO₄, and CuNO₃ or a hydrate thereof.

[0092] Suitably, the copper salt or hydrate thereof is selected from one or more of the group consisting of Cu(NO₃)₂, Cu(OAc)₂, CuCl₂, CuSO₄, and Cu₂CO₃(OH)₂, or a hydrate thereof. Suitably, the copper salt or hydrate thereof is selected from one or more of Cu(NO₃)₂ and Cu₂CO₃(OH)₂ or a hydrate thereof.

[0093] In one embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to copper is about 250:1 to about 50:1.

[0094] In one embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 100:1 to about 10:1. Suitably, the atomic ratio of iron to copper is about 100:1 to about 40:1. Suitably, the atomic ratio of iron to copper is about 80:1 to about 40:1. Suitably, the atomic ratio of iron to copper is about 60:1 to about 40:1.

[0095] In another embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to copper is about 150:1 to about 50:1,

[0096] In another embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 100:1 to about 50:1.

[0097] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and, optionally, one or more of a zinc salt or hydrate thereof, a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[0098] In another embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and, optionally, one or more of a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[0099] In one embodiment, step (i) comprises combining a zinc salt or a hydrate thereof with the iron and chromium salt or hydrate thereof. In one embodiment, in step (i) the zinc salt is a zinc (II) salt or a hydrate thereof. For example, suitable non-limiting examples of zinc salts or hydrates thereof are Zn(NO₃)₂, Zn(OAc)₂, ZnCl₂ and ZnSO₄ or a hydrate thereof. Suitably, the zinc salt or hydrate thereof is Zn(NO₃)₂ or a hydrate thereof.

[00100] In one embodiment, the proportion of iron salt and zinc salt is such that the atomic ratio of iron to zinc is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to zinc is about 250:1 to about 50:1.

[00101] In one embodiment, the proportion of iron salt and zinc salt is such that the atomic ratio of iron to zinc is about 100:1 to about 10:1. Suitably, the atomic ratio of iron to

zinc is about 100:1 to about 40:1. Suitably, the atomic ratio of iron to zinc is about 80:1 to about 40:1. Suitably, the atomic ratio of iron to zinc is about 60:1 to about 40:1. Suitably, the atomic ratio of iron to zinc is about 45:1 to about 40:1, suitably about 42:1.

[00102] In another embodiment, the proportion of iron salt and zinc salt is such that the atomic ratio of iron to zinc is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to zinc is about 150:1 to about 50:1,

[00103] In another embodiment, the proportion of iron salt and zinc salt is such that the atomic ratio of iron to zinc is about 100:1 to about 50:1.

[00104] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zinc salt or a hydrate thereof and, optionally, one or more of a copper salt or hydrate thereof, a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00105] In another embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zinc salt or a hydrate thereof and, optionally, one or more of a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00106] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and, optionally, one or more of a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00107] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and, optionally, a manganese salt or a hydrate thereof.

[00108] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and, optionally, a zirconium salt or a hydrate thereof.

[00109] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and, optionally one or more of a zirconium salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00110] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof.

[00111] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and, optionally a manganese salt or a hydrate thereof.

[00112] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and, optionally, a zirconium salt or a hydrate thereof.

[00113] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00114] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof.

[00115] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00116] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic

compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zinc salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00117] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and a zirconium (III) or (IV) salt or a hydrate thereof.

[00118] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zinc (II) salt or a hydrate thereof and a zirconium (III) or (IV) salt or a hydrate thereof.

[00119] In one embodiment, step (i) essentially consists of combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00120] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00121] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00122] In one embodiment, step (i) essentially consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00123] In step (i) an organic compound comprising one or more function groups selected from a carboxyl, hydroxyl, amido and amino group is combined with the metal salts.

Suitably, the organic compound comprises two or more functional groups selected from a carboxyl, hydroxyl, amido and amino groups. In another embodiment, the organic compound comprises three or more functional groups selected from a carboxyl, hydroxyl, amido and amino groups.

[00124] Suitably, the organic compound is suitable for complexing metal cations, in particular iron cations. Accordingly, suitable organic compounds comprise one or more functional groups selected from carboxylic acids, hydroxyl groups, amide groups or amino groups.

[00125] In one embodiment, the organic compound is selected from a hydroxycarboxylic acid, an aminocarboxylic acid, multicarboxylic acids or salts thereof. Suitably, the organic compound is selected from a hydroxycarboxylic acid and a multicarboxylic acid, or a salt thereof. Alternatively, the organic compound is selected from a hydroxycarboxylic acid and an aminocarboxylic acid, or a salt thereof.

[00126] In one embodiment, the organic compound is a bi- or multi-dentate hydroxycarboxylic acid or a salt thereof.

[00127] In one embodiment, the organic compound is a C₄ to C₁₂ carboxylic acid or urea.

[00128] In one embodiment, the organic compound is selected from glycolic acid, lactic acid, hydracylic acid, hydroxybutyric acid, hydroxyvaleric acid, malic acid, mandelic acid, citric acid, sugar acids, tartronic acid, tartaric acid, oxalic acid, malonic acid, maleic acid, tannic acid, succinic acid, salicylic acid, glutaric acid, adipic acid, glycine, hippuric acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), HEDTA (N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid), alanine, valine, leucine and isoleucine, and salts thereof.

[00129] In one embodiment, the organic compound is selected from glycolic acid, lactic acid, hydracylic acid, hydroxybutyric acid, hydroxyvaleric acid, malic acid, mandelic acid, citric acid, sugar acids, tartronic acid, tartaric acid, oxalic acid, malonic acid, maleic acid, tannic acid, succinic acid, salicylic acid, glutaric acid, adipic acid, hippuric acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid), or a salt thereof.

[00130] In one embodiment, the organic compound is selected from hydroxybutyric acid, hydroxyvaleric acid, malic acid, mandelic acid, citric acid, sugar acids, tartronic acid, tartaric acid, oxalic acid, malonic acid, maleic acid, tannic acid, succinic acid, salicylic acid, glutaric acid, adipic acid, hippuric acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

[00131] In one embodiment, the organic compound is selected from hydroxybutyric acid, hydroxyvaleric acid, malic acid, mandelic acid, citric acid, sugar acids, tartronic acid, tartaric acid, oxalic acid, malonic acid, maleic acid, tannic acid, succinic acid, salicylic acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

[00132] In one embodiment, the organic compound is selected from citric acid, sugar acids, tartaric acid, oxalic acid, salicylic acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

[00133] In one embodiment, the organic compound is selected from citric acid, sugar acids, tartaric acid, oxalic acid, salicylic acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

[00134] In one embodiment, the organic compound is selected from citric acid, tartaric acid, oxalic acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof. Suitably, the organic compound is citric acid or urea.

[00135] In another embodiment, the organic compound is selected from malic acid, salicylic acid, tartaric acid, urea, oxalic acid, citric acid, NTA (nitroilotiracetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

[00136] In one embodiment, the organic compound to metal molar ratio in step (i) is about 0.4:1 to about 10:1. Suitably, the organic compound to metal molar ratio is about 0.4:1 to about 5:1. Suitably, the organic compound to metal molar ratio is about 0.4:1 to about 2:1 or about 0.4:1 to about 1:1.

[00137] In one embodiment, the organic compound to metal molar ratio in step (i) is about 1:1 to about 10:1. Suitably, the organic compound to metal molar ratio is about 1:1 to about 5:1. Suitably, the organic compound to metal molar ratio is about 1:1 to about 3:1 or about 1:1 to about 1:1.

[00138] In one embodiment, the organic compound to metal molar ratio in step (i) is about 0.8:1 to about 10:1. Suitably, the organic compound to metal molar ratio is about 0.8:1 to about 5:1. Suitably, the organic compound to metal molar ratio is about 0.8:1 to about 2:1 or about 0.8:1 to about 1:1.

[00139] In one embodiment, the organic compound to metal molar ratio in step (i) is about 1:1 to about 10:1. Suitably, the organic compound to metal molar ratio is about 1:1 to about 5:1. Suitably, the organic compound to metal molar ratio is about 1:1 to about 2:1.

[00140] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a zinc salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00141] In one embodiment, step (i) comprises combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00142] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a zinc salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00143] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00144] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00145] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00146] In another embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a zirconium salt or a hydrate thereof and a zinc salt or a hydrate thereof.

[00147] In another embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof and a zinc salt or a hydrate thereof.

[00148] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00149] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a manganese salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00150] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and a manganese salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[00151] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from

a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese (II) salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[00152] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, and optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof.

[00153] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[00154] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof and, optionally, a copper salt or a hydrate thereof.

[00155] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and, optionally, a zirconium salt or a hydrate thereof.

[00156] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and, optionally, a zirconium salt or a hydrate thereof.

[00157] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00158] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00159] In one embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from

a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00160] In another embodiment, step (i) comprises combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof.

[00161] In one embodiment, step (i) essentially consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00162] In one embodiment, step (i) essentially consists of combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and a manganese salt or a hydrate thereof.

[00163] In one embodiment, step (i) essentially consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof.

[00164] In one embodiment, step (i) essentially consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00165] In one embodiment, step (i) essentially consists of combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper salt or a hydrate thereof and a zirconium salt or a hydrate thereof.

[00166] In one embodiment, step (i) essentially consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00167] In one embodiment, step (i) consists of/ essentially consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic

compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof.

[00168] In another embodiment, step (i) consists of/ essentially consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof.

[00169] In one embodiment, in step (i), the iron salt or hydrate thereof, or iron oxide or hydrate thereof; chromium salt or hydrate thereof, the organic compound, and optionally the one or more transition metal species, are each combined in solid form under ambient conditions and mixed or milled to form a paste or powder. Suitable techniques for mixing and milling are known in the art and at least include grinding in a pestle and mortar, or bead or ball milling.

[00170] In another embodiment, in step (i), one or more components may be mixed with water, and the components combined to form an aqueous solution or mixture. Suitably, the aqueous solution or mixture is stirred. In one embodiment, the weight ratio of transition metal species and organic compound to water is about 1:1 to about 5:1, suitably about 1:1 to about 3:1, suitably about 2:1.

[00171] The aqueous solution or mixture is suitably dried before proceeding to the calcination step. In one embodiment, the aqueous solution or mixture is dried at a temperature of about 70°C to about 100°C, more suitably about 80°C to about 100°C, in order to remove water. Suitably, the resulting dried material is obtained as a powder or a paste.

[00172] In one embodiment, step (i) comprises (i)(a) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and water; and (i)(b) drying the aqueous product of (i)(a) to provide a dried material.

[00173] In another embodiment, in step (i), the iron salt or hydrate thereof, chromium salt or hydrate thereof and the organic compound, and optionally one or more of a manganese salt or hydrate thereof, a zinc salt or hydrate thereof, a zirconium salt or hydrate thereof and copper salt or hydrate thereof, are each combined in solid form under ambient conditions and

mixed or milled to form a paste or powder. Suitable techniques for mixing and milling are known in the art and at least include grinding in a pestle and mortar, or bead or ball milling.

[00174] In one embodiment, step (i) further comprises combining one or more of an alkali metal species, an alkaline earth metal species and a rare earth metal species. Suitably, step (i) further comprises combining one or more of an alkali metal species and/or an alkaline earth metal species. Suitably, step (i) further comprises combining one or more of an alkali metal species and/or a rare earth metal species. Suitably, step (i) further comprises combining an alkali metal species. The alkali metal species, alkaline earth metal species or rare earth metal species are suitably added in step (i) in the form of a salt, hydroxide, oxide or a hydrate thereof, suitably in the form of a salt or hydrate thereof.

[00175] In one embodiment, the alkali metal species is an alkali metal salt or hydrate thereof. In another embodiment, the alkali metal salt is an alkali metal nitrate, an alkali metal carbonate, an alkali metal bicarbonate, an alkali metal acetate, or a hydrate thereof. In another embodiment, the alkali metal salt is an alkali metal nitrate or an alkali metal carbonate, or a hydrate thereof.

[00176] In one embodiment, the alkali metal is selected from the group consisting of lithium, sodium, potassium and caesium. In another embodiment, the alkali metal is selected from lithium, sodium and potassium.

[00177] Suitably the alkali metal species is selected from potassium nitrate, potassium carbonate, sodium nitrate, sodium carbonate, lithium carbonate, cesium carbonate, or a hydrate thereof.

[00178] In one embodiment, the iron to alkali metal atomic ratio in step (i) is about 100:1 to about 5:1. Suitably, the iron to alkali metal atomic ratio is about 50:1 to about 5:1. Suitably, the iron to alkali metal atomic ratio is about 40:1 to about 5:1, or about 25:1 to about 5:1.

[00179] In another embodiment, the iron to alkali metal atomic ratio in step (i) is about 50:1 to about 5:1. Suitably, the iron to alkali metal atomic ratio is about 50:1 to about 10:1. Suitably, the iron to alkali metal atomic ratio is about 50:1 to about 15:1, or about 50:1 to about 20:1.

[00180] In another embodiment, the iron to alkali metal atomic ratio in step (i) is about 40:1 to about 5:1. Suitably, the iron to alkali metal atomic ratio is about 40:1 to about 10:1. Suitably, the iron to alkali metal atomic ratio is about 40:1 to about 15:1, or about 40:1 to about 20:1. Suitably, the iron to alkali metal atomic ratio is 20:1.

[00181] In one embodiment, the alkaline earth metal species is an alkaline earth metal salt, hydroxide, oxide or hydrate thereof. In another embodiment, the alkaline earth metal species is an alkaline earth metal salt or hydrate thereof.

[00182] In one embodiment, the alkaline earth metal salt is an alkaline earth metal nitrate, an alkaline earth metal carbonate, an alkaline earth metal bicarbonate, an alkaline earth metal acetate, or a hydrate thereof. In another embodiment, the alkaline earth metal salt is an alkaline earth metal nitrate or an alkaline earth metal carbonate, or a hydrate thereof.

[00183] In one embodiment, the alkaline earth metal is selected from the group consisting of magnesium, calcium and barium, suitably magnesium and calcium, more suitably calcium.

[00184] Suitably, the alkaline earth metal species is selected from a calcium salt or hydrate thereof or a magnesium salt or hydrate thereof. In one embodiment, the alkaline earth metal species is selected from calcium nitrate, calcium carbonate, magnesium nitrate and magnesium carbonate, or a hydrate thereof. In another embodiment, the alkaline earth metal species is selected from calcium nitrate and calcium carbonate.

[00185] In one embodiment, the iron to alkaline earth metal atomic ratio in step (i) is about 100:1 to about 5:1. Suitably, the iron to alkaline earth metal atomic ratio is about 50:1 to about 5:1. Suitably, the iron to alkaline earth metal atomic ratio is about 40:1 to about 5:1 or about 25:1 to about 5:1.

[00186] In another embodiment, the iron to alkaline earth metal atomic ratio in step (i) is about 50:1 to about 5:1. Suitably, the iron to alkaline earth metal atomic ratio is about 50:1 to about 10:1. Suitably, the iron to alkaline earth metal atomic ratio is about 50:1 to about 15:1 or about 50:1 to about 20:1.

[00187] In another embodiment, the iron to alkaline earth metal atomic ratio in step (i) is about 40:1 to about 5:1. Suitably, the iron to alkaline earth metal atomic ratio is about 40:1 to about 10:1. Suitably, the iron to alkaline earth metal atomic ratio is about 40:1 to about 15:1 or about 40:1 to about 20:1.

[00188] In one embodiment, the rare earth metal species is a rare earth metal salt, hydroxide, oxide, or a hydrate thereof. In another embodiment, the rare earth metal species is a rare earth metal salt or a hydrate thereof.

[00189] In one embodiment, the rare earth metal salt is a rare earth metal nitrate, a rare earth metal carbonate, a rare earth metal bicarbonate, a rare earth metal acetate, or a hydrate thereof. In one embodiment, the rare earth metal salt is a rare earth metal nitrate or a rare earth metal carbonate, or a hydrate thereof.

[00190] In one embodiment, the rare earth metal is selected from the group consisting of yttrium, lanthanum, cerium, praseodymium and erbium.

[00191] Suitably the rare earth metal species is selected from yttrium nitrate, cerium nitrate, lanthanum nitrate, praseodymium nitrate, erbium nitrate, or a hydrate thereof.

[00192] In one embodiment, the iron to rare earth metal atomic ratio in step (i) is about 200:1 to about 50:1. Suitably, the iron to rare earth metal atomic ratio is about 150:1 to about 50:1. Suitably, the iron to rare earth metal atomic ratio is about 100:1 to about 50:1 or about 100:1 to about 75:1.

[00193] In another embodiment, the iron to rare earth metal atomic ratio in step (i) is about 300:1 to about 50:1. Suitably, the iron to rare earth metal atomic ratio is about 300:1 to about 75:1. Suitably, the iron to rare earth metal atomic ratio is about 200:1 to about 75:1 or about 150:1 to about 75:1.

[00194] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and one or more of an alkali metal species, an alkaline earth metal species and a rare earth metal species.

[00195] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof; and an alkali metal species.

[00196] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic

compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof; and an alkaline earth metal species.

[00197] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof; an alkali metal species and a rare earth metal species.

[00198] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkali metal salt or hydrate thereof.

[00199] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00200] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zinc salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkali metal salt or hydrate thereof.

[00201] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl,

amido and amino group, a zinc salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00202] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a zinc salt or a hydrate thereof and a copper salt or a hydrate thereof; and an alkali metal salt or hydrate thereof.

[00203] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a zinc salt or a hydrate thereof and a copper salt or a hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00204] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; a zinc salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkali metal salt or hydrate thereof.

[00205] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; a zinc salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00206] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; a copper salt or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkali metal salt or hydrate thereof.

[00207] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea; a copper salt

or a hydrate thereof; one or more of a zirconium salt or a hydrate thereof or a manganese salt or hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00208] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and an alkali metal salt or hydrate thereof.

[00209] In one embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00210] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; an alkali metal salt or hydrate thereof and a rare earth metal salt or hydrate thereof.

[00211] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and an alkali metal salt or hydrate thereof.

[00212] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00213] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and an alkali metal salt or hydrate thereof.

[00214] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00215] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and an alkali metal salt or hydrate thereof.

[00216] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and an alkaline earth metal salt or hydrate thereof.

[00217] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and potassium salt or hydrate thereof. Suitably, the atomic ratio of Fe:Cr is about 10:1 and/or the atomic ration of Fe:Zr is about 100:1, and/or the atomic ratio of Fe:K is about 20:1, and/or the atomic ratio of Fe: Zn is about 42:1.

[00218] In another embodiment, step (i) comprises/essentially consists of/consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and calcium salt or hydrate thereof. Suitably, the atomic ratio of Fe:Cr is about 10:1 and/or the atomic ration of Fe:Zr is about 100:1, and/or the atomic ratio of Fe:Ca is about 20:1, and/or the atomic ratio of Fe: Zn is about 42:1.

Step (ii) - Precipitation

[00219] In one embodiment, the method for preparing the pre-catalyst composition comprises step (ii), i.e. combining a solution of an iron salt or a hydrate thereof and an aqueous

basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate.

[00220] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate.

[00221] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally a copper salt or a hydrate thereof, in order to obtain a precipitate.

[00222] In one embodiment, step (ii) essentially consists of combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate.

[00223] In one embodiment, in step (ii) the iron salt or hydrate thereof is an iron (II) or iron (III) salt, or hydrate thereof. For example, suitable non-limiting examples of iron (II) salts or hydrate thereof are FeCl_2 , Fe(OAc)_2 , FeSO_4 , and $\text{Fe(NO}_3)_2$ or a hydrate thereof. Suitable, non-limiting examples of iron (III) salts or hydrate thereof are $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ or a hydrate thereof.

[00224] In one embodiment, the iron salt or hydrate thereof of step (ii) is selected from one or more of the group consisting of FeCl_2 , Fe(OAc)_2 , FeSO_4 , $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, or a hydrate thereof.

[00225] In another embodiment, the iron salt or hydrate thereof of step (ii) is selected from one or more of the group consisting of $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, or a hydrate thereof. In another embodiment, the iron salt or hydrate thereof of step (ii) is selected from one or more of $\text{Fe(NO}_3)_2$ and $\text{Fe(NO}_3)_3$ or a hydrate thereof.

[00226] In one embodiment, step (ii) comprises combining a manganese salt or a hydrate thereof with the iron salt or hydrate thereof. In one embodiment, in step (ii) the manganese salt or hydrate thereof is an manganese (II) or (III) salt or a hydrate thereof, suitably a manganese (II) salt or a hydrate thereof. For example, suitable non-limiting examples of manganese salts or hydrate thereof are $\text{Mn(NO}_3)_2$, MnSO_4 , MnCl_2 , Mn(OAc)_2 , and manganese citrate, or a hydrate thereof. Suitably, the manganese salt is $\text{Mn(NO}_3)_2$ or a hydrate thereof.

[00227] In one embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 250:1 to about 50:1.

[00228] In another embodiment, the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 150:1 to about 50:1.

[00229] In one embodiment, step (ii) comprises combining a zirconium salt or a hydrate thereof with the iron salt or hydrate thereof. In one embodiment, in step (ii) the zirconium salt or hydrate thereof is an zirconium (III) or (IV) salt or a hydrate thereof, suitably a zirconium (IV) salt or a hydrate thereof. For example, suitable non-limiting examples of zirconium salts or hydrate thereof are $Zr(NO_3)_4$, $ZrO(NO_3)_2$, $ZrOCl_2$, zirconium acetate, or a hydrate thereof. Suitably, the zirconium salt is $ZrO(NO_3)_2$ or a hydrate thereof.

[00230] In one embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to zirconium is about 250:1 to about 50:1, suitably about 250:1 to about 75:1.

[00231] In another embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to zirconium is about 150:1 to about 50:1, suitably about 150:1 to about 75:1.

[00232] In another embodiment, the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 100:1 to about 50:1. Suitably, the atomic ratio of iron to zirconium is about 100:1 to about 75:1.

[00233] In one of embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof, a zirconium salt or a hydrate thereof and an aqueous basic solution, and optionally a copper salt or a hydrate thereof, in order to obtain a precipitate.

[00234] In one of embodiment, step (ii) comprises combining a solution of an iron (II) or (III) salt or a hydrate thereof, a zirconium (IV) salt or a hydrate thereof and an aqueous basic solution, and optionally a copper salt or a hydrate thereof, in order to obtain a precipitate.

[00235] In one embodiment, step (ii) comprises combining a copper salt or a hydrate thereof with the iron salt or hydrate thereof. In one embodiment, in step (ii) the copper salt or hydrate thereof is an copper (I) or (II) salt or a hydrate thereof, suitably a copper (II) salt or a hydrate thereof. For example, suitable non-limiting examples of copper salts or hydrate thereof are $Cu(NO_3)_2$, $Cu(OAc)_2$, $CuCl_2$, $CuSO_4$, $Cu_2CO_3(OH)_2$, $CuCl$, Cu_2SO_4 , and $CuNO_3$ or

a hydrate thereof. Suitably, the copper salt or hydrate thereof is selected from one or more of the group consisting of Cu(NO₃)₂, Cu(OAc)₂, CuCl₂, CuSO₄, and Cu₂CO₃(OH)₂, or a hydrate thereof. Suitably, the copper salt or hydrate thereof is selected from one or more of Cu(NO₃)₂ and Cu₂CO₃(OH)₂ or a hydrate thereof.

[00236] In one embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to copper is about 250:1 to about 50:1.

[00237] In another embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to copper is about 150:1 to about 50:1, suitably about 150:1 to about 75:1.

[00238] In another embodiment, the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 100:1 to about 50:1. Suitably, the atomic ratio of iron to copper is about 100:1 to about 75:1.

[00239] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof, a copper salt or a hydrate thereof and an aqueous basic solution, and optionally a zirconium salt or a hydrate thereof, in order to obtain a precipitate.

[00240] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof, a copper salt or a hydrate thereof and an aqueous basic solution, and optionally a manganese salt or a hydrate thereof, in order to obtain a precipitate.

[00241] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof, a copper salt or a hydrate thereof, a manganese salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate.

[00242] In one embodiment, step (ii) comprises combining a solution of an iron (II) or (III) salt or a hydrate thereof, a copper (I) or (II) salt or a hydrate thereof and an aqueous basic solution, and optionally a zirconium salt or a hydrate thereof, in order to obtain a precipitate.

[00243] In one embodiment, step (ii) comprises combining a solution of an iron salt or a hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof and an aqueous basic solution, in order to obtain a precipitate.

[00244] In one embodiment, step (ii) comprises combining a solution of an iron (II) or (III) salt or a hydrate thereof, a zirconium (IV) salt or a hydrate thereof, a copper (I) or (II) salt or a hydrate thereof and an aqueous basic solution, in order to obtain a precipitate.

[00245] In one of embodiment, step (ii) essentially consists of combining a solution of an iron (II) and/or (III) salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate.

[00246] In one embodiment, of the method for preparing a pre-catalyst composition the manganese, copper and/or zirconium salts or hydrates thereof are optionally added in step (i) or (ii), but not both step (i) and step (ii). In one embodiment, the manganese, copper and/or zirconium salts or hydrates thereof are added in step (i) only. In another embodiment, the manganese, copper and/or zirconium salts or hydrates thereof are added in step (ii) only.

[00247] In one embodiment of the method for preparing a pre-catalyst composition the molar ratio of iron salt or hydrate thereof in step (i) to iron salt or hydrate thereof in step (ii) is about 10:1 to about 1:1, suitably about 5:1 to about 2:1.

[00248] In one embodiment, in step (ii) aqueous basic solution is selected from an aqueous ammonia, aqueous urea, an aqueous hydroxide solution, such as aqueous NaOH or KOH, and an aqueous carbonate solution, such as sodium carbonate. Suitably, the aqueous basic solution is aqueous ammonia.

[00249] The aqueous basic solution is used to affect precipitation of a divalent and trivalent iron compounds. The precipitation may be achieved by addition of the aqueous basic solution to a solution of the iron salts or hydrate thereof, preferably an aqueous solution of iron salts or hydrate thereof. The basic solution is added to iron salt solution until the combination has a pH of about 7 to about 14, suitably a pH of about 8 to about 14, suitably a pH of about 9 to about 14, suitably a pH of about 9 to about 12, suitably a pH of about 9, 10 or 11.

[00250] In one embodiment, the precipitate comprises one or more iron species selected from iron oxides or hydroxides, or a hydrate thereof. In one embodiment, the precipitate comprises one or more iron species selected from Fe(OH)_3 , Fe(OH)_2 and FeO(OH) , or a hydrate thereof.

[00251] The precipitate is suitably formed at a temperature in the range of about 10°C to about 100°C. In one embodiment, step (ii) is suitably performed at a temperature in the range of about 20°C to about 100°C. In one embodiment, the step (ii) is suitably performed at a temperature in the range of about 20°C to about 90°C. In another embodiment, step (ii) is suitably performed at a temperature in the range of about 50°C to about 90°C. In another embodiment, step (ii) is suitably performed at a temperature in the range of about 20°C to about 65°C. In another embodiment, step (ii) is suitably performed at a temperature in the range of about 50°C to about 65°C.

[00252] The precipitate may be removed from the mother liquor for instance by filtration and optionally washed and dried. However, in order to avoid difficulty in filtering viscous and gelatinous iron oxides, hydroxides and hydrates thereof, the precipitate and mother liquor may be heated at a temperature in the range of about 10°C to about 100°C in order to provide a wet paste or powder. In one embodiment, in step (ii) a wet paste is suitably formed at a temperature in the range of about 50°C to about 100°C, or about 50°C to about 80°C.

[00253] In one embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00254] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00255] In one embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00256] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00257] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00258] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00259] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00260] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl,

hydroxyl, amido and amino group, a zirconium salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00261] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00262] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00263] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00264] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00265] In one embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00266] In one embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00267] In one embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00268] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00269] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00270] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00271] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a manganese (II) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00272] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00273] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00274] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00275] In another embodiment, the method for preparing the pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

[00276] In another embodiment, the method for preparing the pre-catalyst composition essentially consists of:

(i) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof and, optionally a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

Step (iii) - Calcination

[00277] In one embodiment, the product of step (i) is subjected to calcination to provide a pre-catalyst composition, suitably as a powder. Thus, in certain embodiments above which lack the precipitation step, the calcination may be labelled as step (ii). Nevertheless, the following embodiments are applicable to the calcination step whether labelled step (ii) or (iii).

[00278] In another embodiment, in step (iii) of the method of the invention, the products of steps (i) and (ii) are combined and the combination subjected to calcination to provide a pre-catalyst composition, suitably as a powder.

[00279] Suitably, the product of step (i) is combined with the product of step (ii) and mixed or milled to form a paste or powder. Suitable techniques for mixing and milling are known in the art and at least include grinding in a pestle and mortar, or bead or ball milling. Several different milling techniques are known in the art which may be used in place of bead or ball milling.

[00280] In one embodiment, the combined products of step (i) and (ii) are heated while they are mixed or milled. Suitably, the combination is heated at a temperature in the range of about 10°C to about 100°C while mixing or milling. In one embodiment, the combination is heated at a temperature in the range of about 50°C to about 100°C, or about 50°C to about 80°C. Thereafter a dry paste or powder may be obtained.

[00281] The product of step (i) or the combined products of steps (i) and (ii) are subjected to calcination. Calcination suitably serves to provide combustion or decomposition of the organic compound and any organic salts remaining in the combination, and the formation of metal oxides.

[00282] Suitably the combustion of the organics imparts one or more advantageous properties on the resulting pre-catalyst composition such as nanostructure and advantageous dispersity of metal species and promoters.

[00283] In one embodiment, the calcination is performed at a temperature of between about 400°C to about 1000°C, or about 400°C to about 700°C, or about 400°C to about 600°C, or about 500°C to about 700°C, or about 500°C to about 600°C.

[00284] In another embodiment, the calcination is performed at a temperature of between about 500°C to about 1000°C, or about 500°C to about 800°C, or about 500°C to about 700°C, or about 600°C to about 800°C, or about 600°C to about 700°C.

[00285] In another embodiment, the calcination is performed at a temperature of between about 600°C to about 1000°C, or about 600°C to about 800°C, or about 600°C to about 700°C.

[00286] In another embodiment, the calcination is performed at a temperature of between about 700°C to about 1000°C, or about 700°C to about 800°C, or about 700°C to about 750°C.

[00287] Suitably, the calcination is performed by heating the sample at a heating rate of about 3 to about 10°C per minute, suitably about 5°C per minute. Suitably, the sample is heated up to a temperature of about 500°C, suitably up to about 600°C, suitably up to about 700°C, suitably up to about 750°C, suitably up to about 800°C.

[00288] Suitably the calcination is performed in air, suitably static air. Typically, the calcination will result in decomposition or partial combustion of organic components of the precursor.

[00289] In one embodiment, the combination is calcined for a period of about 1 to about 24 hours, suitably about 1 to about 10 hours, suitably about 2 to about 10 hours.

[00290] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 400°C to about 1000°C for about 1 to 24 hours to provide a pre-catalyst composition.

[00291] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 400°C to about 800°C for about 1 to 24 hours to provide a pre-catalyst composition.

[00292] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 400°C to about 700°C for about 1 to 24 hours to provide a pre-catalyst composition.

[00293] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 400°C to about 600°C for about 1 to 24 hours to provide a pre-catalyst composition.

[00294] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 500°C to about 800°C for about 2 to 10 hours to provide a pre-catalyst composition.

[00295] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 500°C to about 700°C for about 2 to 10 hours to provide a pre-catalyst composition.

[00296] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination at about 500°C to about 600°C for about 2 to 10 hours to provide a pre-catalyst composition.

[00297] In one embodiment, in step (iii), the product of step (i), or the combined product of step (i) and (ii), is/are subjected to calcination by heating at a rate of about 5°C/minute up to about 700°C. Suitably, the product subject to calcination is held at about 700°C for about 4 to 8 hours, suitably about 6 hours.

Optional further steps

[00298] In one embodiment, the method further comprises step (iv), wherein the pre-catalyst composition of step (iii) is further treated with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting the treated pre-catalyst composition to calcination. Suitably, the pre-catalyst composition of step (iii) is impregnated with the one or more transition metal salts or a hydrate thereof.

[00299] Suitably, the transition metal solution comprising one or more transition metal salts or a hydrate thereof is an aqueous solution.

[00300] In one embodiment, the transition metal salt or a hydrate thereof is selected from one or more Pd, Pt, Ru, Rh, Au and Cu salt or hydrate thereof. Suitably, the transition metal salt or a hydrate thereof is selected from one or more of Pd, Pt, Ru, and Cu salt or hydrate thereof. Suitably, the transition metal salt or a hydrate thereof is selected from one or more of Pd, Ru and Cu salt or hydrate thereof.

[00301] In one embodiment, the transition metal salt or a hydrate thereof is a palladium salt or hydrate thereof. Suitably, the palladium salt or hydrate thereof is a palladium (II) salt, or a hydrate thereof. For example, suitable non-limiting examples of palladium (II) salts or hydrate thereof are PdCl₂, Pd(OAc)₂ and Pd(NO₃)₂ or a hydrate thereof. In one embodiment, transition metal salt or hydrate thereof is PdCl₂ or a hydrate thereof.

[00302] In one embodiment, in step (iv), the proportion transition metal salt is such that the atomic ratio of iron to transition metal in the pre-catalyst composition is about 10000:1 to about 10:1. Suitably, the atomic ratio of iron to transition metal is about 1000:1 to about 100:1, suitably about 500:1 to about 100:1.

[00303] In one embodiment, in step (iv), the proportion transition metal salt is such that the atomic ratio of iron to transition metal in the pre-catalyst composition is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to transition metal is about 250:1 to about 50:1, suitably about 250:1 to about 75:1.

[00304] In another embodiment, in step (iv), the proportion of transition metal salt is such that the atomic ratio of iron to transition metal in the pre-catalyst composition is about 150:1 to about 10:1. Suitably, the atomic ratio of iron to transition metal is about 150:1 to about 50:1, suitably about 150:1 to about 75:1.

[00305] In another embodiment, in step (iv), the proportion of transition metal salt is such that the atomic ratio of iron to transition metal is about 100:1 to about 50:1. Suitably, the atomic ratio of iron to transition metal is about 100:1 to about 75:1.

[00306] In one embodiment, the transition metal salt is not a cobalt salt or a hydrate thereof. In another embodiment, the transition metal salt is not a platinum salt or a hydrate thereof. In another embodiment, the transition metal salt is not a nickel salt or a hydrate thereof. In another embodiment, the transition metal salt is not a ruthenium salt or a hydrate thereof. In one embodiment, the transition metal salt is not a Co, Pt, Ni or Ru salt, or a hydrate thereof.

[00307] Once the pre-catalyst composition has been treated with the transition metal salt solution it is suitably dried, for instance at a temperature of about 50°C to about 100°C, and then optionally subjected to calcination.

[00308] In one embodiment, the calcination is performed at a temperature of between about 100°C to about 1000°C, or about 200°C to about 700°C, or about 500°C to about 700°C, or about 400°C to about 600°C, or about 500°C to about 600°C.

[00309] Suitably the calcination is performed in air, suitably static air.

[00310] In one embodiment, the combination is calcined for a period of about 1 to 24 hours, suitably about 1 to about 10 hours, suitably about 2 to about 10 hours.

[00311] In one embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron salt or a hydrate thereof, a chromium salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

optionally (ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting to calcination.

[00312] In one embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron salt or a hydrate thereof, a chromium salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting to calcination.

[00313] In one embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron salt or a hydrate thereof, a chromium salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or a hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting to calcination.

[00314] In one embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron salt or a hydrate thereof, a chromium salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution; and

optionally one or more of a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting to calcination.

[00315] In another embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or a hydrate thereof, a chromium (III) salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof, and a copper (II) salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting to calcination.

[00316] In another embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or a hydrate thereof, a chromium (III) salt or a hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a zirconium (IV) salt or a hydrate thereof, and a copper (II) salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more palladium salts or a hydrate thereof, and optionally subjecting to calcination.

[00317] In another embodiment, the method for preparing a pre-catalyst composition comprises:

(i) combining an iron (II) or (III) salt or a hydrate thereof, a chromium (III) salt or a hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof, and a copper (II) salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more palladium salts or a hydrate thereof, and optionally subjecting to calcination.

[00318] In another embodiment, the method for preparing a pre-catalyst composition essentially consists of:

(i) combining an iron (II) or (III) salt or a hydrate thereof, a chromium (III) salt or a hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zirconium (IV) salt or a hydrate thereof, and a copper (II) salt or a hydrate thereof;

(ii) combining a solution of iron salt or a hydrate thereof, and an aqueous basic solution, in order to obtain a precipitate;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition; and

(iv) treating the pre-catalyst composition of (iii) with a transition metal solution comprising one or more palladium salts or a hydrate thereof, and optionally subjecting to calcination.

[00319] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00320] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron salt or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and one or more of an alkali metal species, an alkaline earth metal species and a rare earth metal species; and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00321] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00322] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; an alkali metal salt or hydrate thereof and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00323] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00324] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a zirconium (IV) salt or a hydrate thereof; an alkali metal salt or hydrate thereof and water.

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00325] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric

acid) or urea, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and water.

- (i)(b) drying the aqueous product of (i)(a) to provide a dried material;
- (ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00326] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; an alkali metal salt or hydrate thereof and water.

- (i)(b) drying the aqueous product of (i)(a) to provide a dried material;
- (ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00327] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; and water.

- (i)(b) drying the aqueous product of (i)(a) to provide a dried material;
- (ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00328] In another embodiment, the method for preparing a pre-catalyst composition comprises/essentially consists of/consists of :

(i)(a) combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C₄ to C₁₂ carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof; an alkali metal salt or hydrate thereof and water.

- (i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the product of (i)(b) to calcination to provide a pre-catalyst composition.

[00329] In one embodiment, the pre-catalyst composition is shaped into pre-catalyst units.

[00330] In another embodiment, the product of step (iii) and/or step (iv) is shaped into a pre-catalyst units, such as pellets or tablets.

[00331] In one embodiment, the products of steps (iii) and/or (iv) are mixed with a lubricant or binder prior to shaping into pre-catalyst units. Suitable lubricants and binders are known in the art. In one embodiment, the lubricant or binder is selected from one or more of the group consisting of sesbania gum powder, calcium aluminate cement or a clay. Suitably, the binder is sesbania gum powder.

[00332] In one embodiment, the lubricant or binder is added to the product of step (iii) and/or (iv) in an amount of about 0.1 % to about 5 % (w/w).

[00333] The shaped pre-catalyst units may be prepared by suitable means known in the art. For instance, the products of steps (iii) and/or (iv) may be combined with lubricant and/or binder and subjected to granulation and tableting in a tablet press, or extruded to in an extruder to give, for example, pellets of suitable dimensions.

[00334] Preferably the shaped pre-catalyst units have maximum and minimum dimensions in the range about 0.5 to about 25 mm, suitably about 0.5 to about 20 mm.

Shaped Composition

[00335] In one aspect, the present invention relates to a shaped composition comprising a pre-catalyst composition obtained or obtainable according to the method of the first aspect as described in any of the above-mentioned embodiments.

[00336] In one embodiment, the shaped composition is in the form of a pellet or a tablet. Suitably, the shaped composition has maximum and minimum dimensions in the range about 0.5 to about 25 mm, suitably about 0.5 to about 20 mm.

[00337] Suitably, the shaped article is a cylindrical pellet or an extruded strip.

[00338] In one embodiment, in addition to the pre-catalyst composition, the shaped composition comprises a lubricant or a binder. In one embodiment, the lubricant or binder is selected from one or more of the group consisting of sesbania gum powder, calcium aluminate cement or a clay. Suitably, the binder is sesbania gum powder.

[00339] In one embodiment, the lubricant or binder is present in the shaped composition in an amount of about 0.1 % to about 5 % (w/w).

Pre-catalyst and Catalyst Composition

[00340] In another aspect, the present invention relates to a pre-catalyst composition obtained or obtainable according to the method of the first aspect as described in any of the above-mentioned embodiments.

[00341] The pre-catalyst composition obtained or obtainable according to the method of the first aspect is suitable for producing a composition comprising carbon monoxide from a feed gas composition comprising carbon dioxide and hydrogen. In particular, the pre-catalyst composition obtained or obtainable according to the method of the first aspect is suitable for use in a reverse water gas shift reaction.

[00342] The pre-catalyst composition obtained or obtainable according to the method of the first aspect has advantageous nano-structure and dispersity of components resulting in high activity and selectivity in a reverse water gas shift reaction

[00343] In another aspect, the present invention provides a method for preparing a catalyst composition comprising:

- (a) providing a pre-catalyst composition obtained or obtainable according to the method of the first aspect, as described any of the above-mentioned embodiments;
- (b) optionally subjecting said pre-catalyst composition to calcination; and
- (c) activating said pre-catalyst composition to obtain a catalyst composition.

[00344] In another aspect, the present invention relates to a catalyst composition obtained or obtainable according to the method of the immediately above aspect.

[00345] The catalyst composition of the above aspects is suitable for producing a composition comprising carbon monoxide from a feed gas composition comprising carbon dioxide and hydrogen. In particular, the catalyst composition according to the above aspects is suitable for use in a reverse water gas shift reaction.

[00346] Suitably, the calcination is performed at a temperature of between about 100°C to about 1000°C, or about 200°C to about 700°C, or about 200°C to about 600°C, suitably about 200°C to about 500°C, more suitably about 300°C to about 450°C. Suitably the calcination is performed in air, suitably static air.

[00347] The calcined pre-catalyst material of step (b) or the pre-catalyst composition of step (a) may be activated, for instance by reduction. Suitably, the material to be activated is exposed to a gaseous composition comprising hydrogen at a temperature of about 250°C to about 500°C, more suitably about 300 to about 350°C.

[00348] In one embodiment, the gaseous composition comprising hydrogen is a mixture of hydrogen and nitrogen. In another embodiment, the gaseous composition is mixture of carbon dioxide and hydrogen gas. In one embodiment, the pre-catalyst activation of (c) occurs in situ in the reaction, i.e. by means of the process gas.

[00349] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, and one or more copper oxide.

[00350] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide; and one or more alkali metal or oxide thereof.

[00351] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, and one or more zinc oxide.

[00352] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide; and one or more alkali metal or oxide thereof.

[00353] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide; and one or more alkaline earth metal or oxide thereof.

[00354] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more zinc oxide.

[00355] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more

chromium oxide, one or more manganese oxide, one or more zinc oxide; and one or more alkali metal or oxide thereof.

[00356] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more zinc oxide; and one or more alkaline earth metal or oxide thereof.

[00357] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more copper oxide; and one or more alkali metal or oxide thereof.

[00358] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more copper oxide; and one or more alkaline earth metal or oxide thereof.

[00359] In another aspect, the present invention provides a pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more copper oxide.

[00360] In another aspect, the present invention provides a pre-catalyst composition consisting essentially of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more copper oxide.

[00361] In another aspect, the present invention provides a pre-catalyst composition consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more copper oxide.

[00362] In another aspect, the present invention provides a pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide and elemental palladium or one or more oxides thereof.

[00363] In another aspect, the present invention provides a pre-catalyst composition essentially consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide and elemental palladium or one or more oxides thereof.

[00364] In another aspect, the present invention provides a pre-catalyst composition consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide and elemental palladium or one or more oxides thereof.

[00365] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more copper oxide and one or more carbon species.

[00366] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide and one or more carbon species.

[00367] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide, one or more alkali metal or oxide thereof and one or more carbon species.

[00368] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide, one or more alkaline earth metal or oxide thereof and one or more carbon species.

[00369] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide and one or more carbon species.

[00370] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide, one or more alkali metal or oxide thereof and one or more carbon species.

[00371] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide, one or more alkaline earth metal or oxide thereof and one or more carbon species.

[00372] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more zinc oxide and one or more carbon species.

[00373] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more zinc oxide, one or more alkali metal or oxide thereof, and one or more carbon species.

[00374] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more manganese oxide, one or more zinc oxide, one or more alkaline earth metal or oxide thereof, and one or more carbon species.

[00375] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide; calcium or an oxide thereof; and one or more carbon species. Suitably, the atomic ratio of Fe:Cr is about 10:1 and/or the atomic ration of Fe:Zr is about 100:1, and/or the atomic ratio of Fe:Ca is about 20:1, and/or the atomic ratio of Fe: Zn is about 42:1.

[00376] In another aspect, the present invention provides a pre-catalyst composition comprising/essentially consisting of/consisting of one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more zinc oxide; potassium or an oxide thereof; and one or more carbon species. Suitably, the atomic ratio of Fe:Cr is about 10:1 and/or the atomic ration of Fe:Zr is about 100:1, and/or the atomic ratio of Fe:K is about 20:1, and/or the atomic ratio of Fe: Zn is about 42:1.

[00377] In one embodiment, the pre-catalyst composition comprises catalytically active nanoparticles.

[00378] As used herein the term “nanoparticle” means a microscopic particle whose size is typically measured in nanometres (nm). A nanoparticle typically has a particle size of from 0.5 nm to 500 nm. For instance, a nanoparticle may have a particle size of from about 0.5 nm to about 200 nm. Suitably, a nanoparticle has a particle size of from about 0.5 nm to about 100 nm, or for instance from about 1 nm to about 50 nm. A particle, for instance a nanoparticle, may be spherical or non-spherical. Non-spherical particles may for instance be plate-shaped, needle-shaped or tubular.

[00379] The term “particle size” as used herein means the diameter of the particle if the particle is spherical or, if the particle is non-spherical, the maximum Feret diameter.

[00380] In one embodiment, the particle size of the catalytically active particles may be in the nanoscale.

[00381] In one embodiment the particle size is determined by microscopy, suitably transmission electron microscopy (TEM).

[00382] In one embodiment, the pre-catalyst composition comprises catalytically active particles sizes of about 100 nm or less. For example, about 80 nm or less; or about 70 nm or less; or about 60 nm or less; or about 50 nm or less; or about 40 nm or less; or about 30 nm or less; or about 20 nm or less; or about 10 nm or less.

[00383] In one embodiment, the pre-catalyst composition comprises a population catalytically active particles having a particle size of about 5 nm to about 100 nm. For example, about 5 nm to about 90 nm; about 5 nm to about 80 nm; or about 5 nm to about 70 nm; or . about 5 nm to about 60 nm; or about 5 nm to about 50 nm; or about 5 nm to about 40 nm; or about 5 nm to about 30 nm; or about 5 nm to about 20 nm.

[00384] In one embodiment, the pre-catalyst composition further comprises a binder or lubricant. Suitable lubricants and binders are known in the art. In one embodiment, the lubricant or binder is selected from one or more of sesbania gum powder, calcium aluminate cement, calcium magnesium oxide (CaMgO_2) or a clay. Suitably, the binder is sesbania gum powder.

[00385] In one embodiment, the lubricant or binder is present in the pre-catalyst composition in an amount of about 0.1 wt.% to about 5 wt.%.

[00386] In one embodiment, the pre-catalyst composition comprises from about 50 to about 90 wt.% of one or more iron oxide. Suitably, the pre-catalyst composition comprises about 60 to about 90 wt. % of one or more iron oxide. Suitably, from about 65 to about 90 wt. % of one or more iron oxide.

[00387] In one embodiment, the pre-catalyst composition comprises from about 5 to about 25 wt.% of one or more chromium oxide. Suitably, the pre-catalyst composition comprises about 5 to about 20 wt. % of one or more chromium oxide. Suitably, from about 5 to about 15 wt. % of one or more chromium oxide.

[00388] In one embodiment, the pre-catalyst composition comprises from about 0.5 to about 15 wt.% of one or more copper oxide. Suitably, the pre-catalyst composition comprises about 1 to about 15 wt. % of one or more copper oxide. Suitably, from about 1 to about 10 wt. % of one or more copper oxide.

[00389] In one embodiment, the pre-catalyst composition comprises from about 0.5 to about 10 wt.% of one or more zirconium oxide. Suitably, the pre-catalyst composition comprises about 1 to about 10 wt. % of one or more zirconium oxide. Suitably, from about 1 to about 5 wt. % of one or more zirconium oxide.

[00390] In one embodiment, the pre-catalyst composition comprises from about 0.5 to about 10 wt.% of one or more manganese oxide. Suitably, the pre-catalyst composition comprises about 1 to about 10 wt. % of one or more manganese oxide. Suitably, from about 1 to about 5 wt. % of one or more manganese oxide.

[00391] In one embodiment, the pre-catalyst composition comprises from about 0.5 to about 15 wt.% of one or more zinc oxide. Suitably, the pre-catalyst composition comprises about 1 to about 15 wt. % of one or more zinc oxide. Suitably, from about 1 to about 10 wt. % of one or more zinc oxide.

[00392] In one embodiment, the pre-catalyst composition comprises about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more zirconium oxides, and about 1 to about 15 wt.% of one or more copper oxides.

[00393] In another embodiment, the pre-catalyst composition comprises about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more zirconium oxides, and about 1 to about 15 wt.% of one or more zinc oxides.

[00394] In one embodiment, the pre-catalyst composition comprises about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more manganese oxides, and about 1 to about 15 wt.% of one or more copper oxides.

[00395] In another embodiment, the pre-catalyst composition essentially consists of about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more manganese oxides, and about 1 to about 15 wt.% of one or more copper oxides.

[00396] In another embodiment, the pre-catalyst composition consists of about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more manganese oxides, and about 1 to about 15 wt.% of one or more copper oxides.

[00397] In one embodiment, the pre-catalyst composition comprises from about 0.01 to about 5 wt.% of elemental palladium or one or more oxides thereof. Suitably, the pre-catalyst composition comprises about 0.05 to about 5 wt. % of elemental palladium or one or more oxides thereof. Suitably, from about 0.05 to about 4 wt. % of elemental palladium or one or more oxides thereof. Suitably, from about 0.05 to about 3 wt. % of elemental palladium or one or more oxides thereof. Suitably, from about 0.05 to about 2 wt. % of elemental palladium or one or more oxides thereof. Suitably, from about 0.05 to about 1 wt. % of elemental palladium or one or more oxides thereof.

[00398] In one embodiment, the pre-catalyst composition comprises about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more zirconium oxides, about 1 to about 15 wt.% of one or more copper oxides and about 0.01 to about 4 wt.% of elemental palladium or one or more oxides thereof.

[00399] In one embodiment, the pre-catalyst composition essentially consists of about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more zirconium oxides, about 1 to about 15 wt.% of one or more copper oxides and about 0.01 to about 4 wt.% of elemental palladium or one or more oxides thereof.

[00400] In one embodiment, the pre-catalyst composition consists of about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more zirconium oxides, about 1 to about 15 wt.% of one or more copper oxides and about 0.01 to about 4 wt.% of elemental palladium or one or more oxides thereof.

[00401] In one embodiment, the pre-catalyst composition has a BET surface area of at least about 20 m²/g, suitably at least about 50 m²/g. BET surface area can be measured according to techniques known in the art. For example, BET surface area may be determined by equilibrium adsorption and desorption isotherms of nitrogen at -196°C for instance.

[00402] In embodiment, the BET surface area of the pre-catalyst composition is at least about 60 m²/g. For example, the pre-catalyst composition may have a BET surface area of at

least about 70 m²/g. For example, the pre-catalyst composition may have a BET surface area of at least about 80 m²/g. For example, the pre-catalyst composition may have a BET surface area of at least about 90 m²/g. For example, the pre-catalyst composition may have a BET surface area of at least 100 m²/g.

[00403] In one embodiment, the pre-catalyst composition has a BET surface area of from about 5 m²/g to about 1000 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 5 m²/g to about 500 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 5 m²/g to about 300 m²/g.

[00404] In one embodiment, the pre-catalyst composition has a BET surface area of from about 20 m²/g to about 1000 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 20 m²/g to about 500 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 20 m²/g to about 300 m²/g.

[00405] In another embodiment, the pre-catalyst composition has a BET surface area of from about 50 m²/g to about 1000 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 50 m²/g to about 500 m²/g. For example, the pre-catalyst composition may have a BET surface area of from about 50 m²/g to about 300 m²/g.

[00406] Suitably, the pre-catalyst composition is used for the producing a composition comprising carbon monoxide from a feed gas composition comprising carbon dioxide and hydrogen. Suitably, the pre-catalyst composition is used in a reverse water gas shift reaction. Further suitable methods in which in the pre-catalyst composition can be used are described below.

Method for producing a composition comprising carbon monoxide

[00407] In another aspect, the present invention relates to a method for producing a composition comprising carbon monoxide, wherein said method comprises contacting a feed gas composition comprising carbon dioxide and hydrogen with a pre-catalyst composition, or a catalyst composition, as described in any of the embodiments above, at a temperature of at least 400°C.

[00408] In one embodiment, the method for producing a composition comprising carbon monoxide comprises providing a pre-catalyst composition by carrying out the methods described above. In another embodiment, the method for producing a composition comprising carbon monoxide comprises providing a catalyst composition by carrying out the methods described above.

[00409] In one embodiment of the claimed methods, the catalyst composition or pre-catalyst composition is charged into a reaction zone. The catalyst having been activated ex situ (for instance by heating, and/or if required by optional oxidation and subsequent reduction e.g. with hydrogen). Alternatively, the pre-catalyst composition may be used directly in the reaction if it is activated in situ, for instance, under the conditions of the reaction.

[00410] The catalyst may be used in a fixed bed, a moving bed or fluidized bed. Suitably, the catalyst is used in a fixed bed reactor. In one embodiment, the pre-catalyst composition or catalyst composition is packed in a fixed bed reactor and the feed gas composition is fed through the bed. In some embodiments, the feed gas composition is continuously fed over the pre-catalyst composition or catalyst composition.

[00411] In one embodiment, the feed gas composition comprising carbon dioxide and hydrogen at a suitable H₂:CO₂ molar ratio is contacted with the bed of catalyst or pre-catalyst composition, and reacted at reaction conditions. Generally, the molar ratio of H₂:CO₂ ranges from about 1:1 to about 10:1, suitably from about 1:1 to about 5:1, more suitably about 1:1 to about 4:1, more suitably about 1:1 to about 3:1, suitably about 1:1 to about 2:1.

[00412] In one embodiment, the feed gas composition is substantially free of oxygen, and/or water. In another embodiment, the feed gas composition is free of oxygen and/or water.

[00413] In another embodiment, the molar ratio of H₂:CO₂ in the feed gas composition is about 1:1, or about 2:1, or about 3:1, or about 4:1.

[00414] The reaction temperatures are elevated. As used herein elevated temperature is a temperature which is elevated with respect to standard ambient temperature, i.e. a temperature of 298.15 K (25 °C). In one embodiment, the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of at least 400°C, suitably at least about 450°C, suitably at least about 500°C, suitably at least about 550°C, suitably at least about 600°C, suitably at least about 650°C.

[00415] In another embodiment the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 400°C to about 1000°C, or about 400°C to about 900°C, or about 400°C to about 800°C, or about 400°C to about 700°C, or about 400°C to about 650°C, or about 400°C to about 600°C, or about 400°C to about 550°C.

[00416] In another embodiment the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 450°C to about 1000°C, or about 450°C to about 900°C, or about 450°C to about 800°C, or about 450°C to about 700°C, or about 450°C to about 650°C, or about 450°C to about 600°C.

[00417] In another embodiment the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 500°C to about 1000°C, or about 500°C to about 900°C, or about 500°C to about 800°C, or about 500°C to about 650°C, or about 500°C to about 600°C.

[00418] In another embodiment the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 600°C to about 1000°C, or about 600°C to about 900°C, or about 600°C to about 800°C, or about 600°C to about 700°C, or about 600°C to about 650°C.

[00419] In another embodiment the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 700°C to about 1000°C, or about 700°C to about 900°C, or about 700°C to about 800°C, or about 700°C to about 750°C.

[00420] The reaction pressure may be below atmospheric pressure, atmospheric pressure, or elevated pressure. In one embodiment, the reaction pressure may be atmospheric or may be elevated pressure. As used herein elevated pressure is a pressure which is elevated with respect to standard ambient pressure, i.e. a pressure of 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm). In one embodiment, the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a pressure of about 100 KPa to about 2000 KPa, or about 100 KPa to about 500 KPa, suitably about 100 KPa to about 400 KPa, suitably about 100 KPa to about 300 KPa, suitably about 100 KPa to about 200 KPa, suitably about 100 KPa to about 150 KPa.

[00421] In another embodiment, the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a pressure of about 0 KPa to about 2000 KPa, or about 0 KPa to about 500 KPa, suitably about 0 KPa to about 400 KPa, suitably about 0 KPa to about 300 KPa, suitably about 0 KPa to about 200 KPa, suitably about 0 KPa to about 150 KPa.

[00422] In another embodiment, the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a pressure of about 0 KPa to about 100 KPa, or about 0 KPa to about 50 KPa.

[00423] In one embodiment, the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a GHSV (gas hourly space velocity) of about 1 to about 20,000 h⁻¹, suitably about 1000 to about 10000 h⁻¹, suitably about 1000 to about 8000 h⁻¹, suitably about 1000 to about 7000 h⁻¹, suitably about 1000 to about 5000 h⁻¹.

[00424] In one embodiment, the method provides a methane selectivity of about 2% or less, more suitably about 1.8 % or less, more suitably about 1.5 % or less, more suitably about 1.0 % or less, more suitably about 0.6 % or less, more suitably about 0.5 % or less, more suitably about 0.4 % or less, more suitably about 0.3 % or less, more suitably about 0.2 % or less, more suitably about 0.1 % or less, more suitably about 0.05 % or less, more suitably about 0.01 vol. % or less.

[00425] Methane selectivity refers to the amount of production of methane as a proportion of the converted CO₂. The methane selectivity (S_{CH4}%) can be calculated according to the following equation:

$$S_{CH4}\% = Y_{CH4\ out}/(Y_{CO2\ in}-Y_{CO2\ out})$$

in which Y_{CO2 in} refers to the CO₂ amount (ml/min) in the feed gas composition and Y_{CO2 out} and Y_{CH4 out} refers to amount of CO₂ and CH₄ respectively in the product stream.

[00426] In one embodiment, the method provides a carbon dioxide conversion of at least about 40%, at least about 50%, suitably at least about 55%, suitably at least about 60%, suitably at least about 65%.

[00427] In another embodiment, the method provides a carbon dioxide conversion of about 50% to about 65%, suitably about 55% to about 65%, suitably about 60% to about 65%.

[00428] The carbon dioxide conversion (X_{CO2}%) can be calculated according to the following equation:

$$X_{CO2}\% = 1 - ((Y_{CO2\ out})/(Y_{CO2\ in}))$$

In which Y_{CO2 in} refers to the CO₂ amount (ml/min) in the feed gas composition and Y_{CO2 out} refers to amount of CO₂ (ml/min) in the product stream.

[00429] In one embodiment, the method provides a carbon monoxide selectivity of at least about 80%, suitably at least about 90%, suitably at least about 95%, suitably at least about 96%, suitably at least about 98%, suitably at least about 99%, suitably at least about 99.5%, suitably at least about 99.9%.

[00430] In one embodiment, the method provides a carbon monoxide selectivity of from about 90% to 100%, suitably from about 95% to 100%, suitably from about 96% to 100%, suitably from about 98% to 100%.

[00431] Carbon monoxide selectivity refers to the amount of production of carbon monoxide as a proportion of the converted CO₂. The carbon monoxide selectivity (S_{CO}%) can be calculated according to the following equation:

$$S_{CO}\% = Y_{CO\text{ out}} / (Y_{CO_2\text{ in}} - Y_{CO_2\text{ out}})$$

in which Y_{CO₂ in} refers to the CO₂ amount (ml/min) in the feed gas composition and Y_{CO₂ out} and Y_{CO out} refers to amount of CO₂ and CO respectively in the product stream.

[00432] In one embodiment, the method provides a carbon dioxide conversion of about 50% to about 65%, a carbon monoxide selectivity of from about 90% to 100%, and a methane selectivity of about 1.8% or less.

[00433] In one embodiment, the method provides a carbon dioxide conversion of about 55% to about 65%, a carbon monoxide selectivity of from about 95% to 100%, and a methane selectivity of about 1.8% or less.

[00434] In another embodiment, the method provides a carbon dioxide conversion of about 55% to about 65%, a carbon monoxide selectivity of from about 95% to 100%, and a methane selectivity of about 0.6% or less.

[00435] In another embodiment, the method provides a carbon dioxide conversion of about 55% to about 65%, a carbon monoxide selectivity of from about 98% to 100%, and a methane selectivity of about 0.01% or less.

[00436] In another embodiment, the method provides a carbon dioxide conversion of about 60% to about 65%, a carbon monoxide selectivity of from about 98% to 100%, and a methane selectivity of about 0.01% or less.

[00437] In another embodiment, the method provides a carbon dioxide conversion of about 60% to about 65%, and a carbon monoxide selectivity of from about 98% or more.

[00438] In another embodiment, the method provides a carbon dioxide conversion of about 60% to about 65%, and a carbon monoxide selectivity of from about 99% or more.

[00439] In another embodiment, the method provides a carbon dioxide conversion of about 60% to about 65%, and a carbon monoxide selectivity of from about 99% or more, and a methane selectivity of about 0.6% or less.

[00440] The method for producing a composition comprising carbon monoxide may comprise preparation of the pre-catalyst composition or catalyst composition described above as a preliminary step.

[00441] The invention will now be further described by the following numbered paragraphs which are not claims:

1. A method for preparing a pre-catalyst composition comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof;

optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.

2. A method for preparing a pre-catalyst composition according to paragraph 1 comprising:

(i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and

(ii) subjecting the material of (i) to calcination to provide a pre-catalyst composition.

3. A method for preparing a pre-catalyst composition according to paragraph 1 or 2, comprising:

(i)(a) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and

water

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the material of (i)(b) to calcination to provide a pre-catalyst composition.

4. A method according to any one of the preceding paragraphs, wherein the iron species is an iron salt or a hydrate thereof.

5. A method according to any one of the preceding paragraphs, wherein the transition metal species is selected from two or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof.

6. A method according to any one of the preceding paragraphs, wherein the transition metal species is selected from one or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, and a zinc salt or hydrate thereof.

7. A method according to any one of the preceding paragraphs, wherein the transition metal species is selected from two or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, and a zinc salt or hydrate thereof.

8. A method according to any one of the preceding paragraphs, wherein the transition metal species is selected from one or more of a manganese salt or hydrate thereof or a zirconium salt or a hydrate thereof; and one or more of a copper salt or a hydrate thereof or a zinc salt or hydrate thereof.

9. A method according to any one of the preceding paragraphs, wherein the transition metal species is selected from:

- (i) a copper salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (ii) a zinc salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (iii) a copper salt or hydrate thereof and a zirconium salt or hydrate thereof; or
- (iv) a zinc salt or hydrate thereof and a zirconium salt or hydrate thereof.

10. A method according to any one of the preceding paragraphs, wherein step (i) further comprises combining one or more of an alkali metal species, an alkaline earth metal species and a rare earth metal species.

11. A method according to paragraph 10, wherein the alkali metal species, alkaline earth metal species or rare earth metal species are added in step (i) in the form of a salt or a hydrate thereof.

12. A method according to paragraph 10 or 11, wherein the alkali metal species is selected from one or more of potassium nitrate, potassium carbonate, sodium nitrate, sodium carbonate, lithium carbonate and cesium carbonate, or a hydrate thereof.

13. A method according to any one of paragraphs 10 to 12, wherein the iron to alkali metal atomic ratio in step (i) is about 100:1 to about 5:1.

14. A method for preparing a pre-catalyst composition comprising:

(i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group; and

optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof;

optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;

(iii) subjecting the product of (i), or the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

15. A method according to any one of the preceding paragraphs, wherein in step (i) the iron salt or hydrate thereof is an iron (II) or iron (III) salt or hydrate thereof.

16. A method according any one of the preceding paragraphs, wherein the iron salt or hydrate thereof of step (i) is selected from one or more of the group consisting of FeCl_2 , Fe(OAc)_2 , FeSO_4 , $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ or a hydrate thereof.

17. A method according to any one of the preceding paragraphs, wherein the iron salt or hydrate thereof of step (i) is one or more of $\text{Fe(NO}_3)_2$ and $\text{Fe(NO}_3)_3$ or a hydrate thereof.

18. A method according to any one of the preceding paragraphs, wherein the chromium salt or hydrate thereof is a chromium (III) salt or a hydrate thereof.

19. A method according to any one of the preceding paragraphs, wherein the chromium salt or hydrate thereof is selected from one or more of the group consisting of $\text{Cr(NO}_3)_3$, CrCl_3 , Cr(Ac)_3 and Cr(OH)_3 or a hydrate thereof.

20. A method according to any one of the preceding paragraphs, wherein the chromium salt or hydrate thereof is $\text{Cr(NO}_3)_3$ or a hydrate thereof.

21. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and chromium salt is such that the atomic ratio of iron to chromium is about 100:1 to about 5:4.

22. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and chromium salt is such that the atomic ratio of iron to chromium is about 20:1 to about 5:4.

23. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a manganese salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

24. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a manganese salt or a hydrate thereof and a copper salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

25. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining an iron (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound comprising one or more functional groups selected from a carboxyl, hydroxyl, amido and amino group, a copper (II) salt or a hydrate thereof and a manganese (II) salt or a hydrate thereof.

26. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a manganese salt or a hydrate thereof and a zinc salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

27. A method according to any one of the preceding paragraphs, wherein the manganese salt or hydrate thereof is selected from one or more of $Mn(NO_3)_2$, $MnSO_4$, $MnCl_2$, $Mn(OAc)_2$, and manganese citrate or a hydrate thereof.

28. A method according to any one of the preceding paragraphs, wherein the manganese salt or hydrate thereof is $Mn(NO_3)_2$ or a hydrate thereof.

29. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and manganese salt is such that the atomic ratio of iron to manganese is about 250:1 to about 10:1. Suitably, the atomic ratio of iron to manganese is about 250:1 to about 50:1, suitably about 250:1 to about 75:1.

30. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a zirconium salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

31. A method according to any one of the preceding paragraphs, wherein the zirconium salt or hydrate thereof is an zirconium (III) or (IV) salt or a hydrate thereof, suitably a zirconium (IV) salt or a hydrate thereof.

32. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a copper salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

33. A method according to any one of the preceding paragraphs, wherein the copper salt or hydrate thereof is a copper (I) or (II) salt or a hydrate thereof, suitably a copper (II) salt or a hydrate thereof.

34. A method according to any one of the preceding paragraphs, wherein step (i) comprises combining a zinc salt or a hydrate thereof with the iron and chromium salt or hydrate thereof.

35. A method according to any one of the preceding paragraphs, wherein the zinc salt or hydrate thereof is a zinc (II) salt or a hydrate thereof, suitably selected from Zn(NO₃)₂, Zn(OAc)₂, ZnCl₂ and ZnSO₄ or a hydrate thereof.

36. A method according to any one of the preceding paragraphs, wherein the organic compound comprises two or more functional groups selected from a carboxyl, hydroxyl, amido and amino groups.

37. A method according to any one of the preceding paragraphs, wherein the organic compound is a C₄ to C₁₂ carboxylic acid or urea.

38. A method according to any one of the preceding paragraphs, wherein the organic compound is selected from citric acid, tartaric acid, oxalic acid, urea, EDTA (ethylenediaminetetraacetic acid), NTA (nitroilotiracetic acid), DTPA (diethylenetriaminepentaacetic acid), and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), or a salt thereof.

39. A method according to any one of the preceding paragraphs, wherein the organic compound is citric acid or urea.

40. A method according to any one of the preceding paragraphs, wherein the organic compound to metal molar ratio in step (i) is about 0.4:1 to about 10:1.

41. A method according to any one of the preceding paragraphs, wherein the organic compound to metal molar ratio in step (i) is about 1:1 to about 10:1.

42. A method according to any one of paragraphs 1 and 14 to 41, wherein the method comprises step (ii).

43. A method according to any one of paragraphs 1 and 14 to 42, wherein in step (ii) the iron salt or hydrate thereof is an iron (II) or iron (III) salt, or hydrate thereof.

44. A method according to any one of paragraphs 1 and 14 to 43, wherein the iron salt or hydrate thereof of step (ii) is selected from one or more of the group consisting of FeCl_2 , Fe(OAc)_2 , FeSO_4 , $\text{Fe(NO}_3)_2$, $\text{Fe(NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ or a hydrate thereof.

45. A method according to any one of paragraphs 1 and 14 to 44, wherein the iron salt or hydrate of step (ii) is selected from one or more of the group consisting of $\text{Fe(NO}_3)_2$ and $\text{Fe(NO}_3)_3$ or a hydrate thereof.

46. A method according to any one of paragraphs 1 and 14 to 45, wherein step (ii) essentially consists of combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution to obtain a precipitate.

47. A method according to any one of paragraphs 1 and 14 to 45, wherein step (ii) comprises combining a zirconium salt or a hydrate thereof with the iron salt or hydrate thereof, suitably a zirconium (IV) salt or a hydrate thereof.

48. A method according to any one of paragraphs 1 and 14 to 45, wherein step (ii) comprises combining a copper salt or a hydrate thereof with the iron salt or hydrate thereof, suitably a copper (II) salt or a hydrate thereof.

49. A method according to any one of the preceding paragraphs, wherein the zirconium salt or hydrate thereof is selected from one or more of the group consisting of $\text{Zr(NO}_3)_4$, $\text{ZrO}(\text{NO}_3)_2$, ZrOCl_2 , zirconium acetate or a hydrate thereof.

50. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 250:1 to about 10:1.

51. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and zirconium salt is such that the atomic ratio of iron to zirconium is about 100:1 to about 50:1.

52. A method according to any one of the preceding paragraphs, wherein the copper salt or hydrate thereof is selected from one or more of the group consisting of Cu(NO₃)₂, Cu(OAc)₂, CuCl₂, CuSO₄, Cu₂CO₃(OH)₂, CuCl, Cu₂SO₄, and CuNO₃ or a hydrate thereof.

53. A method according to any one of the preceding paragraphs, wherein the copper salt or hydrate thereof is selected from one or more of the group consisting of Cu(NO₃)₂ and Cu₂CO₃(OH)₂ or a hydrate thereof.

54. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 250:1 to about 10:1.

55. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and copper salt is such that the atomic ratio of iron to copper is about 100:1 to about 50:1.

56. A method according to any one of the preceding paragraphs, wherein the proportion of iron salt and zinc salt is such that the atomic ratio of iron to copper is about 100:1 to about 50:1.

57. A method according to any one of paragraphs 1 and 14 to 56, wherein the aqueous basic solution is selected from an aqueous ammonia, aqueous urea, an aqueous hydroxide solution, such as aqueous NaOH or KOH, and an aqueous carbonate solution, such as sodium carbonate.

58. A method according to any one of paragraphs 1 and 14 to 57, wherein the basic solution is added in step (ii) until the combination has a pH of about 7 to about 14.

59. A method according to any one of paragraphs 1 and 14 to 58, wherein step (ii) is performed at a temperature in the range of about 20°C to about 90°C.

56. A method according to any one of paragraphs 1 and 14 to 59, wherein step (iii) comprises combining the product of step (i) and the product of step (ii) by mixing or milling to form a paste or powder.

57. A method according to any one of the preceding paragraphs, wherein the calcination is performed at a temperature of between about 400°C to about 1000°C, suitably about 500°C to about 700°C.

58. A method according to any one of the preceding paragraphs, wherein in step (iii) the combination is calcined for a period of about 1 to 24 hours, suitably about 2 to about 10 hours.

59. A method according to any one of the preceding paragraphs, wherein the method further comprises:

(iv) treating the pre-catalyst composition of step (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting the treated pre-catalyst composition to calcination.

60. A method according to paragraph 59, wherein the transition metal solution comprising one or more transition metal salts or a hydrate thereof is an aqueous solution.

61. A method according to paragraph 59 or 60, wherein the transition metal solution comprises one or more transition metal salts or a hydrate thereof selected from a Pd, Pt, Ru, Rh, Au and Cu salt or hydrate thereof.

62. A method according to any one of paragraphs 59 to 61, wherein the transition metal salt solution comprises a palladium salt or hydrate thereof.

63. A method according to any one of paragraph 59 to 62, wherein the transition metal salt solution consists of one or more palladium salts or a hydrate thereof.

64. A method according to any one of paragraphs 59 to 63, wherein the palladium salt or hydrate thereof is a palladium (II) salt, or a hydrate thereof.

65. A method according to paragraph 64, wherein the palladium (II) salt or hydrate thereof is selected from one or more of the group consisting of PdCl_2 , $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{NO}_3)_2$ or a hydrate thereof.

66. A method according to any one of paragraphs 59 to 65, wherein in step (iv), the proportion of transition metal salt is such that the atomic ratio of iron to transition metal in the pre-catalyst composition is about 250:1 to about 10:1.

67. A method according to any one of paragraphs 59 to 65, wherein in step (iv), the proportion of transition metal salt is such that the atomic ratio of iron to transition metal in the pre-catalyst composition is about 100:1 to about 50:1.

68. A method according to any one of paragraphs 59 to 67, wherein in step (iv), the transition metal salt is not a Co, Pt, Ni or Ru salt, or a hydrate thereof.

69. A method according to any one of paragraphs 59 to 68, wherein in step (iv), the calcination is performed at a temperature of between about 100°C to about 1000°C, suitably about 500°C to about 700°C.

70. A method according to any one of the preceding paragraphs, wherein the product of step (iii) and/or step (iv) are shaped into a pre-catalyst units, such as pellets or tablets.

71. A method according to any one of the preceding paragraphs, wherein the products of steps (iii) and/or (iv) are mixed with a lubricant or binder prior to shaping into pre-catalyst units.

72. A method according to paragraphs 70 or 71, wherein the lubricant or binder is selected from one or more of the group consisting of sesbania gum powder, calcium aluminate cement or a clay.

73. A method according to any one of paragraphs 70 to 72, wherein the lubricant or binder is added to the product of step (iii) and/or (iv) in an amount of about 0.1 % to about 5 % (w/w).

74. A pre-catalyst composition obtained or obtainable according to the method of any one of paragraphs 1 to 73.

75. A pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, one or more copper oxide and elemental palladium or one or more oxides thereof.

76. A pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more copper oxide.

77. A pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, and one or more zinc oxide.

78. A pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more zirconium oxide, and one or more copper oxide.

79. A pre-catalyst composition comprising one or more iron oxide, one or more chromium oxide, one or more manganese oxide, and one or more zinc oxide.

80. A pre-catalyst composition according to any one of paragraphs 75 to 79, further comprising one or more of an alkali metal, alkaline earth metal and rare earth metal, or an oxide thereof.

81. A pre-catalyst composition according to any one of paragraphs 75 to 80, further comprising a binder or lubricant.

82. A pre-catalyst composition according to paragraph 81, wherein the lubricant or binder is selected from one or more of the group consisting of sesbania gum powder, calcium aluminate cement, calcium magnesium oxide (CaMgO_2) or a clay.

83. A pre-catalyst composition according to paragraph 81 or 82, wherein the lubricant or binder is present in the pre-catalyst composition in an amount of about 0.1 wt.% to about 5 wt.%.

84. A pre-catalyst composition according to any one of paragraphs 75 to 83, wherein the pre-catalyst composition comprises from about 50 to about 90 wt.% of one or more iron oxide.

85. A pre-catalyst composition according to any one of paragraphs 75 to 84, wherein the pre-catalyst composition comprises from about 5 to about 25 wt.% of one or more chromium oxide.

86. A pre-catalyst composition according to any one of paragraphs 75 to 85, wherein the pre-catalyst composition comprises from about 0.5 to about 15 wt.% of one or more copper oxide.

87. A pre-catalyst composition according to any one of paragraphs 75 to 86, wherein the pre-catalyst composition comprises from about 0.5 to about 10 wt.% of one or more zirconium oxide.

88. A pre-catalyst composition according to any one of paragraphs 75 to 87, wherein the pre-catalyst composition comprises from about 0.5 to about 15 wt.% of one or more zinc oxide.

89. A pre-catalyst composition according to any one of paragraphs 75 to 88, wherein the pre-catalyst composition comprises from about 0.01 to about 5 wt.% of elemental palladium or one or more oxides thereof.

90. A pre-catalyst composition comprising 60-90 wt.% of one or more iron oxides, 5 to 20 wt.% of one or more chromium oxides, 1 to 10 wt.% of one or more zirconium oxides, 1 to 15 wt.% of one or more copper oxides and 0.01 to 4 wt.% of elemental palladium or one or more oxides thereof.

91. A pre-catalyst composition according to paragraph 90, comprising about 60 to about 90 wt.% of one or more iron oxides, about 5 to about 20 wt.% of one or more chromium oxides, about 1 to about 10 wt.% of one or more manganese oxides, and about 1 to about 15 wt.% of one or more copper oxides

92. A pre-catalyst composition according to any one of paragraphs 75 to 88, comprising potassium or an oxide thereof or calcium or an oxide thereof, and one or more carbon species.

93. A pre-catalyst composition according to any one of paragraphs 75 to 92 suitable for producing a composition comprising carbon monoxide from a feed gas composition comprising carbon dioxide and hydrogen.

94. A pre-catalyst composition according to any one of paragraphs 75 to 93 suitable for use in a reverse gas shift reaction.

95. A method for preparing a catalyst composition comprising:

- (a) providing a pre-catalyst composition according to any one of paragraphs 74 or 75 to 94;
- (b) optionally subjecting said pre-catalyst composition to calcination; and
- (c) activating said pre-catalyst composition to obtain a catalyst composition.

96. A method according to paragraph 95, wherein the calcination is performed at a temperature of between about 100°C to about 1000°C, suitably about 200°C to about 500°C.

97. A method according to paragraph 95 or 96, wherein step (c) further comprises grinding or milling the calcined pre-catalyst composition in order to reduce the particle size prior to activation.

98. A method according to any one of paragraphs 95 to 97, wherein in step (c) the pre-catalyst composition to be activated is exposed to a gaseous composition comprising hydrogen at a temperature of about 250°C to about 500°C.

99. A catalyst composition obtained or obtainable according to the method of paragraphs 95 to 98.

100. A method for producing a composition comprising carbon monoxide, wherein said method comprises contacting a feed gas composition comprising carbon dioxide and hydrogen with a pre-catalyst composition according to any one of paragraphs 74 or 75 to 94, or a catalyst composition according to paragraph 99 at a temperature of at least 400°C, suitably about 600°C.

101. A method according to paragraph 100, wherein the feed gas composition has a molar ratio of H₂:CO₂ of from about 1:1 to about 10:1.

102. A method according to paragraph 101, wherein the feed gas composition has a molar ratio of H₂:CO₂ of about 1:1 to about 4:1.

103. A method according to any one of paragraphs 100 to 102, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of at least 500°C.

104. A method according to any one of paragraphs 100 to 102, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 400°C to about 1000°C.

105. A method according to any one of paragraphs 100 to 102, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 450°C to about 600°C.

106. A method according to any one of paragraphs 101 to 105, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a pressure of about 100 KPa to about 500 KPa.

107. A method according to any one of paragraphs 101 to 106, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a GHSV (gas hourly space velocity) of about 1 to about 20,000 h⁻¹, suitably about 1000 to about 5000 h⁻¹.

108. A method according to any one of paragraphs 101 to 107, wherein the method provides a methane selectivity of about 2% or less.

109. A method according to any one of paragraphs 101 to 108, wherein the method provides a methane selectivity of about 0.6% or less.

110. A method according to any one of paragraphs 101 to 109, wherein the method provides a carbon dioxide conversion of at least about 55%.

111. A method according to any one of paragraphs 101 to 110, wherein the method provides a carbon dioxide conversion of at least about 60%.

112. A method according to any one of paragraphs 101 to 111, wherein the method provides a carbon monoxide selectivity of at least about 98%.

EXAMPLES

I. Preparation of the pre-catalyst compositions

[00442] The pre-catalyst compositions were prepared using an organic combustion method, optionally in combination with precipitation and/or impregnation methods.

I.A Example 1

[00443] For example, in a first step the following compounds were combined as follows:

- Fe(NO₃)₃. 9H₂O 171 g (Fischer Chemicals)
- Cr(NO₃)₃.4H₂O, 21.1 g (Sigma Aldrich, Cr₂O₃ content: 19 wt.%)
- ZrO(NO₃)₂.xH₂O 2.1 g (Sigma Aldrich)
- Cu(NO₃)₂.4H₂O 2.1 g (Sigma Aldrich)
- Citric acid 240g (Sigma Aldrich)

[00444] Fe(NO₃)₃.9H₂O (iron(III) nitrate nonahydrate), Cr(NO₃)₃.4H₂O (Chromium(III) nitrate hydrate), ZrO(NO₃)₂.xH₂O (zirconium(IV) oxynitrate hydrate), Cu(NO₃)₂.4H₂O (copper(II) nitrate hydrate) and citric acid were mixed in the amounts above and ground in a pestle and mortar under ambient conditions for 1 hour, until a nearly dry paste was formed.

[00445] In a second step, 50.5 g of Fe(NO₃)₃.9H₂O was added to 500ml of water while stirring at 50-90°C for 3 hours. Subsequently, aqueous ammonia (NH₃.H₂O) solution (25 wt.%) was added drop-wise in order to adjust the pH value to 11. A precipitate formed and the resultant slurry was aged at 50 to 80°C for 10 hours whilst continuously stirring, until the volume of the solution was reduced to less than about 100ml and a sludge produced.

[00446] In a third step, the sludge from the second step was gradually added to the paste from the first step whilst continuously mixing at a temperature of about 50 to 80°C, for up to 10 hours, to obtain a viscous solid mixture which was solid when cooled to room temperature. The solid was then transferred to crucibles and put into a muffle furnace (Carbolite Laboratory Muffle Furnace max. 1100°C) and the temperature increased gradually from room temperature to 600°C at a rate of 2°C/min and then heated at 600°C for 5 hours before being left in the muffle oven to cool down to room temperature overnight. A brown-red powder was obtained (**Pre-catalyst A**).

[00447] A portion of the calcined brown-red powder was combined with 1.8% by weight of sesbania gum powder and milled at ambient conditions (Xuman crusher 34000 rotate/min) for 2 hours, then extruded (Beiyang Lixing Extruder 0041) to provide the pre-catalyst composition as cylindrical pellets.

I.B Example 2

[00448] In a fourth step, Pre-catalyst A (10g, dried powder) was treated with 5 ml of 0.05% PdCl₂ solution (Aladdin Chemical), statically left in air for 4 hours at ambient conditions, dried at 100°C for 3 hours and then calcined in a muffle furance (Luoyang Sigma Instrument Manufacture Co., Ltd, SGM. M10/13) at 600°C for 2 hours then cooled down. The cooled product of the calcination was further washed with water to remove any chloride ions and then dried and calcined at 600°C , then cooled down to room temperature to give **Pre-catalyst B** as a powder. This powder was manually pressed to give pellets using a manual powder tablet machine (769YP-15A).

I.C Example 3

[00449] In another example, the following was combined as a first step:

- Fe(NO₃)₃. 9H₂O 171.7 g (Fischer Chemicals)
- Cr(NO₃)₃.xH₂O, 23.7 g (Sigma Aldrich, Cr₂O₃ content: 19 wt.%)
- Mn(NO₃)₂.4H₂O 1.4 g (Sigma Aldrich)
- Cu(NO₃)₂.xH₂O 2.4 g (Sigma Aldrich)
- Citric acid 243g (Sigma Aldrich)

[00450] Similar to the method described above in Example 1, these components were mixed and ground in a pestle and mortar under ambient conditions for 1 hour, until a nearly dry paste was formed.

[00451] A precipitate was prepared from iron salts and a base as described in the second step of Example 1 and the resultant sludge was added to the dry paste of the first step.

[00452] The combination was dried at about 100°C for 4 hours and then the viscous sludge transferred to a quartz crucible and heated at 2°C/min to 600°C and held for 4 hours in a muffle furnace (Carbolite Laboratory Muffle Furnace max. 1100°C) to give a brown-red powder (**Pre-catalyst C**).

[00453] The catalyst is mixed with sesbania gum powder (1.2%) and then pressed into pellets using a manual powder tablet press machine (769YP-15A).

I.D Example 4

[00454] The same materials as for Pre-catalyst C (Example 3) were combined in a first step: Fe(NO₃)₃. 9H₂O (171.7 g), Cr(NO₃)₃.xH₂O (23.7 g), Mn(NO₃)₂.4H₂O (1.4 g), Cu(NO₃)₂.xH₂O (2.4 g) and citric acid (243g), and ground in a pestle and mortar under ambient conditions until a nearly dry paste was formed. However, in contrast with the second step used in the examples above, this material was not combined with an iron salt precipitate. Rather the nearly dry paste of the first step was directly transferred to a quartz boat and heated in a muffle furnace in static air at heating rate 2°C/min to 600°C and held for 5 hours (Carbolite Laboratory Muffle Furnace max. 1100°C) to give a brown-red powder (**Pre-catalyst D**).

[00455] The above powder is pelletized using a manual powder tablet machine (769 YP -15A) to provide the pre-catalyst composition as a pellet.

I.E Example 5 – Pre-catalyst compositions 1 to 34

[00456] Pre-catalyst compositions were prepared by an Organic Combustion Method (OCM); citric acid was used as the organic compound unless stated otherwise. Typically, a Fe-Cr-Cu-Mn pre-catalyst composition was prepared from citric acid (99%, Acros Organics), iron (III) nitrate nonahydrate (98%, Sigma-Aldrich or Alfa Aesar), chromium (III) nitrate nonahydrate (99%, Sigma-Aldrich), copper(II) nitrate hemi(pentahydrate) (98%, Thermo Scientific) and manganese (II) nitrate (50%, w/w aq. Soln, Thermo Scientific), in a molar ratio of citric acid: (Fe + Cr + Cu + Mn) = 1:1 and a weight ratio of (Fe- and Cr- and Cu- and Mn- precursors + citric acid)/water of 2:1.

[00457] The method consisted of mixing the metal salts, citric acid and water in a beaker. This initial mixture was stirred overnight to form a homogeneous aqueous solution and heated at 80°C for 1-2 h to obtain a citric acid-based slurry. The slurry was then dried at 80-100 °C overnight in the drying oven. Then, the obtained viscous paste was heated at 5 °C/min to 700 °C and maintained for 6 hours to produce a powder.

[00458] Pre-catalyst compositions with different transition metals (e.g. Zn, Co, Ni, Zr to replace Cu or Mn) promoters were also prepared using the same method.

[00459] Fe-Cr-Zn-Mn, Fe-Cr-Co-Mn, Fe-Cr-Ni-Mn, Fe-Cr-Zr-Mn pre-catalysts were prepared using zinc nitrate hexahydrate (98%, Thermo Scientific), cobalt(II) nitrate

hexahydrate (98%, Sigma-Aldrich), nickel(II) nitrate hexahydrate (98%, Sigma-Aldrich) and zirconium(IV) oxynitrate hydrate (99%, Sigma-Aldrich) as transition metal precursors replacing copper(II) nitrate hemi(pentahydrate) (98%, Thermo Scientific), respectively.

[00460] Fe-Cr-Cu-Zn, Fe-Cr-Cu-Co, Fe-Cr-Cu-Ni and Fe-Cr-Cu-Zr pre-catalysts were prepared with zinc nitrate hexahydrate (98%, Thermo Scientific), cobalt(II) nitrate hexahydrate (98%, Sigma-Aldrich), nickel(II) nitrate hexahydrate (98%, Sigma-Aldrich) and zirconium(IV) oxynitrate hydrate (99%, Sigma-Aldrich) as transition metal precursors replacing manganese (II) nitrate (50%, w/w aq. Soln, Thermo Scientific), respectively.

[00461] Similarly, Fe-Cr-Cu-Zr-Li, Fe-Cr-Cu-Zr-Na, Fe-Cr-Cu-Zr-K, Fe-Cr-Cu-Zr-Cs, Fe-Cr-Cu-Zr-Mg, Fe-Cr-Cu-Zr-Ca were prepared with Fe-Cr-Cu-Zr (100:10:2.4:1) as the basis by adding alkali metals (Li, Na, K, Cs) and alkaline earth metals (Mg, Ca) using lithium carbonate (99%, Sigma-Aldrich), sodium nitrate (97%, Acros Organics), potassium nitrate (99%, Sigma-Aldrich) and cesium nitrate (99.8%, Thermo Scientific) to the initial mixture, respectively. Typically, the molar ratio of Fe: alkali metal (or alkaline earth metal) used was 20:1.

[00462] Fe-Cr-Zn-Zr-K-Y, Fe-Cr-Zn-Zr-K-La, Fe-Cr-Zn-Zr-K-Ce, Fe-Cr-Zn-Zr-K-Pr, Fe-Cr-Zn-Zr-K-Er pre-catalysts were prepared with Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) as the basis by adding rare earth metals (Y, La, Ce, Pr, Er) in salt form, such as yttrium(III) nitrate hexahydrate (99.8%, Aldrich), lanthanum(III) nitrate hexahydrate (99%, Fluka), cerium(III) nitrate hexahydrate (99.8%, Aldrich), praseodymium(III) nitrate hexahydrate (99.9%, Aldrich) and erbium(III) nitrate pentahydrate (99.9%, Aldrich) to the initial mixture, respectively. Typically, the atomic ratio of Fe: rare earth metal used was 100:1.

[00463] Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) pre-catalysts were also prepared using organic compounds other than citric acid, specifically; malic acid (99%, Acros Organics), salicylic acid (99.0%, SigmaAldrich), tannic acid (ACS reagent, Sigma-Aldrich), urea (Bio-Reagent, Sigma-Aldrich), oxalic acid (99.0%, Sigma-Aldrich), nitrilotriacetic acid (NTA, 99%, Sigma-Aldrich), N-(2-hydroxyethyl) ethylenediamine-N,N',N'-triacetic acid (HEDTA, 98%, Sigma-Aldrich), diethylenetriaminepentaacetic acid (DTPA, 98%, Sigma-Aldrich), tannic acid (ACS reagent, Sigma-Aldrich), ethylenediamine Tetraacetic Acid (EDTA, 99.5%, Fisher Scientific), ascorbic acid (99%, Alfa Aesar) and lactic acid (\approx 90% (T), Sigma-Aldrich).

[00464] Otherwise, pre-catalyst compositions were prepared with citric acid as the organic compound. The composition of different metals in the pre-catalyst compositions is expressed as atomic molar ratios.

[00465] The above described method yielded pre-catalyst compositions 1 to 34 (see Table A, below).

Table A

Pre-catalyst	Description
01	Fe-Cr-Cu-Mn (100:10:2.4:1)
02	Fe-Cr-Zn-Mn (100:10:2.4:1)
03	Fe-Cr-Co-Mn (100:10:2.4:1)
04	Fe-Cr-Ni-Mn (100:10:2.4:1)
05	Fe-Cr-Zr-Mn (100:10:2.4:1)
06	Fe-Cr-Cu-Zn (100:10:2.4:1)
07	Fe-Cr-Cu-Co (100:10:2.4:1)
08	Fe-Cr-Cu-Ni (100:10:2.4:1)
09	Fe-Cr-Cu-Zr (100:10:2.4:1)
10	Fe-Cr-Cu-Zr-Li (100:10:2.4:1:5)
11	Fe-Cr-Cu-Zr-Na (100:10:2.4:1:5)
12	Fe-Cr-Cu-Zr-K (100:10:2.4:1:5)
13	Fe-Cr-Cu-Zr-Cs (100:10:2.4:1:5)
14	Fe-Cr-Cu-Zr-Mg (100:10:2.4:1:5)
15	Fe-Cr-Cu-Zr-Ca (100:10:2.4:1:5)
16	Fe-Cr-Zn-Zr (100:10:2.4:1)
17	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5)
18	Fe-Cr-Zn-Zr-K-Y (100:10:2.4:1:5:1)
19	Fe-Cr-Zn-Zr-K-La (100:10:2.4:1:5:1)
20	Fe-Cr-Zn-Zr-K-Ce (100:10:2.4:1:5:1)
21	Fe-Cr-Zn-Zr-K-Pr (100:10:2.4:1:5:1)
22	Fe-Cr-Zn-Zr-K-Er (100:10:2.4:1:5:1)
23	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + malic acid
24	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + salicylic acid
25	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + tartaric acid
26	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + urea
27	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + oxalic acid
28	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + NTA
29	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + HEDTA
30	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + DTPA
31	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + tannic acid
32	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + EDTA
33	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + ascorbic acid

Pre-catalyst	Description
34	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5) + lactic acid

II. Reverse water gas shift reaction with Catalysts A to D

[00466] In general, the pre-catalyst composition is loaded into a stainless steel fixed bed reactor. The pre-catalyst composition is then pre-reduced using hydrogen whilst heating. The reactor is then switched to feed in the desired reaction gas mixture of CO₂+xH₂ to the desired reaction temperature. The pressure is adjusted to the target pressure, and the flow rate of the gas mixture is adjusted as necessary. The exit gas is analysed using Lunan GC 6890A equipped with a TCD detector at 100°C.

[00467] Pre-catalyst compositions A to D were reduced for 1 hour under a flow of 10% H₂ carried by N₂ whilst heating at a rate of 2°C/min up to 600°C prior to reactions to activate the catalyst composition and provide catalyst compositions A to D respectively. Each catalyst composition was then reacted with a feed gas composition consisting of 3:1 H₂:CO₂ at temperature of about 600°C and at ambient pressure.

[00468] The catalyst composition performance is provided in Table 1 below.

Table 1

Catalyst	CO ₂ conversion (%)	CO selectivity (%)	CH ₄ selectivity (%)
No catalyst	9.2	85.1%	ND
A	57	96.2	1.8
B	61.4	98.8	0
C	63.5	99.0	0
D	56.8	95.8	0.6
GHSV=6000h ⁻¹ , Ambient pressure, 600°C			

[00469] It is observed that without catalyst less than 10% of CO₂ converted to CO at 600°C. However, catalyst composition A converted 57% of CO₂ into CO with a trace amount of methane produced. When catalyst A is impregnated with palladium, (i.e. catalyst composition B), under the same conditions, CO₂ conversion rises to 61.4%, with no methane detected.

[00470] When the zirconium component of pre-catalyst composition A is replaced with a manganese component (i.e. pre-catalyst composition C), it is seen that the CO₂ conversion

of the corresponding catalyst composition (catalyst composition C) increased to 63.5%, with a CO selectivity of 99% and no methane detected.

[00471] In comparison with the hybrid combustion and precipitation method adopted in the preparation of catalyst composition C, catalyst composition D was prepared using a combustion method but without a precipitation step. CO₂ conversion over catalyst composition D is 56.8%, and CH₄ selectivity is 0.6%.

III. Reverse water gas shift reaction with Catalysts 1 to 34

[00472] In general, the pre-catalyst composition is loaded into a stainless-steel fixed bed reactor with an inner diameter of 1.0 cm with a typical loading of 1.2 g pre-catalyst and 4.8 g SiC load. A feed gas mixture with a H₂ to CO₂ ratio of 3:1 and N₂ (as an internal standard gas) is used at a GHSV (gas hourly space velocity) of 2500 mL/(g·h) in order to activate the pre-catalyst to form in situ the active catalyst composition. Then the reactor was heated at 5°C/min up to 600 °C under atmospheric pressure unless stated otherwise. The exit gas was analysed using an online Gas Chromatograph (Agilent 8890 GC) with flame ionization (FID) and thermal conductivity detectors (TCD).

[00473] In Table 2, the data was collected at an operating temperature of 600 °C, GHSV of 2500 ml/(g·h) and pressure of 0-0.5 bar. The effect of various metals on the catalytic performance is shown. Utilizing catalyst Fe-Cr-Cu-Mn (100:10:2.4:1) as the basis, various transition metals have replaced either Cu or Mn. Catalyst 16 (Fe-Cr-Zn-Zr) showed best CO₂ conversion and minimal CH₄ selectivity.

Table 2

Catalyst	Description	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
01	Fe-Cr-Cu-Mn (100:10:2.4:1)	52.12	99.79	0.21
02	Fe-Cr-Zn-Mn (100:10:2.4:1)	55.08	100.00	0.00
03	Fe-Cr-Co-Mn (100:10:2.4:1)	55.28	97.57	2.43
04	Fe-Cr-Ni-Mn (100:10:2.4:1)	46.49	96.27	3.73
05	Fe-Cr-Zr-Mn (100:10:2.4:1)	51.92	99.70	0.30
06	Fe-Cr-Cu-Zn (100:10:2.4:1)	46.81	99.71	0.29
07	Fe-Cr-Cu-Co (100:10:2.4:1)	53.08	95.95	4.05
08	Fe-Cr-Cu-Ni (100:10:2.4:1)	50.08	95.54	4.46
09	Fe-Cr-Cu-Zr (100:10:2.4:1)	59.15	98.40	1.60
16	Fe-Cr-Zn-Zr (100:10:2.4:1)	61.35	99.87	0.13

[00474] The effect of alkali metals and alkaline earth metals on the catalyst performance is shown in Table 3. The data was collected at an operating temperature of 600 °C, GHSV of 2500 ml/(g·h) and pressure of 0-0.5 bar. It can be seen from Table 3, the addition of alkali metals and alkaline earth metals, such as Li, Na, K, Cs and Ca serves to eliminate any CH₄ selectivity.

[00475] The results from catalyst-14 and catalyst-15 showed the effect of alkaline earth metals on the catalyst performance and CH₄ selectivity. The addition of Ca eliminates CH₄ selectivity.

Table 3

Catalyst	Description	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
09	Fe-Cr-Cu-Zr (100:10:2.4:1)	59.15	98.40	1.60
10	Fe-Cr-Cu-Zr-Li (100:10:2.4:1:5)	52.86	100.00	0.00
11	Fe-Cr-Cu-Zr-Na (100:10:2.4:1:5)	53.72	100.00	0.00
12	Fe-Cr-Cu-Zr-K (100:10:2.4:1:5)	57.05	100.00	0.00
13	Fe-Cr-Cu-Zr-Cs (100:10:2.4:1:5)	53.06	100.00	0.00
14	Fe-Cr-Cu-Zr-Mg (100:10:2.4:1:5)	54.04	99.80	0.20
15	Fe-Cr-Cu-Zr-Ca (100:10:2.4:1:5)	56.93	100.00	0.00

[00476] The effect of rare earth metals on the catalyst performance is shown in Table 4. The data was collected at an operating temperature of 600 °C, GHSV of 2500 ml/(g·h) and pressure of 0-0.5 bar. All rare earth metals have very similar performance and no CH₄ selectivity.

Table 4

Catalyst	Description	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
17	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5)	59.14	100.00	0.00
18	Fe-Cr-Zn-Zr-K-Y (100:10:2.4:1:5:1)	56.03	100.00	0.00
19	Fe-Cr-Zn-Zr-K-La (100:10:2.4:1:5:1)	53.61	100.00	0.00
20	Fe-Cr-Zn-Zr-K-Ce (100:10:2.4:1:5:1)	56.28	100.00	0.00

Catalyst	Description	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
21	Fe-Cr-Zn-Zr-K-Pr (100:10:2.4:1:5:1)	58.42	100.00	0.00
22	Fe-Cr-Zn-Zr-K-Er (100:10:2.4:1:5:1)	58.91	100.00	0.00

[00477] The effect of organic compounds used for pre-catalyst composition preparation on the catalyst performance is shown in Table 5. The data was collected at an operating temperature of 600 °C, GHSV of 2500 ml/(g·h) and pressure of 0-0.5 bar. The catalysts Fe-Cr-Zn-Zr-K prepared with citric acid, malic acid, salicylic acid, tartaric acid, urea, oxalic acid, NTA, HEDTA, DTPA, tannic acid, EDTA, ascorbic acid and lactic acid showed similar conversion on CO₂, 100% CO selectivity and no CH₄ selectivity.

Table 5

Catalyst	Description	Organic compounds	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
17	Fe-Cr-Zn-Zr-K (100:10:2.4:1:5)	Citric acid	59.14	100	0
23		Malic acid	57.24	100	0
24		Salicylic acid	55.42	100	0
25		Tartaric acid	56.19	100	0
26		Urea	54.51	100	0
27		Oxalic acid	54.10	100	0
28		NTA	58.14	100	0
29		HEDTA	56.39	100	0
30		DTPA	56.90	100	0
31		Tannic acid	55.75	100	0
32		EDTA	61.43	100	0
33		Ascorbic acid	60.97	100	0
34		Lactic acid	57.22	100	0

[00478] The effect of operating pressure on the catalyst performance is shown in Table 6. The data was collected at an operating temperature of 600 °C, GHSV of 2500 ml/(g·h) and pressure from 0 to 3 bar (gauge pressure).

Table 6

Catalyst	Reaction bed temperature (°C)	GHSV [mL/(g·h)]	Operation pressure /bar	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
17	600	2500	0	59.11	100	0.00

Catalyst	Reaction bed temperature (°C)	GHSV [mL/(g·h)]	Operation pressure /bar	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
Fe-Cr-Zn-Zr-K (100:10:2.4:1:5)			1	58.65	99.95	0.05
			2	58.51	99.77	0.23
			3	57.83	96.04	3.96

[00479] The effect of reaction bed temperature on the catalyst performance is shown in Table 7. The data was collected at a range of operating temperatures from 400 °C to 800 °C with 50 °C intervals, GHSV of 2500 ml/(g·h) and pressure of 0-0.5 bar.

Table 7

Catalyst	Operation pressure/ bar	GHSV [mL/(g·h)]	Reaction bed temperature (°C)	CO ₂ Conversion/%	CO Selectivity/%	CH ₄ Selectivity/%
¹⁷ Fe-Cr-Zn-Zr-K (100:10:2.4:1:5)	0-0.5	2500	400	23.99	100.00	0.00
			450	38.27	100.00	0.00
			500	48.02	100.00	0.00
			550	53.72	100.00	0.00
			600	58.80	100.00	0.00
			650	63.45	100.00	0.00
			700	66.97	99.82	0.18
			750	69.64	99.80	0.20
			800	72.33	99.82	0.18

IV. Catalyst Characterisation

[00480] The powder X-ray diffraction (XRD) analyses of catalysts used a Cu K α (0.154056 nm) X-ray source (25 kV, 40 mA) on a Bruker D8 Advance diffractometer. Diffraction patterns were recorded over a 10-80° 2 θ angular range using a step size of 0.02°. Crystallite sizes were determined using the Scherrer equation.

[00481] X-Ray Photoelectron Spectroscopy (XPS) of the sample was performed using a Thermo Fisher Scientific Nexsa spectrometer. Samples were analysed using a micro-focused monochromatic Al X-ray source (72 W) over an area of approximately 400 mm. Data were recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively. Charge neutralisation was achieved using a combination of low energy electrons and argon ions. The resulting spectra were analysed

using Casa XPS peak fitting software and sample charging corrected using the C 1s signal at 284.8 eV as reference.

[00482] Transmission electron microscopy (TEM) and energy dispersive X-ray tomography within the scanning transmission electron microscope (STEM/EDX) imaging was carried out on a 200kV analytical TEM (JEOL 2100) equipped with OI Aztec. A small amount of the powder sample was dry cast on to a holey carbon coated Cu grid before analysis.

[00483] The powder X-ray diffraction (XRD) spectrum of various pre-catalysts compositions is presented in Figure 1.

[00484] The surface elemental compositions and oxidation states of the metals of catalyst precursor 17 were analysed by using XPS in the region of 0-1100 eV. The survey spectrum (Figure 2a) indicated that the sample contains Fe, Cr, Zn, Zr, K, C and O. Figure 2b shows the XPS spectrum of the Fe 2p region, which can be fitted with two spin-orbit doublets corresponding to the Fe 2p^{3/2} and Fe 2p^{1/2} peaks with a binding energy gap of 13.5 eV and a shakeup satellite which is assigned to Fe³⁺, most of peaks can be assigned to Fe³⁺, and small amount of them as Fe²⁺, which indicates Fe₂O₃ with small amounts of Fe₃O₄.

[00485] Figure 2c shows the Cr 2p XPS spectra, which showed most of chromium as Cr₂O₃ (Cr (III) oxide in the figure). In addition, in Figures 2d, 2e, 2f show the Zr 3d, Zn 2p and K 2p at 181.9 eV/183.9 eV, 1021.4 eV/1044.5 eV, and 292.7 eV/295.4 eV, respectively.

[00486] Figure 2h shows the O 1s, XPS spectra with a main peak at 529.9 eV, clearly originating from the presence of metal-O bonds.

[00487] The XPS spectra of the C 1s present (Figure 2g) showed the peak of C-C, C=O, and C-O at 284.8 eV, 288.4 eV and 286.4 eV, respectively, that carbon is due to the carbon residue due to the calcination of citric acid, and the peak of C=O can be attributed to the citric acid residues which have not fully decomposed.

[00488] The transmission electron microscopy (TEM) of a pre-catalyst composition 17 is shown in Figure 3. Overview images at low to intermediate magnification show a variety of particle sizes and shapes. Two size ranges were immediately visible: large particles in hundreds of nm to micron range (Figure 3a) and smaller particles in the 5-20nm range (Figure 3b).

[00489] Figure 3 c-f show the high resolution TEM (HRTEM), the smaller particles were mostly attached to the surface of the larger particles and some evidence of carbonaceous

material covering both large and small particles could also be detected. At higher magnification the lattice parameters of the small particles can be resolved and FFTs show that there is a number of different d-spacings. D spacings of 0.37 nm and 0.47nm were found more frequently. This is due to a combination of Fe₂O₃ and Fe₃O₄ among some less frequently found patterns. Some of the larger particles are assign to Fe₂O₃ (lattice spacings of 0.37 – 112) whereas the smaller particles at the edge of the large particles appear to have more characteristics of Fe₃O₄ (lattice spacing 0.47 – 111). Figure 3f showed the image of area with large Fe₂O₃ crystal with smaller Fe₃O₄ crystals at the edge.

[00490] Energy dispersive X-ray tomography within the scanning transmission electron microscope (STEM/EDX) of catalyst precursor 17 is shown in Figure 4, EDX of different areas showed a variation in chemical content, ranging from >80% Fe in some areas to various ratios of Fe and Oxygen as well as areas which contained small amounts of Cr or Zn. The different elements images showed similar shape, which indicate their uniform dispersion.

[00491] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference in their entirety and to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein (to the maximum extent permitted by law).

[00492] All headings and sub-headings are used herein for convenience only and should not be construed as limiting the invention in any way.

[00493] The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise paragraphed. No language in the specification should be construed as indicating any non-paragraphed element as essential to the practice of the invention.

[00494] The citation and incorporation of patent documents herein is done for convenience only and does not reflect any view of the validity, patentability, and/or enforceability of such patent documents.

[00495] This invention includes all modifications and equivalents of the subject matter recited in the paragraphs appended hereto as permitted by applicable law.

CLAIMS

1. A method for preparing a pre-catalyst composition comprising:
 - (i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and
optionally one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof;
optionally (ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution; and optionally one or more of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof and a copper salt or a hydrate thereof, in order to obtain a precipitate;
(iii) subjecting the product of (i), or the combined products of (i) and (ii), to calcination to provide a pre-catalyst composition.
2. A method for preparing a pre-catalyst composition according to claim 1 comprising:
 - (i) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof; an organic compound comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and
one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and
 - (ii) subjecting the material of (i) to calcination to provide a pre-catalyst composition.
3. A method for preparing a pre-catalyst composition according to claim 1 or 2, comprising:
 - (i)(a) combining an iron species selected from an iron salt or hydrate thereof, or an iron oxide or hydrate thereof; a chromium salt or hydrate thereof, an organic compound

comprising one or more functional groups selected from the group consisting of a carboxyl, hydroxyl, amido and amino group; and

one or more transition metal species selected from the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, a zinc salt or hydrate thereof, a cobalt salt or hydrate thereof and a nickel salt or hydrate thereof; and

water

(i)(b) drying the aqueous product of (i)(a) to provide a dried material;

(ii) subjecting the material of (i)(b) to calcination to provide a pre-catalyst composition.

4. A method according to any one of claims 1 to 3, wherein the transition metal species of step (i) is selected from two or more of the group consisting of a manganese salt or hydrate thereof, a zirconium salt or a hydrate thereof, a copper salt or a hydrate thereof, and a zinc salt or hydrate thereof.

5. A method according to any one of claims 1 to 4, wherein the transition metal species is:

- (a) a copper salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (b) a zinc salt or hydrate thereof and a manganese salt or hydrate thereof; or
- (c) a copper salt or hydrate thereof and a zirconium salt or hydrate thereof; or
- (d) a zinc salt or hydrate thereof and a zirconium salt or hydrate thereof.

6. A method according to any one of the preceding claims, wherein step (i) further comprises combining one or more of an alkali metal species, an alkaline earth metal species and a rare earth metal species.

7. A method according to any one of the preceding claims, wherein step (i) further comprises combining one or more of an alkali metal species selected from an alkali metal salt or hydrate thereof.

8. A method according to claim 7, wherein the alkali metal salt or hydrate thereof is selected from potassium nitrate, potassium carbonate, sodium nitrate, sodium carbonate, lithium carbonate and cesium carbonate, or a hydrate thereof.

9. A method according to any one of the preceding claims, wherein the iron species is an iron salt or hydrate thereof.
10. A method according to any one of the preceding claims, wherein the iron salt or hydrate of step (i) is one or more of $\text{Fe}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ or a hydrate thereof.
11. A method according to any one of the preceding claims, wherein the chromium salt or hydrate thereof is selected from one or more of the group consisting of $\text{Cr}(\text{NO}_3)_3$, CrCl_3 , $\text{Cr}(\text{Ac})_3$ and $\text{Cr}(\text{OH})_3$ or a hydrate thereof.
12. A method according to any one of the preceding claims, wherein the proportion of iron salt and chromium salt is such that the atomic ratio of iron to chromium is about 20:1 to about 5:4.
13. A method according to any one of the preceding claims, wherein the organic compound comprises two or more functional groups selected from a carboxyl, hydroxyl, amido and amino groups.
14. A method according to any one of the preceding claims, wherein the organic compound is a C_4 to C_{12} carboxylic acid or urea.
15. A method according to any one of the preceding claims, wherein the organic compound is citric acid.
16. A method according to any one of claims 1 to 3, wherein step (i) consists of combining an iron (II) or (III) salt or hydrate thereof, a chromium (III) salt or hydrate thereof, an organic compound selected from a C_4 to C_{12} carboxylic acid (suitably citric acid) or urea, a zinc (II) salt or a hydrate thereof; a zirconium (IV) salt or a hydrate thereof; a calcium salt or hydrate thereof or a potassium salt or hydrate thereof; and optionally water.
17. A method according to any one of the preceding claims, wherein the calcination step is performed at a temperature of between about 400°C to about 1000°C.
18. A method according to claim 1, wherein said method comprises:
 - (i) combining an iron salt or hydrate thereof, a chromium salt or hydrate thereof, an organic compound selected from citric acid or urea, a manganese salt or a hydrate thereof and a copper salt or a hydrate thereof;

(ii) combining a solution of an iron salt or a hydrate thereof and an aqueous basic solution;

(iii) subjecting the combined products of (i) and (ii) to calcination to provide a pre-catalyst composition.

19. A method according to any one of claims 1 and 4 to 18, wherein the method further comprises:

(iv) treating the pre-catalyst composition of step (iii) with a transition metal solution comprising one or more transition metal salts or a hydrate thereof selected from a Pd, Co, Ni, Pt, Ru, Rh, Au and Cu salt or hydrate thereof, and optionally subjecting the treated pre-catalyst composition to calcination.

20. A method according to claim 19, wherein the transition metal solution comprises a palladium salt or hydrate thereof.

21. A pre-catalyst composition obtained or obtainable according to the method of any one of claims 1 to 20.

22. A method for preparing a catalyst composition comprising:

- (a) providing a pre-catalyst composition according to claim 21;
- (b) optionally subjecting said pre-catalyst composition to calcination; and
- (c) activating said pre-catalyst composition to obtain a catalyst composition.

23. A catalyst composition obtained or obtainable according to the method of claim 22.

24. A method for producing a composition comprising carbon monoxide, wherein said method comprises contacting a feed gas composition comprising carbon dioxide and hydrogen with a pre-catalyst composition according to claim 21, or a catalyst composition according to claim 23, at a temperature of at least 400°C.

25. A method according to claim 24, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a temperature of about 450°C to about 650°C.

26. A method according to claim 24 or 25, wherein the feed gas composition is contacted with the pre-catalyst composition or catalyst composition at a pressure of about 100 KPa to about 150 KPa.

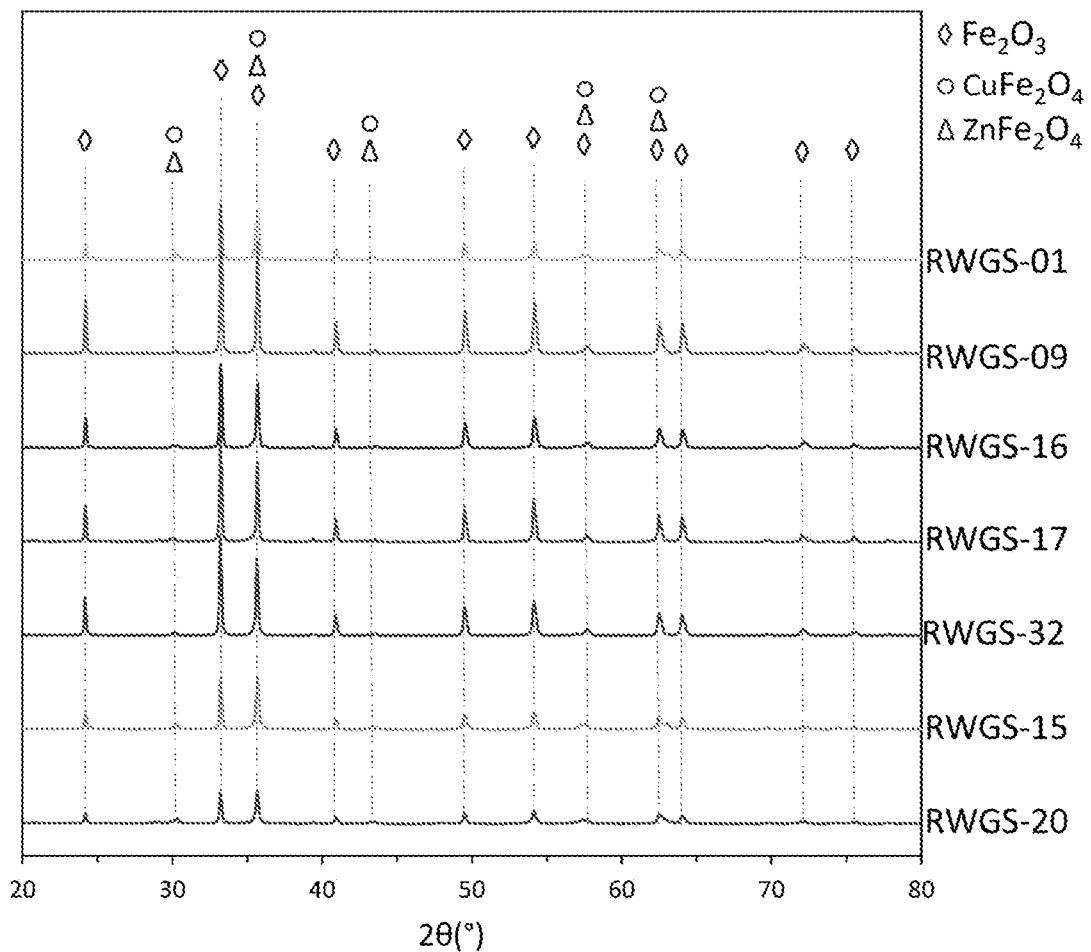
Fig. 1

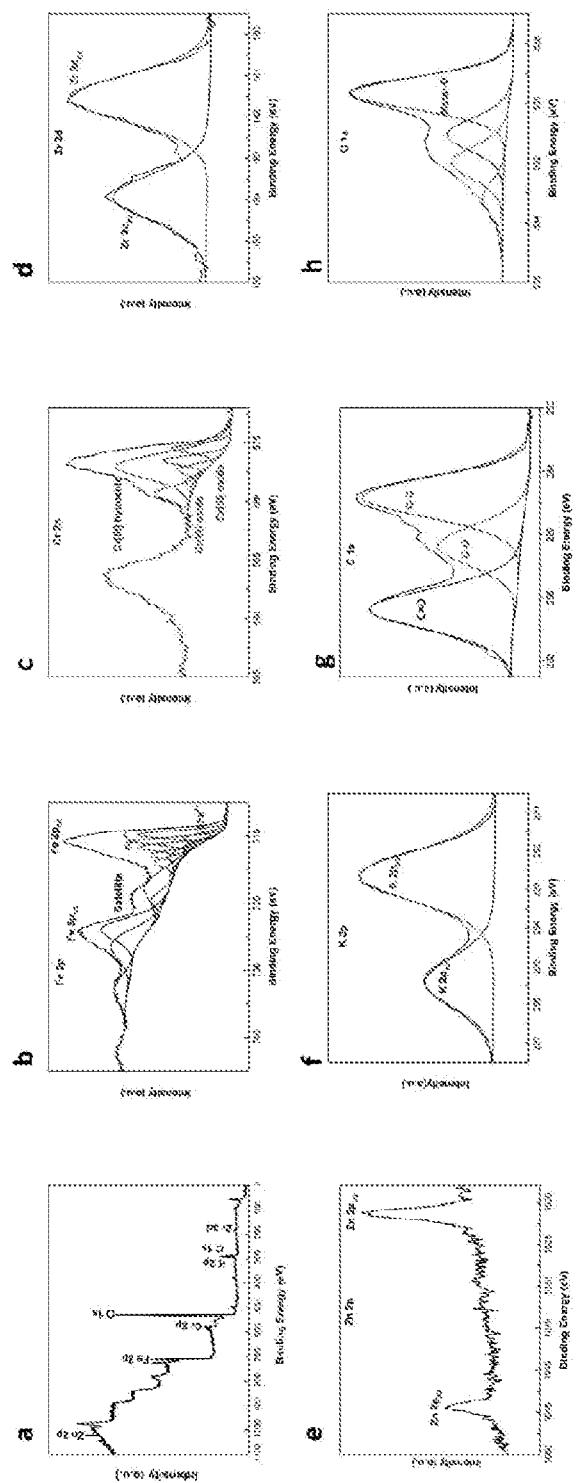
Fig. 2

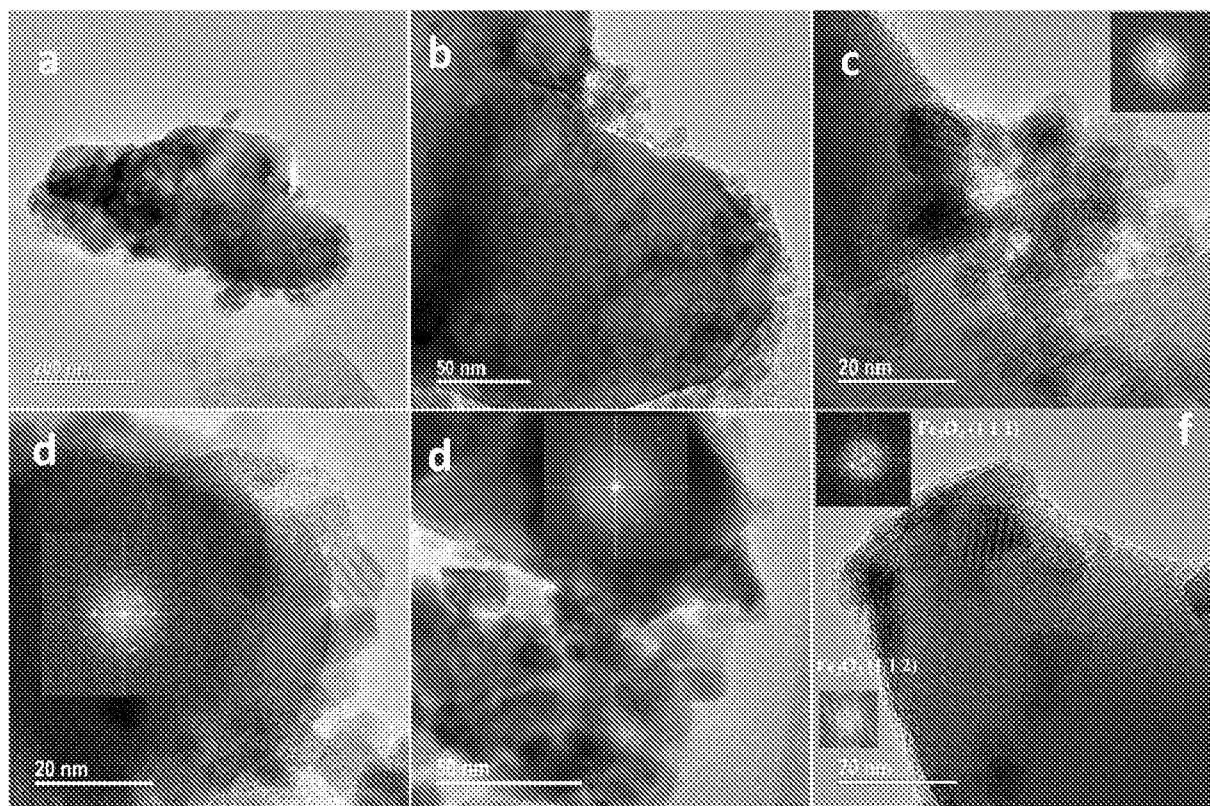
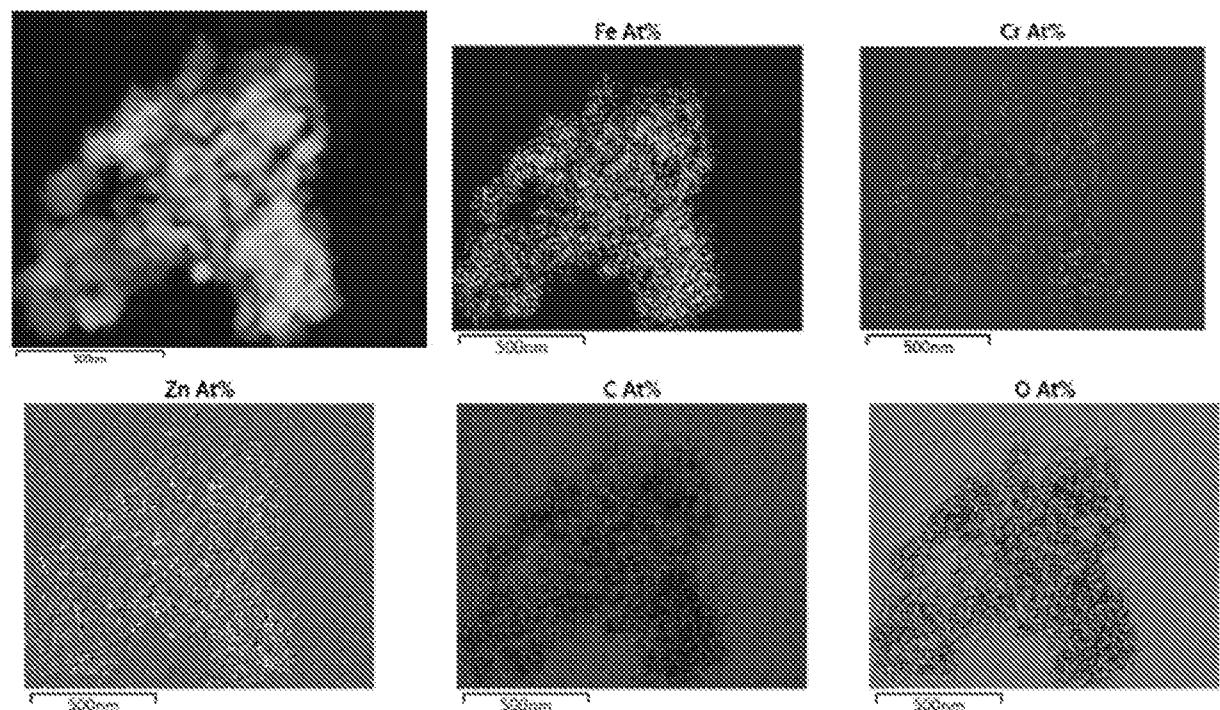
Fig. 3

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2023/051503

A. CLASSIFICATION OF SUBJECT MATTER

INV.	C07C29/151	B01J23/745	B01J23/26	B01J23/72	B01J21/06
	B01J23/34	B01J23/75	B01J23/755	B01J23/04	B01J23/02
	B01J23/10	B01J37/04	B01J37/08	B01J37/18	B01J37/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C B01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104 148 087 B (ZIBO ZAMR NEW MATERIAL RESOURCE CO LTD) 22 June 2016 (2016-06-22) example 2	1-6, 17, 21-23 7-16, 18-20
X	----- US 2018/327259 A1 (ALEXANDER ANNE-MARIE CHRISTINA [GB] ET AL) 15 November 2018 (2018-11-15)	21-23
Y	paragraphs [0071] - [0074]; example 1	7-16, 18-20, 24-26
A	----- US 8 431 511 B2 (MIRONOV OLEG [US]; KUPERMAN ALEXANDER E [US] ET AL.) 30 April 2013 (2013-04-30) claims 24-27	13-15
	----- -/-	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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22 August 2023

29/08/2023

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer
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Campbell, Paul

INTERNATIONAL SEARCH REPORTInternational application No
PCT/GB2023/051503**C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 101 644 975 B1 (KOREA ENERGY RESEARCH INST [KR]) 4 August 2016 (2016-08-04) claims 21-22 -----	24-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2023/051503

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
CN 104148087	B	22-06-2016	NONE	
US 2018327259	A1	15-11-2018	AU 2016344491 A1 BR 112018008318 A2 CA 3001506 A1 CN 108349731 A DK 3368472 T3 EA 201891053 A1 EP 3368472 A1 GB 2546131 A PL 3368472 T3 US 2018327259 A1 US 2020354215 A1 WO 2017072481 A1	26-04-2018 30-10-2018 04-05-2017 31-07-2018 15-06-2020 31-10-2018 05-09-2018 12-07-2017 07-09-2020 15-11-2018 12-11-2020 04-05-2017
US 8431511	B2	30-04-2013	NONE	
KR 101644975	B1	04-08-2016	KR 101644975 B1 US 2017113207 A1 WO 2017069340 A1	04-08-2016 27-04-2017 27-04-2017