

ENCAPSULATED NANOPARTICLES

Field

[0001] The invention relates to encapsulated nanoparticles and to processes for making them.

Priority

[0002] The present application claims priority from Singapore Patent Application No. 201208096-6, the entire contents of which are incorporated herein by cross-reference.

Background

[0003] Design and synthesis of highly dispersed metal oxides nanoparticles on supports with excellent thermal stability are of great importance for heterogeneous catalysis and other applications such as chemical looping combustion.

[0004] Nano-sized metals/metal oxides, e.g. transition metals/metal oxides, with high reactivity and selectivity are of great importance as catalyst for industrial heterogeneous catalytic process due to their smaller particle size and high surface area. However, agglomeration and coalescence of nanoparticles (i.e. sintering) results in a loss of active surface area of the nanoparticles, causing undesired catalyst deactivation. Catalyst deactivation via sintering occurs at high temperatures and creates large financial and environmental costs associated with catalyst regeneration and renewal. The sintering of supported nanoparticles is typically attributed to mass-transport mechanisms involving crystallite or atomic migration. The high temperature and reactive gas conditions encountered during catalysis often accelerate the sintering rate. For example, sintering of catalysts is commonly observed in reactions such as methanol synthesis and reforming over Cu based catalysts, steam and CO₂ reforming of methane over Ni based-catalyst and Fischer–Tropsch reaction over Fe-based and Co-based catalysts, CO oxidation over Pt-based catalysts, catalytic biomass tar decomposition over iron oxide catalysts, SO₂ oxidation over transition metal oxides (V₂O₅- or iron oxide-based) catalysts, NO reduction over CuO-based catalysts and methane oxidation over CoO_x catalysts etc. One common approach to address this issue is to use inert support to disperse the nanoparticles. Even so, sintering of the nanoparticles is still unavoidable, especially at high metal loadings.

[0005] On the other hand, metal oxides as oxygen carriers have been extensively investigated for chemical looping combustion (CLC) with inherent CO₂ separation, which is an alternative combustion technology for fossil fuel utilization. In the CLC system, fuel reacts with an oxygen carrier in a fuel reactor, producing CO₂ and H₂O and the oxygen carrier is reduced to a metal or metal oxide with lower valence. Then the reduced oxygen carrier is circulated into an air reactor, where it is reoxidized. The CLC system can provide high concentration of CO₂ after a simple water condensation for CO₂ capture. It not only avoids the complex and energy intensive separation of diluted CO₂ produced from the conventional combustion but also avoids NO_x production due to relatively low reaction temperature. Therefore CLC has the potential to replace conventional combustion. In the CLC system, four promising oxygen carriers, NiO, Fe₂O₃, CuO and Mn₃O₄, have been widely applied in the demonstration CLC devices because of their high reversible oxygen release capacity. However, a major problem is the loss of oxygen release capacity of oxygen carriers due to serious sintering.

[0006] Recently, a novel core-shell structured nanocomposite has been developed by Schüth for catalytic application. His study showed that Au cores in spherical ZrO₂ shells (Au@ZrO₂) have high activity for CO oxidation at about 240 °C without sintering (Arnal, P.M., Comotti, M. and Schüth, F. *Angew. Chem. Int. Ed.*, 2006, 45, 8224). In this work, metals or metal oxides served as core materials and porous inert oxides such as SiO₂ and ZrO₂ served as shell materials to prevent the sintering of core. In addition, the porous inert shell was able to provide effective mass transportation channels for the reactants and products to and from the reaction sites in the core.

[0007] To date, core-shell structured nanocomposites with metals or metal oxides core and porous silica shell have been prepared using a similar synthetic strategy, in which metal or metal oxide nanoparticles were first synthesized either by direct reduction of noble metal salts using reducing agents such alcohol, NaHB₄ and hydrazine in the presence of surfactant or hydrothermal method or microemulsion for base metal oxides. The formation of metal or metal oxide core was then followed by deposition of silica shell and final removal of structure-directing polymer templates. However, these complex synthesis procedures and low productivity limit large scale application of the novel core-shell structured metals or metal oxides catalysts, since the preparation cost is a crucial factor for the successful application of a new structured material. For example, particles size and distribution in the preparation need to be carefully controlled by, for example, controlling metal salt concentration, the ratio of metal

salt to surfactants, pH, etc. Also, high temperature and high pressure conditions are commonly necessary. Additionally, the difficult separation of nanoparticles from solution can be only performed by high speed centrifuge, and hence use of a reaction volume-limited autoclave is required. Therefore, a process for high quality and scalable synthesis of core/shell composites are still a big challenge.

[0008] There is therefore a need for an improved process for manufacturing composites comprising metal or metal oxide particles embedded in porous ceramic materials. Such a process would preferably be inexpensive, readily scalable and use moderate temperatures and pressures.

Summary of Invention

[0009] According to a first aspect of the present invention, there is provided a process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, said process comprising:

- a) Preparing a solution comprising a soluble salt of the metal, and a surfactant;
- b) Adjusting the solution to a basic pH at which a hydroxide of the metal precipitates from the solution;
- c) Preparing an aqueous suspension of the hydroxide of the metal, said suspension being at pH greater than 7, optionally greater than 10;
- d) Adding to the suspension, with agitation (such as stirring), an alkoxysilane, so as to form composites comprising the hydroxide of the metal at least partially, optionally completely, coated with silica; and
- e) Calcining the composites obtained in step d) so as to produce the composite substance.

[00010] The following options may be used in conjunction with the first aspect either individually or in any suitable combination.

[00011] The metal may be a transition metal. It may be a precious metal. It may be a rare earth metal. It may be selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Sn, Pb, Sb, Bi, La, Ce and Gd. Mixtures of any two or more of these may also be used. In some

embodiments the metal is selected from the group consisting of Cu, Ni, Cr, V, Co, Mn, Zn and Fe.

[00012] The surfactant may be a soluble polymer surfactant. It may be a polyelectrolyte. It may be an alkylammonium salt. It may be cationic or it may be anionic or it may be non-ionic or it may be zwitterionic. Suitable mixtures of surfactants may also be used. In certain instances, cosurfactants may also be used. The soluble polymer surfactant may be for example a carbohydrate polymer, a polyaniline, a polyimide, a polyvinylpyrrolidone, a polyvinyl alcohol, etc. The polyelectrolyte may be for example a polypeptide, a glycosaminoglycan, a DNA or polydiallyldimethylammonium chloride (PDPA).

[00013] The alkylammonium salt may comprise a C₈-C₁₈ alkyl group attached directly to a quaternary nitrogen atom. It may be a tetraalkylammonium salt. It may be a C₈-C₁₈ alkyltri(C₁-C₄ alkyl)ammonium salt. The alkylammonium salt may be for example a cetyltrimethylammonium salt.

[00014] The solution of step a) may be an aqueous solution. It may have a ratio of the soluble salt of the metal to the surfactant (e.g. alkylammonium salt) of between about 1:10 and about 10:1 on a molar basis. It may have a ratio of the soluble salt of the metal to the surfactant (e.g. alkylammonium salt) of between about 1:2 and about 2:1 on a molar basis.

[00015] Step b) may comprise adding to the solution of step a) a water soluble hydroxide salt. The water soluble hydroxide salt may be sodium hydroxide or may be potassium hydroxide or may be ammonium hydroxide or may be a mixture of any two or all of these.

[00016] The process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix may comprise step b') separating the precipitated hydroxide of the metal from the solution. Step c) may include the step of resuspending the hydroxide of the metal in an aqueous liquid, e.g. in water. Step c) may also include adjusting the suspension of the resuspended hydroxide of the metal to a pH greater than 7, or greater than 10.

[00017] The alkoxysilane may be a trialkoxysilane or a tetraalkoxysilane. It may be tetraethoxysilane or tetramethoxysilane. The alkoxysilane may be added at a molar ratio to the metal hydroxide of between about 1:8 and about 8:1. It may be added at a molar ratio to the

metal hydroxide of between about 1:2 and about 2:1. The alkoxysilane may be added in alcoholic solution. It may be added at a rate of about 1 to about 100 micromol/second.

[00018] Step d) may additionally comprise stirring the suspension following addition of the alkoxysilane, said stirring being continued for at least about 10 hours, or at least about 24, 36 or 48 hours, or for about 10 to about 60 hours, or from about 24 to 60, 36 to 48, 48 to 60 or 30 to 40 hours, e.g. for about 12, 18, 24, 30, 36, 42, 48, 54 or 60 hours. The process may comprise step d'), conducted between steps d) and e), of separating the particles formed in step d) from the suspension and washing said particles with an aqueous liquid. The aqueous liquid may be deionised water.

[00019] Step e) may comprise heating the particles for at least about 1 hour. It may comprise heating the particles for about 1 to about 5 hours. It may comprise heating the particles for about 2 hours. The heating may be to a temperature of about 400 to about 700 °C, e.g. to about 500 °C.

[00020] The process may additionally comprising step f) reducing the oxide of the metal within the porous silica matrix so as to form particles of the metal within the porous silica matrix. Step f) may comprise exposing the oxide of the metal to hydrogen or to one or more other reducing agents. Thus when step f) is included in the process, the process is one for preparing a composite substance comprising particles of a metal dispersed in a porous silica matrix.

[00021] The oxide of the metal, or, in the event that step f) is conducted, the metal, may be catalytically active. The oxide of the metal, or, in the event that step f) is conducted, the metal, may be catalytically active for a reaction selected from the group consisting of methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer–Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction and methane oxidation. The oxide of the metal may be usable as an oxidant in chemical looping combustion.

[00022] In a specific example of the first aspect the process comprises:

- a) Preparing an aqueous solution comprising a soluble salt of the metal and a cetyltrimethylammonium salt;
- b) Adding to the solution from step a) a sodium hydroxide solution so as to precipitate a hydroxide of the metal from the solution;
- b') Separating the precipitated hydroxide of the metal from the solution;

- c) Resuspending the hydroxide of the metal in an aqueous liquid and adjusting the resulting suspension to a pH greater than 7, optionally greater than 10;
- d) Adding to the suspension, with stirring, an alcoholic solution of tetraalkoxysilane, so as to form particles comprising the hydroxide of the metal at least partially coated with silica;
- d') Separating the particles formed in step d) from the suspension and washing said particles with water; and
- e) Calcining the particles obtained in step d) at about 500°C for about 1 to about 5 hours so as to produce the composite substance.

[00023] In one embodiment, there is provided a process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, said metal being selected from the group consisting of Cu, Ni, Cr, V, Co, Mn, Zn and Fe, said process comprising:

- a) Preparing a solution comprising a soluble salt of the metal, and a C₈-C₁₈ alkyltri(C₁-C₄ alkyl)ammonium salt in a ratio of the soluble salt of the metal to the C₈-C₁₈ alkyltri(C₁-C₄ alkyl)ammonium salt of between about 1:2 and about 2:1 on a molar basis;
- b) Adjusting the solution to a basic pH at which a hydroxide of the metal precipitates from the solution, said adjusting comprising adding sodium hydroxide or potassium hydroxide or ammonium hydroxide;
- c) Preparing an aqueous suspension of the hydroxide of the metal, said suspension being at pH greater than 7, optionally greater than about 10;
- d) Adding to the suspension, with agitation such as stirring, an alkoxysilane such as tetraethoxysilane or tetramethoxysilane, wherein the molar ratio of the alkoxysilane to the metal hydroxide is between about 1:2 and about 2:1, so as to form composites comprising the hydroxide of the metal at least partially, optionally completely, coated with silica, and stirring the suspension following addition of the alkoxysilane for at least about 10 hours; and
- e) Calcining the composites obtained in step d) for about 1 to about 5 hours at a temperature of about 400 to about 700°C so as to produce the composite substance.

[00024] In another embodiment, there is provided a process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, wherein the metal is Cu, Ni, Co, Mn, or Fe and wherein said process comprising:

- a) Preparing a solution comprising a soluble salt of the metal and a C₈-C₁₈ alkyltri(C₁-C₄ alkyl)ammonium salt in a ratio of the soluble salt of the metal to the C₈-C₁₈ alkyltri(C₁-C₄ alkyl)ammonium salt of between about 1:2 and about 2:1 on a molar basis;
- b) Adjusting the solution to a basic pH at which a hydroxide of the metal precipitates from the solution, said adjusting comprising adding sodium hydroxide or potassium hydroxide;
- c) Preparing an aqueous suspension of the hydroxide of the metal, said suspension being at pH greater than 7, optionally greater than about 10;
- d) Adding to the suspension, with agitation such as stirring, an alkoxysilane, e.g. tetraethoxysilane or tetramethoxysilane, wherein the molar ratio of the alkoxysilane to the metal hydroxide is between about 1:2 and about 2:1, so as to form composites comprising the hydroxide of the metal at least partially, optionally completely, coated with silica, and stirring the suspension following addition of the alkoxysilane for at least about 10 hours;
- e) Calcining the composites obtained in step d) for about 1 to about 5 hours at a temperature of about 400 to about 700°C so as to produce the composite substance; and
- f) exposing the oxide of the metal to hydrogen or to one or more other reducing agents so as to reduce the oxide of the metal within the porous silica matrix so as to form particles of the metal within the porous silica matrix.

[00025] In yet another embodiment, there is provided a process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, wherein the metal is Cu, Ni, or Fe, said process comprising:

- a) Preparing a solution comprising a soluble salt of the metal and a cetyltrimethylammonium salt in a ratio of the soluble salt of the metal to the cetyltrimethylammonium salt of between about 1:10 and about 10:1 on a molar basis;
- b) Adjusting the solution to a basic pH at which a hydroxide of the metal precipitates from the solution, said adjusting comprising adding sodium hydroxide or potassium hydroxide;
- c) Preparing an aqueous suspension of the hydroxide of the metal, said suspension being at pH greater than 7, optionally greater than about 10;
- d) Adding to the suspension, with agitation such as stirring, an alkoxysilane, e.g. tetraethoxysilane or tetramethoxysilane, wherein the molar ratio of the alkoxysilane to the metal hydroxide is between about 1:8 and about 8:1 and the alkoxysilane is added in

alcoholic solution at a rate of about 1 to about 100 micromol/second, so as to form composites comprising the hydroxide of the metal at least partially, optionally completely, coated with silica, and stirring the suspension following addition of the alkoxysilane for at least about 10 hours;

- e) Calcining the composites obtained in step d) for about 1 to about 5 hours at a temperature of about 400 to about 700°C so as to produce the composite substance; and
- f) exposing the oxide of the metal to hydrogen or to one or more other reducing agents so as to reduce the oxide of the metal within the porous silica matrix so as to form particles of the metal within the porous silica matrix.

[00026] In a further embodiment, there is provided a process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, wherein the metal is Cu, Ni, Cr, V, Co, Mn, Zn or Fe, said process comprising:

- a) Preparing an aqueous solution comprising a soluble salt of the metal and a cetyltrimethylammonium salt;
- b) Adding to the solution from step a) a sodium hydroxide solution so as to precipitate a hydroxide of the metal from the solution;
- b') Separating the precipitated hydroxide of the metal from the solution;
- c) Resuspending the hydroxide of the metal in an aqueous liquid and adjusting the resulting suspension to a pH greater than 7, optionally greater than about 10;
- d) Adding to the suspension, with stirring, an alcoholic solution of tetraalkoxysilane, wherein the molar ratio of the tetraalkoxysilane to the metal hydroxide is between about 1:8 and about 8:1 and the alcoholic solution is added at a rate of about 1 to about 100 micromol/second, so as to form particles comprising the hydroxide of the metal at least partially coated with silica;
- d') Separating the particles formed in step d) from the suspension and washing said particles with water; and
- e) Calcining the particles obtained in step d) at about 500°C for about 1 to about 5 hours so as to produce the composite substance.

[00027] According to a second aspect of the present invention, there is provided a composite substance prepared by the process according to the first aspect above.

[00028] According to a third aspect of the present invention, there is provided a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix. There

is also provided a composite substance comprising particles of a metal dispersed in a porous silica matrix. The composite substance of the third aspect may be made, or makable, by the process of the first aspect.

[00029] The following options may be used in conjunction with the second or third aspects either individually or in any suitable combination.

[00030] The metal may be a transition metal. It may be a precious metal. It may be a rare earth metal. The metal may be selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Sn, Pb, Sb, Bi, La, Ce and Gd. It may be selected from the group consisting of Cu, Ni, Cr, V, Co, Mn, Zn and Fe. The porous silica matrix may be mesoporous. It may have pores of about 1 to about 5 nm diameter. The porous silica matrix may have pores of about 2 to about 3 nm diameter. The porous silica matrix may additionally have pores of about 10 to about 100 nm diameter. It may additionally have pores of about 10 to about 50 nm diameter. The particles of the oxide of the metal may have a mean particle diameter of about 2 to about 10 nm. They may have a mean particle diameter of about 5 nm. They may be substantially monodispersed in particle size. They may be nanoparticles.

[00031] The composite substance may be in particulate form. The particles of said substance may have an aspect ratio (i.e. length to diameter ratio) of at least about 10. The oxide of the metal may be a copper oxide and the composite substance may be in rod-like structures. The rod-like structures may have a diameter of about 10 to about 100nm, or may have a diameter of about 20 to about 50nm. The oxide of the metal may be nickel oxide or may be iron oxide and the substance may have a sheet like structure, whereby, if particles of the substance have an aspect ratio of at least about 10, the aspect ratio refers to a ratio of length to thickness of sheets of the sheet like structure. Each particle of said composite substance may comprise a plurality of particles of the oxide of the metal dispersed therein. Each particle of said composite substance may comprise, on average, at least about 100 particles of the oxide of the metal dispersed therein.

[00032] The composite substance may have a BET surface area of at least about 200 m²/g, or may have a BET surface area of at least about 500 m²/g. The composite substance may have a BET surface area of from about 200 to about 1000 m²/g or from about 400 to about 700 m²/g or

from about 500 to about 700 m²/g. The composite substance may have pores extending continuously from an outside surface of the silica matrix to an outside surface of the oxide of the metal so as to allow a reactant to penetrate to the surface of the oxide of the metal.

[00033] In one embodiment, there is provided a composite substance comprising particles of a metal, or of an oxide of the metal, dispersed in a porous silica matrix, wherein the metal is selected from the group consisting of Cu, Ni, Cr, V, Co, Mn, Zn and Fe, wherein the porous silica matrix has pores of about 2 to about 3 nm diameter and additionally has pores of about 10 to about 50 nm diameter, and wherein the composite substance is in particulate form.

[00034] In another embodiment, there is provided a composite substance comprising particles of a metal, or an oxide of the metal, dispersed in a porous silica matrix, wherein the metal is selected from the group consisting of Cu, Ni, Co, Mn, and Fe, wherein the porous silica matrix has pores of about 2 to about 3 nm diameter and additionally has pores of about 10 to about 50 nm diameter, wherein the particles of the oxide of the metal have a mean particle diameter of about 5nm, and wherein the composite substance is in particulate form and the particles of said substance have an aspect ratio (i.e. length to diameter ratio) of at least about 10.

[00035] In further embodiment, there is provided a composite substance comprising particles of copper oxide, wherein the composite substance is in rod-like structures having a diameter of about 20 to about 50nm, wherein the composite substance is in particulate form and has a BET surface area of from about 200 to about 1000 m²/g, and wherein the porous silica matrix comprises pores that extend continuously from an outside surface of the silica matrix to an outside surface of the oxide of the metal so as to allow a reactant to penetrate to the surface of the oxide of the metal.

[00036] In yet a further embodiment, there is provided a composite substance comprising particles of nickel oxide or iron oxide, wherein the composite substance is in sheet like structures have an aspect ratio of at least about 10, wherein the aspect ratio refers to a ratio of length to thickness of sheets of the sheet like structure, wherein the composite substance is in particulate form and has a BET surface area of from about 200 to about 1000 m²/g, and wherein the porous silica matrix comprises pores that extend continuously from an outside surface of the silica matrix to an outside surface of the oxide of the metal so as to allow a reactant to penetrate to the surface of the oxide of the metal.

[00037] According to a fourth aspect of the present invention, there is provided use of the composite substance according to the second or third aspects above in an application selected from the group consisting of methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer–Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction, methane oxidation and chemical looping combustion.

[00038] According to a fifth aspect of the present invention, there is provided a process for oxidising a fuel comprising exposing said fuel to a composite substance according to the second or third aspects above at sufficient temperature for combustion of the fuel. In this aspect, the composite substance comprises particles of an oxide of the metal dispersed in a porous silica matrix.

[00039] The following options may be used in conjunction with the fifth aspect either individually or in any suitable combination.

[00040] The temperature may be at least about 500 °C, or may be between about 500 and 1000 °C, or may be about 850 °C. The metal may be copper. The process may be chemical looping combustion.

[00041] In one embodiment, there is provided a process for oxidising a fuel comprising exposing said fuel to a composite substance according to the second or third aspects above, said the composite substance comprising particles of copper oxide dispersed in a porous silica matrix, at a temperature of at least about 500 °C, for combustion of the fuel.

[00042] In another embodiment, there is provided a chemical looping combustion process for oxidising a fuel comprising exposing said fuel to a composite substance according to the second or third aspects above, the composite substance comprising particles of an oxide of the metal dispersed in a porous silica matrix, at a temperature between about 500 and 1000 °C, for combustion of the fuel.

Brief Description of Drawings

[00043] Figure 1 is a scheme of the synthesis of highly dispersed CuO nanoparticles encapsulated in porous SiO₂ matrix;

[00044] Figure 2 shows TEM images of $\text{Cu}(\text{OH})_2$ capped by CTAB (a,b), $\text{Cu}(\text{OH})_2$ encapsulated in SiO_2 matrix (c,d) and CuO encapsulated in porous SiO_2 matrix;

[00045] Figure 3 shows *in situ* XRD patterns of Cu phase in SiO_2 matrix (a) and average particles size of Cu phase (b) as function of temperature;

[00046] Figure 4 shows N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of 50wt% CuO encapsulated in SiO_2 matrix calcinated at 500 °C;

[00047] Figure 5 shows a H_2 TPR (Temperature-Programmed Reduction) curve of 50wt% CuO encapsulated in SiO_2 matrix calcinated at 500 °C. The reduction peak is located between 150 and 250 °C, indicating that the CuO core is accessible by H_2 gas and CuO can be reduced readily;

[00048] Figure 6 shows TEM images of 50wt% CuO encapsulated in SiO_2 matrix calcinated at 500 °C after TPR analysis: the core-shell structure remains stable after the $\text{CuO}@\text{SiO}_2$ was reduced to $\text{Cu}@\text{SiO}_2$ by H_2 at 150-300 °C and heated up to 850 °C;

[00049] Figure 7 shows a performance comparison of 50wt% CuO encapsulated in SiO_2 matrix calcinated at 500 °C (a) and commercial CuO nanopowder in CLC application (b) at 850 °C;

[00050] Figure 8 shows TEM images of $\text{Ni}(\text{OH})_2$ capped by CTAB (a) and 50 wt% NiO encapsulated in SiO_2 matrix (b,c) calcinated at 500 °C and N_2 adsorption-desorption isotherms(d) and pore size distribution (e) of 50 wt% NiO encapsulated in SiO_2 matrix calcinated at 500 °C; and

[00051] Figure 9 shows TEM images (a, b), N_2 adsorption-desorption isotherms (c) and pore size distribution (d) of 50wt% Fe_2O_3 encapsulated in SiO_2 matrix calcined at 500 °C.

Description of the Invention

[00052] In the present specification, the terminology A@B refers to A encapsulated within B. Therefore, for example, $\text{MeOx}@\text{SiO}_2$ refers to a metal oxide encapsulated within silica.

[00053] The present invention relates in a particular embodiment to a simple and efficient method of synthesizing highly dispersed metal oxides nanoparticles encapsulated in a SiO_2 matrix ($\text{MeO}_x@ \text{SiO}_2$). The silica may be porous, and in particular it may be mesoporous, microporous or a combination of microporous and mesoporous. Microporous materials are considered to be those that have pores of less than about 2nm in mean diameter, and mesoporous materials are considered to be those having pores of about 2 to about 50nm in mean diameter. The formation of this nanocomposite can be performed at room temperature and atmospheric pressure with almost 100% recovery yield of metal and SiO_2 . Most previously existing synthetic techniques for making related materials require hydrothermal or microemulsion methods for the formation of core nanoparticles, which impose complexity, low yield and high cost of the synthesis. By contrast, the simplicity and high yield of the present method make the present invention commercially viable. It is usable for large-scale production of various types of heterogeneous catalysts, including noble metal, transition metal and transition metal oxide catalysts, which possess high thermal stability, high surface area and therefore high catalytic performance. These catalysts may be utilized in a wide range of important heterogeneous catalysis processes such as methanol synthesis and reforming over Cu based catalysts, steam and CO_2 reforming of methane over Ni based-catalysts, Fischer-Tropsch synthesis over Fe-based and Co-based catalysts, CO oxidation over Pt-based catalysts, catalytic biomass tar decomposition over iron oxide catalysts, SO_2 oxidation over transition metal oxides (V_2O_5 - or iron oxide-based) catalysts, NO reduction over CuO-based catalysts and methane oxidation over CoO_x catalysts etc. The present invention can also be used in preparing nano-sized oxygen carriers such as NiO, Fe_2O_3 , CuO and Mn_3O_4 for advanced chemical looping combustion.

[00054] A novel aspect of the present invention is the preparation of a metal hydroxide precipitate ($\text{Me}(\text{OH})_x$) as the first step in place of the complex synthesis of metal or metal oxides commonly used in conventional methods. The inventors have surprisingly found that simply by controlling the feeding rate of the precursor metal salt (and thus the precipitation rate of the resulting metal hydroxide) and by using a cationic surfactant such as cetyltrimethylammonium bromide (CTAB), the metal hydroxide may be produced as very fine nanoparticles with a specific shape. It is thought that this is a product of self assembly. Thus it is hypothesised that hydrogen bonding between OH groups in $\text{Me}(\text{OH})_x$ and a cationic N^+ in the cationic surfactant have an effect in controlling the crystal growth direction while the hydrophobic tail of the surfactant keeps the particle sizes in the nanoscale. In some forms the invention uses surfactants other than cationic ammonium based surfactants. In this case, it is

hypothesised that related associations may direct a similar self-assembly process so as to achieve the desired structure. A further novel aspect of the invention is the coating of a porous SiO_2 shell on $\text{Me}(\text{OH})_x$ core by *in situ* polymerization of a silane such as tetraethoxysilane (TEOS), forming a porous, optionally mesoporous, high surface area shell. Silanes such as TEOS can function as cross-linking agents and as precursors of solid-state SiO_2 . Hydrolysis of these compounds can result in sol-gel SiO_2 via the formation of Si-O-Si linkages. By controlling the pH, substantially mono-dispersed porous SiO_2 may be formed on the nano-sized $\text{Me}(\text{OH})_x$ cores. Conversion of as-formed core-shell structured $\text{Me}(\text{OH})_x@ \text{SiO}_2$ into $\text{MeO}_x@ \text{SiO}_2$ and removal of structure-directing agent can be easily achieved by calcination.

[00055] Metal oxide catalysts encapsulated in SiO_2 ($\text{MeO}_x@ \text{SiO}_2$), transition metal and noble metal catalysts in SiO_2 ($\text{Me}@ \text{SiO}_2$) prepared by this method are usable as high performance catalysts in several important industrial processes. NiO , Fe_2O_3 , CuO and Mn_3O_4 encapsulated in SiO_2 can be used in chemical looping combustion application. In each of these cases, the silica may be porous, optionally mesoporous. The technology can also find application in biosensor and drug delivery applications.

[00056] Thus in an embodiment, the invention relates to synthesis of highly dispersed metal or metal oxide nanoparticles encapsulated in mesoporous SiO_2 matrix and their application in heterogeneous catalysis and chemical looping combustion.

[00057] Disclosed herein is a simple, efficient and environmentally benign method of synthesizing highly dispersed metal oxides nanoparticles encapsulated in a SiO_2 matrix ($\text{MeO}_x@ \text{SiO}_2$). The method comprises three key steps: (1) preparation of metal hydroxide precipitates ($\text{Me}(\text{OH})_x$), commonly at room temperature and atmospheric pressure; (2) *in situ* coating of SiO_2 on $\text{Me}(\text{OH})_x$ core using structure-directing agent; (3) conversion of as-formed core-shell structured $\text{Me}(\text{OH})_x@ \text{SiO}_2$ into $\text{MeO}_x@ \text{SiO}_2$ and removal of structure-directing agent by calcination. The MeO_x encapsulated in SiO_2 nanocomposites prepared by this method not only possess high dispersion of MeO_x , commonly with narrow particle size distribution (average particles size of around 5 nm), but also generally have high surface area (about 300 to 500 m^2/g) with richly accessible mesopores to metal oxides and excellent thermal stability at high temperatures. Furthermore, the loading of metal oxide in the composites can be increased up to 50% or even more while maintaining small particle sizes. The synthetic process is sufficiently simple that it is readily scalable to commercial production. These features provide

the composites with broad application prospects and commercial value as catalysts and oxygen carriers in heterogeneous catalysis and other applications.

[00058] By selecting suitable metal salts, transition metal oxides such as CuO, NiO, V₂O₅, Co₃O₄, MnO₂, ZnO and Fe₂O₃ etc. encased in a SiO₂ matrix can be prepared based on the above synthetic strategy. The inventors have also shown that by suitable reduction reactions, metal (e.g. transition metal) oxides encased in a SiO₂ shell may be reduced to the corresponding metals encased in SiO₂ without collapse of the core-shell structure. Therefore the inventors have found a simple, widely applicable method to prepare MeOx@SiO₂ and Me@SiO₂.

[00059] The present invention provides process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix. In one form of this process, a solution is prepared comprising a soluble salt of the metal and an alkylammonium salt. The solution is adjusted to a basic pH at which a hydroxide of the metal precipitates from the solution.

[00060] The precipitated hydroxide is then used to prepare a basic suspension, to which is added an alkoxysilane, thereby forming composites comprising the hydroxide of the metal at least partially, optionally completely, coated with silica. These composites are then calcined so as to produce the composite substance.

[00061] The metal is commonly a transition metal, although other metals may at times be used, for example precious metals and rare earth metals. Suitable metals include Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Sn, Pb, Sb, Bi, La, Ce and Gd. In some cases, mixtures of any two or more of these metals may be used.

[00062] Suitable surfactants for use in the present process include alkylammonium salts. The alkylammonium salt may comprise a C8-C18 alkyl group attached directly to a quaternary nitrogen atom. It may comprise 1, 2, 3 or 4 such groups directly attached to the quaternary nitrogen. Each alkyl group may be, independently, C8 to C18, or C8 to C12 or C12 to C18 or C10 to C14, e.g. C8, C9, C10, C11, C12, C13, C14, C15, C16, C17 or C18. In some cases one or more groups attached to the quaternary nitrogen are no C8 to C18 alkyl groups. In this case they may for example be aryl groups, arylalkyl groups, alkylaryl groups or some other groups. In other cases one or more of the groups may be short chain alkylgroups, e.g. C1 to C8, or C1 to

C4, or C4 to C8, e.g. C1, C2, C3, C4, C5, C6, C7 or C8. In some instances the alkylammonium salt is a C8-C18 alkyltri(C1-C4 alkyl)ammonium salt, e.g. a C8-C18 alkyltrimethylammonium salt such as a cetyltrimethylammonium salt. The counterion may be any suitable counterion, e.g. a halide (Cl, Br, I), and may be organic or inorganic. In some instances, other cationic surfactants may be used, or even other surfactants such as non-ionics, anionics or zwitterionics.

[00063] The solution of the metal salt may be an aqueous solution. Other than water, it may have no other solvents, or may have no organic solvents, or may have a cosolvent, e.g. a water miscible organic solvent (e.g. methanol, ethanol, acetone, THF etc.). If a cosolvent is present, it should be in sufficiently low concentration that it does not cause components of the solution to precipitate. It will be understood that in the present context, the term "soluble" in reference to solutes in the solution indicates that it is soluble in the solvent used. It may in particular be soluble in the desired concentration and at the desired temperature in said solvent.

[00064] The ratio of the metal salt to the alkylammonium salt in the solution is commonly between about 1:10 and about 10:1 on a molar basis or between about 1:5 and 5:1, 1:2 and 2:1, 2:3 and 3:2, 1:10 and 1:1, 1:5 and 1:1, 1:2 and 1:1, 2:3 and 1:1, 10:1 and 1:1, 5:1 and 1:1, 2:1 and 1:1, 3:2 and 1:1 or some other suitable range. It may be about 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9 or 1:10.

[00065] The step of adjusting the pH may comprise adding a hydroxide salt, for example sodium hydroxide or potassium hydroxide, to the solution. These may be added as a solution, e.g. an aqueous solution, or may be added as solids. Sufficient may be added to achieve the desired pH. In some instances the pH may be adjusted by addition of sufficient of a buffer having an appropriate buffering pH. Alternatively, the solution may be added to the hydroxide salt (optionally itself in solution). The addition in any event may be conducted with stirring or other suitable agitation. It may be conducted sufficiently rapidly to achieve a desired particle size of metal hydroxide (commonly less than about 10nm). It may be added rapidly. It may be added for example at a rate of about 5 L/min, or between about 10 L/min and about 1 L/min, e.g. between about 6 L/min and about 1 L/min, or between about 4 L/min and about 10 L/min, or between about 4 L/min and about 6 L/min, e.g. about 10 L/min, 9 L/min, 8 L/min, 7 L/min, 6 L/min, 5 L/min, 4 L/min, 3 L/min, 2 L/min or 1 L/min.

[00066] The pH adjustment causes the metal hydroxide to precipitate from the solution. This may then be separated by any suitable method (e.g. settling/decanting, centrifuging, filtration, etc.) and resuspended. It may be washed, e.g. with water, prior to being resuspended. In this case, the resuspended metal hydroxide should be at a pH of greater than about 7, or greater than about 8, 9, 10, 10.5, 11 or 11.5, e.g. at a pH of about 10, 10.5, 11, 11.5 or 12. This may be achieved by resuspending the metal hydroxide and then adjusting the pH of the resulting suspension to the desired pH (e.g. as described above) or may comprise suspending the separated metal hydroxide in a liquid of the appropriate pH.

[00067] The alkoxysilane which is added to the metal hydroxide suspension commonly comprises (optionally consists essentially of) a trialkoxysilane or a tetraalkoxysilane or a mixture of these. In some instances a relatively small proportion (e.g. less than about 10% by weight) of a dialkoxysilane or in cases a monoalkoxysilane may be used. The alkoxy group(s) on the silane may, independently, comprise C1 to C6 alkyl groups which may be straight chain or (if C3 or greater) branched. They may be C1, C2, C3, C4, C5 or C6. Common examples include tetraethoxysilane or tetramethoxysilane. If a trialkoxysilane is used, it will be understood that the resulting silica matrix will be an organosilica matrix. The trialkoxysilane may have an alkyl group on the central silicon atom, or an aryl group, each of which may be optionally substituted (e.g. with an amine group, a thiol group, a hydroxyl group or some other suitable group). The alkoxysilane may be added in an organic solution. The solvent may be a water miscible organic solvent, e.g. acetone, THF, THP, methanol, ethanol, isopropanol etc. The solvent may be an alcoholic solvent. The alcohol solvent may have the same alkyl group as the, or an, alkoxy group on the alkoxysilane (e.g. if the alkoxysilane is an ethoxysilane, the solvent may be ethanol).

[00068] The alkoxysilane may be added at a molar ratio to the metal hydroxide of between about 1:8 and about 8:1, or between about 1:5 and 5:1, 1:2 and 2:1, 2:3 and 3:2, 1:8 and 1:1 1:5 and 1:1, 1:2 and 1:1, 2:3 and 1:1, 8:1 and 1:1, 5:1 and 1:1, 2:1 and 1:1, 3:2 and 1:1 or some other suitable range. It may be added at a molar ratio of about 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 3:2, 1:1, 2:3, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9 or 1:10. It may be added at a rate of about 1 to about 100 micromol/second, or of about 1 to 50, 1 to 20, 1 to 10, 1 to 5, 1 to 2, 2 to 100, 5 to 100, 10 to 100, 20 to 100, 50 to 100, 5 to 50, 5 to 20 or 20 to 50 micromol/second, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90 or 100 micromol/second, or at some other suitable rate. The rate may be at any suitable rate to obtain the desired structure.

[00069] The suspension may be agitated, e.g. stirred, swirled, sonicated, shaken etc., either during or following addition of the alkoxysilane or both. The agitation may be continued for a time (taken either from commencement of addition of the alkoxysilane or from completion of said addition) of at least about 10 hours, or at least about 12, 18, 24, 30, 36, 42, 48, 54 or 60 hours, or from about 10 to about 60 hours, or from about 24 to 60, 36 to 48, 12 to 24, 18 to 30 or 24 to 48 hours, e.g. about 10, 12, 14, 16, 20, 24, 32, 40, 48, 54 or 60 hours although in some instances it may be continued for longer than this. This leads to a sol-gel process in which porous silica structures are formed around the metal hydroxide particles.

[00070] The resulting particles may be separated from the suspension. They may be washed, e.g. with an aqueous liquid, optionally with water. The separating may comprise one or more of settling/decanting, centrifuging, filtration, etc. The washing may comprise suspending, optionally agitating, the particles in a washing liquid and then separating them therefrom, or may comprise passing the washing liquid through a bed of the particles, or may comprise some other form of washing.

[00071] The particles may be calcined. This may serve to remove substantially all organic matter from the particles. In particular it may serve to remove the surfactant, or at least the organic portions of it. If a trialkoxysilane (or di- or mono-alkoxysilane) is used for formation of the silica matrix, the calcining may also serve to remove the attendant organic groups from the silane. The calcining may comprise heating for at least about 0.5 hours, or for at least about 1, 2, 3, 4 or 5 hours, or for about 0.5 to about 5 hours, or for about 0.5 to 2, 0.5 to 1, 1 to 5, 2 to 5 or 1 to 3 hours, e.g. for about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5 hours. The calcining may be for sufficient time and at sufficient temperature to achieve a suitable degree of removal of organics, e.g. at least about 90%, or at least about 95 or 99%. The calcining may also convert the metal hydroxide to the corresponding metal oxide. The calcining may be in air or may be in an inert atmosphere, e.g. nitrogen, carbon dioxide, argon, helium etc. The calcining may be at a temperature of at least about 400°C, or at least about 450, 500, 550, 600, 650 or 700°C, or at about 400 to about 700°C, or at about 400 to 600, 400 to 500, 500 to 700, 600 to 700 or 500 to 600°C. It may be at about 400, 450, 500, 550, 600, 650 or 700°C or may be at higher temperature. It may be at a sufficient temperature to remove organics from the composite substance and/or to convert encapsulated metal hydroxide nanoparticles to the corresponding metal oxide. It will be understood that the higher the temperature used, in general the shorter the time required for adequate calcining. The calcining should be at a temperature that is not

sufficient to melt the silica matrix. It may be at a temperature that is not sufficient to melt the metal oxide and/or metal.

[00072] The process described above is capable of producing particles of a porous silica matrix having metal oxide particles dispersed therethrough. These may be useful as catalysts in cases where the metal oxide is catalytically active, or they may be useful as reagents in cases where the metal oxide is capable of acting as a reagent such as an oxidant. In such cases the porous silica matrix provides mechanical protection to the active catalyst/reagent particles whilst allowing access to reagents and allowing egress of products.

[00073] In some instances however the metal itself may be a more active catalyst. In this case, it may be desirable to reduce the metal oxide to the metal within the porous silica matrix so as to form particles of the metal within the porous silica matrix. This may comprise exposing the metal oxide to hydrogen or to one or more other reducing agents. In particular it may comprise exposing the particles to the reducing agent(s), since the porosity of the silica matrix allows access to the metal oxide particles. A suitable reducing agent is hydrogen gas, however the skilled person will readily appreciate other reducing agents which may be suitable. The reducing agent may be a fluid. It may be a liquid or may be a gas or may be a plasma or may be mixture of any two or more of these. It may be a solution (e.g. a solution of an active reductant in a solvent). It may be capable of passing through pores of the porous silica matrix so as to access the particles of the oxide of the metal. It may have sufficiently low viscosity as to be capable of passing through said pores.

[00074] Thus the metal, or the metal oxide may be catalytically active for one or more reactions including methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer-Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction and methane oxidation. The metal oxide may be useful as an oxidant in chemical looping combustion.

[00075] The invention also encompasses a composite substance prepared, or preparable, by the process described above. The composite substance of the present invention comprises particles of an oxide of a metal, or of a metal itself, dispersed in a porous silica matrix. The porous silica matrix may have pores of about 0.5 to about 5 nm diameter, or about 0.5 to 2, 1 to 3, 3 to 4 to 5, 1 to 5 or 2 to 4 nm. It may have a population of pores having a mean pore diameter of about

0.5, 1, 2, 3, 4 or 5nm. It may additionally or alternatively have pores of about 10 to about 500 nm diameter, or of about 10 to 200, 10 to 100, 10 to 50, 10 to 20, 20 to 500, 50 to 500, 100 to 500, 200 to 500, 20 to 200, 50 to 200, 50 to 100, 100 to 300 or 30 to 70nm. It may have a population of pores having a mean diameter of about 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450 or 500nm. It may have a bimodal pore distribution. In this instance, it may have a first population of pores is in the range of about 0.5 to about 5nm and a second population of pores is in the range of about 10 to about 100nm. It is thought that, in the case of a bimodal distribution of pores, the smaller pore population may be due to the intrinsic nanoporosity of the sol-gel silica matrix and that the larger pore population may be due to spaces between aggregated silica particles. It will be understood that the two populations of a bimodal distribution may at times overlap slightly. However in such instances, a graph of pore size distribution will clearly indicate two populations of pores by the presence of two clearly defined maxima in the graph. The pore size distribution, or each mode of the pore size distribution, may be narrow.

[00076] The particles of the oxide of the metal (or of the metal itself) may have a mean particle diameter of about 2 to about 10nm, or about 2 to 5, 5 to 10 or 3 to 7nm, e.g. about 2, 3, 4, 5, 6, 7, 8, 9 or 10nm. They may be substantially monodispersed in particle size. They may have at least about 90% of particles within 20% of the mean particle size, or within 10 or 5% thereof. The particles of the oxide of the metal, or of the metal itself, may represent at least about 20% by weight of the composite substance, or at least about 25, 30, 35, 40, 45 or 50% by weight, or between about 20 and about 70% by weight, or about 20 to 50, 20 to 30, 30 to 70, 50 to 70, 50 to 60, 30 to 50 or 40 to 50%, e.g. about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65 or 70% by weight. They may be substantially spherical, or may be some other shape, e.g. polyhedral, acicular, ovoid, oblate spherical, needle like, discoid, platelet-like or irregular.

[00077] The composite substance may be particulate or it may be monolithic. In the event that it is particulate, the particles thereof may have an aspect ratio (i.e. length to diameter ratio) of at least about 10, or at least about 15, 20, 25, 30, 35, 40, 45 or 50, or about 10 to about 50, or about 10 to 30, 10 to 20, 20 to 50 or 20 to 30, e.g. about 10, 15, 20, 25, 30, 35, 40, 45 or 50. The particles may have a rod-like morphology. Alternative morphologies include spherical, polyhedral, ovoid, oblate spherical, acicular and irregular. In some instances, mixtures of morphologies may be present. In some instances the particles of the composite substances may be in the form of aggregates of particles having any one or more of these shapes. The particles

(or aggregates) of the composite substance may have a mean diameter of about 0.1 to about 10 microns or about 0.1 to 1, 1 to 10, 1 to 5, 5 to 10, 0.5 to 5 or 0.5 to 1 microns, e.g. about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 or 10 microns.

[00078] In one particular embodiment, the metal oxide is copper oxide. In this case the composite substance may be in rod-like structures. These typically have a diameter of about 10 to about 100 nm, and may be within the range of about 10 to 50, 10 to 20, 20 to 100, 50 to 100 or 20 to 50nm, e.g. about 10, 20, 30, 40, 50, 60, 70, 80, 90 or 100 nm.

[00079] In another particular embodiment, the metal oxide is nickel oxide or iron oxide. In this case the substance may have a sheet like structure. In the sheetlike structure, the aspect ratio refers to a ratio of length to thickness of the sheets.

[00080] In the composite substance of the invention, each particle commonly comprises a plurality of particles of the metal oxide, or of the metal, dispersed therein. These particles may be distributed substantially homogeneously therethrough, or may be distributed unevenly.

[00081] On average, each particle of the composite substance may comprise at least about 100 particles of the oxide of the metal dispersed therein, or at least about 150, 200, 250, 300, 350, 400, 450 or 500 particles therein, or about 100 to about 1000 particles, or about 100 to 500, 100 to 200, 200 to 1000, 500 to 1000 or 300 to 700 particles, e.g. about 100, 150, 200, 250, 300, 340, 400, 450, 500, 600, 700, 800, 900 or 1000 particles, although at times there may be more than this.

[00082] The composite substance may have a BET surface area of at least about 200 m²/g, or at least about 250, 300, 350, 400, 450, 500, 600, 700, 800, 900 or 1000 m²/g, or from about 200 to about 1000 m²/g or about 200 to 500, 200 to 300, 300 to 500, 300 to 1000, 500 to 1000, 400 to 700 or 500 to 800 m²/g, e.g. about 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900 or 1000 m²/g.

[00083] The composite substance preferably has pores extending continuously from an outside surface of the silica matrix to an outside surface of the oxide of the metal so as to allow a reactant to penetrate to the surface of the oxide of the metal. The composite substance may have a porosity of at least about 5%, or at least about 10, 15, 20, 25, 30, 35, 40, 45 or 50%, or about 5

to about 50%, or about 5 to 25, 5 to 10, 10 to 50, 20 to 50 or 20 to 40%, e.g. about 5, 10, 15, 20, 25, 30, 35, 40, 45 or 50%, although porosities of greater this may be possible.

[00084] The composite substance of the invention may be used for a variety of applications. These primarily relate to the use of the substance as a catalyst. Typical reactions that may be catalysed by the substance include methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer–Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction, methane oxidation and chemical looping combustion. The nature of the reaction to be catalysed will depend on the nature of the metal oxide or metal particles which are dispersed within the silica matrix. Thus in general, a reaction that may be catalysed by (or that may otherwise use) a particular metal (e.g. transition metal) or metal oxide (e.g. transition metal oxide) may also be catalysed by (or otherwise use) the composite substance of the invention in which the particular metal or metal oxide is in the form of particles dispersed through particles of the composite substance. In this context, the term “otherwise use” may refer to use as a reagent, use as a scavenger for poisons and/or by-products or any other relevant use.

[00085] The composite substance may be resistant to sintering at the temperatures encountered in use.

[00086] A specific example is where the metal oxide is capable of high temperature oxidation of a substrate. A suitable metal for this application is copper, whereby the dispersed particles are copper oxide. In this example, a fuel is exposed to a composite substance according to a suitable composite material according to the invention at sufficient temperature for combustion of the fuel. The temperature is commonly at least about 500 °C, or at least about 600, 700, 800, 900 or 1000 °C, or between about 500 and about 1000 °C, or about 500 to 900, 500 to 800, 600 to 1000, 700 to 1000, 800 to 1000, 600 to 800, 700 to 900 or 800 to 900 °C, e.g. about 500, 550, 600, 650, 700, 750, 800, 850, 900, 950 or 1000 °C.

[00087] In another example the composite substance may be used in chemical looping combustion. Suitable metal oxide nanoparticles for this application include NiO, Fe₂O₃, CuO and Mn₃O₄.

Description of Embodiments

Examples

Synthesis of MeOx@SiO₂:

[00088] **Synthesis of CuO@SiO₂:** In a typical synthesis of 50 wt% CuO@SiO₂, 6.08 g of Cu(NO₃)₂ and 10 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 400 ml H₂O followed by the addition of 80 ml of NaOH water solution with 4.0 g NaOH by pouring at room temperature. The light-blue Cu(OH)₂ precipitate capped with CTAB was then collected by centrifugation. The precipitate was dispersed into 320 ml of water to form a suspension. The pH value of the suspension was adjusted to above 12. Subsequently, 7.6 ml of tetraethoxysilane (TEOS) in 80 ml ethanol was slowly dropped into the suspension and maintained at room temperature for 48 h under constant stirring to form SiO₂ shell coated onto the Cu(OH)₂ precipitate. After centrifugation, the as-received Cu(OH)₂ with SiO₂ shell was washed thoroughly with deionized water to remove sodium residue in the composite, and dried at 80°C. Finally, 50 wt% CuO@SiO₂ was obtained by calcination in air at 500 °C for 2 h.

[00089] **Synthesis of other MeOx@SiO₂:** The synthesis procedures of 50% NiO@SiO₂ and 50wt% Fe₂O₃@SiO₂ are the same as the above the synthesis of 50 wt% CuO@SiO₂. Ni(NO₃)₂·6H₂O (7.8 g) and Fe(NO₃)₃·9H₂O (10.3 g) were used as precursor for the preparation of Ni(OH)₂ and Fe(OH)₃ respectively.

Characterization

[00090] The particles size and morphology of MeOx@SiO₂ were characterized by transmission electron microscopy (TEM, HR-TEM, JEOL JEM-2010F). The crystallization size and phase transformation were determined by X-ray diffraction using a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation ($\lambda = 0.154$ nm) and *in situ* X-ray diffractometer, respectively. N₂ adsorption-desorption isotherms were collected on Micromeritics ASAP 2420 V2.05 (V2.05 J). H₂ temperature-programmed reduction (H₂-TPR) measurements were carried out with 50 mg of fresh catalysts. Before measurement, the sample was thermally treated under Ar stream at 200 °C for 2h to remove moisture and other contaminants. The reactor was heated from 30 °C to 850 °C at a rate of 10 °C /min in 50 ml/min of 5% of H₂/Ar. The hydrogen consumption was monitored by thermal conductivity detector (TCD).

Chemical looping combustion measurement

[00091] A fix-bed reactor was used to test the reactivity of MeOx@SiO_2 as oxygen carrier (OC). 0.5 g of MeOx@SiO_2 was placed in the middle of a quartz tube with an inner diameter of 10 mm, using quartz wool to hold the sample in place. Quartz chips were placed from the ends of the tube towards the sample for even distribution of gases reducing the dead volume and back mixing of gas in the tube. The tube was placed in a furnace and heated constant at 850 °C. The reduction reaction of CH_4 with OC and the oxidation reaction of air with OC were performance by the following: The as-prepared OC was heated up in the flow of Ar to the reaction temperature 850 °C, then 10% CH_4 (Ar balanced) was introduced at the flow rate of 100 ml/min for 5 min for reduction. Then CH_4 supply was stopped and argon gas was flowed through the reactor to purge the remaining methane gas. After running argon gas for 5 min, purified air 50 ml/min was run through the reactor to oxidize the metal for 5 min. Then, argon gas was run for 5 min to purge the oxygen gas and methane was flowed through the reactor to cycle the whole reaction. The flue gases from reactor were monitored by mass spectrometer.

Results and Discussion

[00092] The present method of synthesizing metal oxides/silica core-shell structured nanocomposites comprises three key steps: (1) preparation of metal hydroxides precipitates (Me(OH)_x) at room temperature and atmospheric pressure instead of complex synthesis of metal or metal oxides in the conventional method; (2) *in situ* coating of SiO_2 on Me(OH)_x core using structure-directing agent; (3) conversion of as-received core-shell structured $\text{Me(OH)}_x\text{@SiO}_2$ into MeOx@SiO_2 and removal of structure-directing agent by calcinations. The fourth step is for Me@SiO_2 : (4) conversion of MeOx to Me by H_2 reduction or reduction using agents such as H_2 , NaBH_4 , hydrazine, ethylene glycol etc.

[00093] Synthesis and characterization of CuO , NiO and Fe_2O_3 encaged in SiO_2 matrix prepared based on the synthetic strategy are as follows:

50% CuO encapsulated in SiO_2 matrix

[00094] Fig. 1 illustrates the synthesis of 50wt% CuO nanoparticles encapsulated in SiO_2 matrix using the synthetic strategy described above. First, Cu(OH)_2 precipitate capped by CTAB was prepared through fast pouring addition of NaOH into $\text{Cu(NO}_3)_2$ solution containing CTAB. Second, a silica shell was deposited *in situ* on the surface of Cu(OH)_2 under the direction of CTAB as template. Third, Cu(OH)_2 was converted into CuO and CTAB was removed by

calcination, leaving mesopores in the silica shell, finally resulting in highly dispersed CuO nanoparticles encapsulated in silica matrix.

[00095] TEM images in Figure 2 show the morphologies of Cu compounds and SiO₂ at the different synthetic steps. The Cu(OH)₂ precipitates capped by CTAB have a random nanowired or nanoribboned like structure, consisting of Cu(OH)₂ nanoparticles (Figure 2 a and b). After *in situ* coating of SiO₂ under the direction of CTAB, as shown in Figure 2 c and d, the random Cu(OH)₂ was transformed into an order bundled like structure, mostly like due to SiO₂ interaction, in which Cu(OH)₂ nanoparticles are highly dispersed in the silica matrix and each nanoparticle is separated by a nano-scale silica layer. Finally by calcination at 500 °C, highly dispersed CuO nanoparticles were formed in the SiO₂ matrix (Figure 2 e and f). The average particles size calculated from XRD pattern is 6.6 nm.

[00096] In order to further understand the transformation of Cu phase during the synthesis, *in situ* XRD analysis was carried out in air at a test temperature from 25 °C to 850 °C at a heating rate of 5 °C/min. XRD patterns were obtained at each particular temperature, staying at that temperature for 3 min. As seen in Figure 3a, the Cu phase is copper hydroxide in the temperature range between 25 °C to 150 °C. When the temperature is increased to 250 °C, the Cu phase is completely transformed from Cu(OH)₂ into CuO. The crystal size of Cu as a function of temperature is shown in Figure 3b. It can be seen that the particles size of 10.6 nm for Cu(OH)₂ at 25 °C rapidly decreases to 2.8 nm for CuO at 250 °C. This is thought to be due to the decrease of lattice contraction from Cu(OH)₂ to CuO. Thereafter, the particle size very slow grows to 4 nm at 750 °C and rapidly increase to 7.6 nm as temperature increases to 850 °C. This indicates that the CuO/SiO₂ composite have good thermal stability.

[00097] The texture structure of the 50% CuO encased in a silica matrix calcinated at 500°C was characterized by nitrogen physisorption. N₂ adsorption-desorption isotherms of the nanocomposites are shown in Figure 4a display type IV isotherms with the relatively fast increase of the adsorption amount in the low pressure (P/P_0) range of 0.2 to 0.3, indicating the presence of mesopority. The mesopore size distribution (Figure 4b) shows a sharp peak centered at 2.5 nm with the average pore size of 5.3 nm, exhibiting a uniform mesopore structure. The BET surface area and BJH desorption cumulative volume of pore calculated is 576 m²/g and 0.76 m³/g, respectively, indicating that the SiO₂ matrix has a highly mesoporous structure.

[00098] The accessibility of the core in the core-shell structured materials for reactants is of great importance for catalytic reaction and gas solid reaction. Figure 5 shows H_2 TPR curve measured from 30 °C to 850 °C at a rate of 10 °C/min of 50wt% CuO encapsulated in a SiO_2 matrix calcinated at 500 °C. Most of CuO in the composite can be easily reduced at below 300°C, which is comparable to the reduction behavior of commercial CuO nanoparticle powders. Furthermore, by comparison of the peak area of same weight of standard CuO powder, CuO loading in the composite was calculated to be 45%, which is very close to the nominal content of 50% in the the present product, indicating that more than 90% of the CuO nanoparticles are accessible for reaction and the SiO_2 matrix can provide efficient channels for reactants diffusion to CuO cores. The bundled like structure still is retained and the Cu nanoparticles are still encapsulated in the SiO_2 matrix after been reduced in H_2 up to 850°C, as shown in TEM images (Figure 6 a and b) . The particles size is still below 10 nm. This further identifies that the present materials have a good thermal stability.

[00099] CuO as an oxygen carrier has very high reactivity and selectivity to methane combustion, however, a serious sintering problem of Cu metal is encountered in the CLC application. Consequently the composite substance of the present invention comprising 50% CuO in a SiO_2 matrix was investigated under the operation conditions of CLC. Figure 7 shows its performance in CLC application. The reaction was carried out at 850 °C. It can be seen that after 10-cycle operation, the composite has no substantial decay in performance. However, commercial CuO nanoparticles lose most of their activity after only one cycle, due to serious Cu sintering. This indicates that CuO encapsulated into a silica matrix has excellent thermal stability in spite of the large CuO particles formed after reaction. Previously, CuO supported on inert materials with less than 20 wt% of Cu loading has been used in the demonstration device to avoid serious Cu sintering. Hence with the increase of Cu loading up to 50 wt% in the present invention, which may be achieved without sintering, the reaction efficiency can be greatly enhanced.

Other metal oxides encapsulated in SiO_2 matrix

[000100] 50wt% NiO nanoparticles encapsulated in a SiO_2 matrix was also prepared using the same procedure as described above for CuO. As shown in Figure 8, $Ni(OH)_2$ has a layered structure, which is different from the nanowire or nanoribbon $Cu(OH)_2$ precipitate (Figure 8a). This is thought to be due to different crystal growth mechanisms of $Cu(OH)_2$ and $Ni(OH)_2$.

After coating with SiO₂ and calcination at 500°C, highly dispersed NiO formed in the SiO₂ matrix with particle size less than 5 nm (Figure 8 b and c). The average particles size obtained from XRD pattern was 2.6 nm. N₂ adsorption and desorption isotherms obtained of the nanocomposites (Figure 8d) also show that they have a mesoporous structure with high BET surface area of 406 m²/g and pore volume of 1.3 m³/g. The pore size distribution shown in Figure 8e show two peaks in which one sharp peak centered at 2.2 nm may be due to the body of SiO₂ matrix and other broad peak at 33.3 nm may be ascribed to the interstitial space between the agglomerated particles of SiO₂ matrix, due to its irregular shape as observed in Figure 8 b.

[000101] The synthetic technology was extended to prepare 50 wt% Fe₂O₃ encapsulated in SiO₂. Figure 9a and b shows TEM images of this product. It can be observed that Fe₂O₃ nanoparticles with particle size <5 nm are highly distributed in SiO₂ matrix and each Fe₂O₃ particle is well separated from adjacent particles by a SiO₂ layer. The texture structure characterized by N₂ adsorption and desorption isotherms is shown in Figure 9c. There is an increase of N₂ amount at low pressure range, indicating the composites are mesoporous. The high BET surface area and pore volume are 532 m²/g and 1.7 m³/g, respectively. They have a similar pore size distribution to NiO encapsulated in SiO₂ (Figure 9d), where two peaks can be found at 2.3 nm and 220 nm.

[000102] Other metal oxides, such as Co₃O₄, V₂O₅, Mn₃O₄ and ZnO, can be encapsulated in a porous silica matrix using the method described herein.

Conclusions

[000103] A simple and efficient method of synthesizing highly dispersed metal oxides nanoparticles encapsulated in a porous SiO₂ matrix using metal hydroxide precipitates as key intermediates instead of metal or metal oxides nanoparticles in the conventional method was developed. Three kinds of metal oxides (CuO, NiO and Fe₂O₃) encapsulated in porous SiO₂ matrix were successfully prepared. The metal oxides encased in SiO₂, which are nanocomposites, prepared by this method not only possess high dispersion of metal oxides with narrow distribution and average particles size of around 5 nm, but also high surface area (300~500 m²/g) with richly accessible mesopores to metal oxides and excellent thermal stability at high temperature. Furthermore, the loading of metal oxides in the composites can be increased up to 50% or even more. The synthetic process is so simple that it is readily scalable to commercial

production. These features provide the composites with broad application prospects and commercial value as catalysts and oxygen carriers in heterogeneous catalysis and chemical looping combustion.

[000104] The SiO₂-encapsulated metal oxides of the present invention can be extended to many transition metal oxides other than Cu, Ni and Fe oxides. These include V₂O₅, ZnO, Co₃O₄, MnO₂ which have been widely used as oxide catalysts. The inventors have also shown that transition metals encapsulated in porous SiO₂ matrix, Me@SiO₂ can be easily prepared by reducing redox MeO_x@SiO₂. Noble metals (Pt, Au, Pd, Rh etc) encapsulated in a porous SiO₂ matrix can be synthesized by this method as well. All of these can find applications in various heterogeneous catalysis processes.

CLAIMS

1. A process for preparing a composite substance comprising particles of an oxide of a metal dispersed in a porous silica matrix, said process comprising:
 - a) preparing a solution comprising a soluble salt of the metal and a surfactant;
 - b) adjusting the solution to a basic pH at which a hydroxide of the metal precipitates from the solution;
 - c) preparing an aqueous suspension of the hydroxide of the metal, said suspension being at pH greater than 7;
 - d) adding to the suspension, with agitation, an alkoxysilane, so as to form composites comprising the hydroxide of the metal at least partially coated with silica; and
 - e) calcining the composites obtained in step d) so as to produce the composite substance.
2. The process of claim 1 wherein the metal is a transition metal, precious metal or rare earth metal.
3. The process of claim 1 or claim 2 wherein the metal is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Sn, Pb, Sb, Bi, La, Ce, Gd.
4. The process of any one of claims 1 to 3 wherein the surfactant is a soluble polymer surfactant, a polyelectrolyte or an alkylammonium salt.
5. The process of any one of claims 1 to 4 wherein the surfactant is a soluble polymer surfactant which is a carbohydrate polymer, a polyaniline, a polyimide, a polyvinylpyrrolidone or a polyvinyl alcohol.
6. The process of any one of claims 1 to 4 wherein the surfactant is a polyelectrolyte which is a polypeptide, a glycosaminoglycan, a DNA or a polydiallyldimethylammonium chloride.
7. The process of any one of claims 1 to 4 wherein the surfactant is an alkylammonium salt which comprises a C8-C18 alkyl group attached directly to a quaternary nitrogen atom.
8. The process of any one of claims 1 to 4 wherein the surfactant is a tetraalkylammonium salt.

9. The process of claim 8 wherein the alkylammonium salt is a C8-C18 alkyltri(C1-C4 alkyl)ammonium salt.
10. The process of claim 9 wherein the alkylammonium salt is a cetyltrimethylammonium salt.
11. The process of any one of claims 1 to 10 wherein the solution of step a) is an aqueous solution.
12. The process of any one of claims 1 to 11 wherein the solution of step a) has a ratio of the soluble salt of the metal to the alkylammonium salt of between about 1:10 and about 10:1 on a molar basis.
13. The process of any one of claims 1 to 12 wherein step b) comprises adding to the solution of step a) a water soluble hydroxide salt.
14. The process of any one of claims 1 to 14 comprising step b') separating the precipitated hydroxide of the metal from the solution, and step c) includes the step of resuspending the hydroxide of the metal in an aqueous liquid.
15. The process of claim 14 wherein step c) also includes adjusting the suspension of the resuspended hydroxide of the metal to a pH greater than 7.
16. The process of any one of claims 1 to 15 wherein the alkoxysilane is a trialkoxysilane or a tetraalkoxysilane.
17. The process of claim 16 wherein the alkoxysilane is tetraethoxysilane or tetramethoxysilane.
18. The process of any one of claims 1 to 17 wherein the alkoxysilane is added at a molar ratio to the metal hydroxide of between about 1:8 and about 8:1.
19. The process of any one of claims 1 to 18 wherein the alkoxysilane is added in alcoholic solution.
20. The process of any one of claims 1 to 19 wherein the alkoxysilane is added at a rate of about 1 to about 100 micromol/second.

21. The process of any one of claims 1 to 20 wherein step d) additionally comprises stirring the suspension following addition of the alkoxysilane, said stirring being continued for at least about 10 hours.
22. The process of any one of claims 1 to 21 comprising step d'), conducted between steps d) and e), of separating the particles formed in step d) from the suspension and washing said particles with an aqueous liquid.
23. The process of any one of claims 1 to 22 wherein step e) comprises heating the particles for at least about 1 hour at a temperature of about 400 to about 700 °C.
24. The process of any one of claims 1 to 23 additionally comprising step f) reducing the oxide of the metal within the porous silica matrix so as to form particles of the metal within the porous silica matrix.
25. The process of claim 24 wherein step f) comprises exposing the oxide of the metal to hydrogen.
26. The process of any one of claims 1 to 25 wherein the oxide of the metal, or, in the event that step f) is conducted, the metal, is catalytically active.
27. The process of claim 26 wherein oxide of the metal, or, in the event that step f) is conducted, the metal, is catalytically active for a reaction selected from the group consisting of methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer-Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction and methane oxidation
28. The process of any one of claims 1 to 23 wherein the oxide of the metal is usable as an oxidant in chemical looping combustion.
29. The process of claim 1 comprising:
 - a) preparing an aqueous solution comprising a soluble salt of the metal and a cetyltrimethylammonium salt;
 - b) adding to the solution from step a) a sodium hydroxide solution so as to precipitate a hydroxide of the metal from the solution;
 - b') separating the precipitated hydroxide of the metal from the solution;

- c) resuspending the hydroxide of the metal in an aqueous liquid and adjusting the resulting suspension to a pH greater than 7;
 - d) adding to the suspension, with stirring, an alcoholic solution of tetraalkoxysilane, so as to form particles comprising the hydroxide of the metal at least partially coated with silica;
 - d') separating the particles formed in step d) from the suspension and washing said particles with water; and
 - e) calcining the particles obtained in step d) at about 500°C for about 1 to about 5 hours so as to produce the composite substance.
30. A composite substance preparable by the process of any one of claims 1 to 29.
31. A composite substance comprising particles of a metal or an oxide of the metal dispersed in a porous silica matrix.
32. The composite substance of claim 30 or claim 31 wherein the metal is a transition metal.
33. The composite substance of any one of claims 30 to 32 wherein the metal is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Sn, Pb, Sb, Bi, La, Ce, Gd.
34. The composite substance of any one of claims 30 to 33 wherein the porous silica matrix has pores of about 1 to about 5 nm diameter.
35. The composite substance of claim 34 wherein the porous silica matrix additionally has pores of about 10 to about 100 nm diameter.
36. The composite substance of any one of claims 30 to 35 wherein the particles of the metal or of the oxide of the metal have a mean particle diameter of about 2 to about 10nm.
37. The composite substance of any one of claims 30 to 36 wherein the particles of the metal or of the oxide of the metal are substantially monodispersed in particle size.
38. The composite substance of any one of claims 30 to 37 which is in particulate form.
39. The composite substance of claim 38 wherein particles of said substance have an aspect ratio of at least about 10.
40. The composite substance of claim 38 or claim 39 wherein the oxide of the metal is copper oxide and the composite substance is in the form of rod-like structures.

41. The composite substance of claim 40 wherein the rod-like structures have a diameter of about 10 to about 100 nm.
42. The composite substance of claim 38 or claim 39 wherein the oxide of the metal is nickel oxide or iron oxide and wherein the substance has a sheet like structure, whereby, if particles of the substance have an aspect ratio of at least about 10, the aspect ratio refers to a ratio of length to thickness of sheets of the sheet like structure.
43. The composite substance of any one of claims 30 to 42 wherein each particle of said composite substance comprises a plurality of particles of the oxide of the metal dispersed therein.
44. The composite substance of claim 43 wherein, on average, each particle of said composite substance comprises at least about 100 particles of the oxide of the metal dispersed therein.
45. The composite substance of any one of claims 30 to 44 having a BET surface area of at least about 200 m²/g.
46. The composite substance of any one of claims 30 to 45 wherein pores extend continuously from an outside surface of the silica matrix to an outside surface of the metal or oxide of the metal so as to allow a reactant to penetrate to the surface of the oxide of the metal.
47. Use of the composite substance of any one of claims 30 to 46 in an application selected from the group consisting of methanol synthesis and reforming, steam and CO₂ reforming of methane, Fischer-Tropsch synthesis, CO oxidation, catalytic biomass tar decomposition, SO₂ oxidation, NO reduction, methane oxidation and chemical looping combustion
48. A process for oxidising a fuel comprising exposing said fuel to a composite substance according to any one of claims 30 to 46 at sufficient temperature for combustion of the fuel.
49. The process of claim 48 wherein the sufficient temperature is at least about 500°C.
50. The process of claim 48 or claim 49 wherein the metal is copper.
51. The process of any one of claims 48 to 50 wherein said process is chemical looping combustion.