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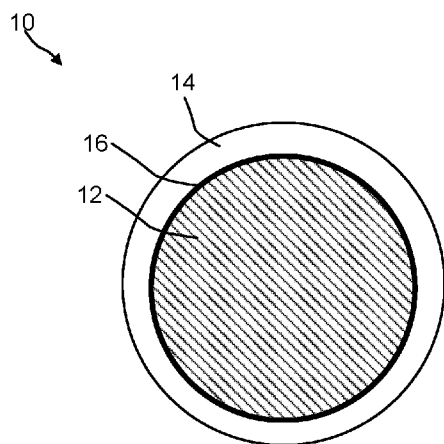


FIG. 1

(57) Abstract: Supported catalysts having a core-shell structure for the direct oxidation of hydrocarbons are described. The supported catalyst can include a catalytic metal-containing nanostructure core and a metal oxide support shell encompassing the catalytic metal-containing nanostructure core. Methods of making and of using the supported catalyst are also described.



CORE-SHELL CATALYSTS FOR SELECTIVE OXIDATION OF HYDROCARBONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/643,282 filed March 15, 2018, and U.S. Provisional Patent Application No. 62/648,175 filed March 26, 2018. The entire contents of each of the above-referenced disclosures are specifically incorporated herein.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns a supported catalyst having a core-shell structure. The catalyst can include a catalytic metal-containing nanostructure and a metal oxide support shell that encompasses the catalytic metal containing nanostructure core. The metal oxide support shell can include silicon dioxide (SiO₂) and titanium dioxide (TiO₂).

B. Description of Related Art

[0003] Propylene oxide (PO) is a versatile bulk chemical intermediate that can be widely used in the production of a variety of derivatives such as polyurethane, polyester resins. However, propylene oxidation is one of the most difficult oxidation reactions to conduct. Commercialized processes to convert propylene to propylene oxide can include either using hydrochlorination methods or organic peroxides (*e.g.*, *tert*-butyl hydroperoxide, ethylbenzene hydroperoxide and cumene hydroperoxide) methodology. Hydrochlorination methods use caustic chemicals that have environmental concerns and are less economical. Methods employing organic peroxides can generate by-products that can be difficult or costly to separate from the propylene oxide. Methods using hydrogen peroxide and a TS-1 zeolite to convert propylene to propylene oxide are also known (*e.g.*, HPPO process). However, the hydrogen peroxide used in these processes is produced through a quinone redox process that can be economically non-viable, and large scale production of hydrogen peroxide through this process can pose safety issues.

[0004] Other methods for producing PO can include direct oxidation of propylene with oxygen. In these methods, gold supported catalysts have been shown to have the highest activity. The activity can be dependent on the size of the gold atom. By way of example, U.S. Patent No. 7,973,184 to Haruta *et al.* describes a catalyst having gold clusters on the surface of

an aqueous-alkali-treated titanasilicate support where gold clusters having an average particle diameter of less than 2 nm gave the best performances. By comparison, non-alkali treated catalysts had low conversion and no propylene oxide selectivity.

[0005] While various methods to produce propylene oxide from propylene have been described, there exists a need for more efficient and cost effective methods.

SUMMARY OF THE INVENTION

[0006] A discovery has been found that provides a solution to at least some of the problems associated with direct oxidation of hydrocarbons (*e.g.*, direct oxidation of alkenes to form epoxides or alcohols). The solution is premised on using a supported catalyst having a catalytic metal-containing nanostructure core and a metal oxide support shell that includes SiO₂ and TiO₂. This supported catalyst can be used in a direct oxidation of alkene to an epoxide reaction (*e.g.*, propylene to propylene oxide) or an aromatic hydrocarbon to an aromatic alcohol reaction (*e.g.*, benzene to phenol). The structure of the shell, in combination with the catalytic core, is believed to drive these reactions. The structure of the shell can have three designs: 1) a monolayer or submonolayer of TiO₂ positioned between a layer of SiO₂ and the metal core; 2) a porous composite layer of TiO₂ and SiO₂ having a small aperture size (*e.g.*, less than 10 nm) with the TiO₂ distributed in the SiO₂ (*e.g.*, TiO₂ homogenized or blended in SiO₂); or 3) a porous SiO₂ layer encompassing the metal core with TiO₂ loaded in the apertures. Without wishing to be bound by theory, it is believed that having such a core-shell type structure can lead to more interaction of the active metal surface with the TiO₂, thereby providing a more stable catalyst with enhanced epoxide or alcohol selectivity.

[0007] In a particular aspect of the invention, supported catalysts that include a core-shell structure having a catalytic metal-containing nanostructure core and a metal oxide support shell encompassing the catalytic metal-containing nanostructure core are described. The shell can include (a) a titania (TiO₂) layer encompassing the metal-containing nanostructure core and a silica (SiO₂) layer encompassing the TiO₂ layer, (b) a porous composite layer comprising a SiO₂ layer with TiO₂ distributed therein, or (c) a porous SiO₂ layer encompassing the metal-containing nanostructure core having apertures loaded with TiO₂. In some instances, the porous composite or the porous SiO₂ layer can have average aperture size (*e.g.*, pore diameter) of less than 10 nm, preferably less than 5 nm, more preferably less than 2 nm. The total shell and/or the silica layer has an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 100 nm, more preferably 10 to 50 nm. A molar ratio of titanium to silicon (Ti:Si) at the inner

surface of the shell or the Ti:Si composite layer can be from 1:5 to 1:100, preferably 1:10 to 1:50. In some instances, the SiO₂ layer can have an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 50 nm. In a particular aspect, the shell is the TiO₂ layer encompassing the metal-containing nanostructure core and the SiO₂ layer encompassing the TiO₂ layer. The TiO₂ layer can be a monolayer or a submonolayer. In another aspect of the present invention, the shell is the composite porous layer of TiO₂ and SiO₂ with the TiO₂ distributed in the SiO₂. The composite can have an average aperture (*e.g.*, pore) diameter of less than 10 nm, preferably less than 5 nm, more preferably less than 2 nm. In yet another aspect of the invention, the shell is a porous SiO₂ layer encompassing the metal-containing nanostructure with TiO₂ loaded into apertures of the SiO₂. In a preferred embodiment, the metal-containing nanostructure comprises gold (Au) or an oxide thereof. The Au nanostructure can have a 0.5 nm to 5 nm, preferably 1 nm to 3 nm, or about 2 nm.

[0008] Embodiments of the present invention also describe methods of producing core-shell catalysts of the present invention. A method can include (a) obtaining a catalyst precursor material that can include a metal-containing nanostructure core encompassed by a silica (SiO₂) layer, (b) etching the SiO₂ layer to form apertures in the SiO₂ layer, (c) contacting the catalyst precursor material of step (b) with a titania (TiO₂)-precursor solution under conditions sufficient to load the TiO₂-precursor solution in the apertures of the SiO₂ layer, and (d) calcining the catalyst precursor material of step (c), preferably at 250 °C to 400 °C, to form a catalyst having a metal-containing nanostructure core encompassed by a SiO₂ layer comprising TiO₂ in the apertures of the SiO₂ layer. The TiO₂-precursor solution of step (b) can include a surfactant (*e.g.*, ionic, cationic, anionic or the like) and the step (b) etching conditions can include: (i) subjecting the catalyst precursor material to conditions (*e.g.*, acidic) to remove the surfactant from the SiO₂ layer; and (ii) heating the catalyst precursor material of step (i) at a temperature of 200 °C to 500 °C, or 225 to 400 °C, or about 300 °C.

[0009] Another method of producing core-shell catalysts can include: (a) contacting a solution of a metal-containing nanostructure (*e.g.*, Au), a cationic surfactant, and a titania (TiO₂)-precursor material with a silica (SiO₂)-precursor material under conditions sufficient to produce a catalyst precursor material having the metal-containing nanostructure encompassed by a TiO₂ layer and a SiO₂ layer, where the TiO₂ layer is positioned between the metal-containing nanostructure and the SiO₂ layer; (b) etching the SiO₂ layer to form apertures in the SiO₂ layer; and (c) calcining the catalyst precursor material of step (b), preferably at 250 °C to 500 °C, to form a catalyst having a metal-containing nanostructure encompassed by a SiO₂

layer containing TiO_2 in the void apertures of the silica layer. The step (b) etching step can also include contacting the catalyst precursor of step (b) with a TiO_2 -precursor solution under conditions sufficient to load the additional TiO_2 -precursor solution in the apertures of the SiO_2 layer. In some embodiments, the TiO_2 -precursor solution can be basic and the TiO_2 -precursor can be tetraethyl orthotitanate or tetrabutyl orthotitanate. In other embodiments, the TiO_2 -precursor solution can be acidic and TiO_2 -precursor can be titanium tetrachloride. Etching can include contacting the step (b) catalyst precursor with an inorganic acid at a temperature of 5 to 95 °C for 1 to 10 hours. In some instances, the catalyst precursor material can be dried prior to calcining. The resulting catalyst can have a silicon (Ti:Si) molar ratio is 1:10 to 1:50, preferably 1:10 to 1:30, on the inner surface of the shell.

[0010] In yet another instance, processes for oxidation of hydrocarbons are described. A process can include contacting an alkene or an aromatic hydrocarbon and an oxygen source with any of the catalysts of the present invention under conditions suitable to produce an alkene oxide or an aromatic alcohol. In some embodiments, the alkene is propylene, the conditions can include a temperature of 100 °C to 400 °C, preferably 200 °C to 300 °C, and the alkene oxide is propylene oxide. The aromatic hydrocarbon can be benzene and the produced aromatic alcohol can be phenol.

[0011] In the context of the present invention 20 embodiments are described. Embodiment 1 is a supported catalyst having a core-shell structure comprising a catalytic metal-containing nanostructure core and a metal oxide support shell encompassing the catalytic metal-containing nanostructure core, wherein the shell comprises: (a) a titania (TiO_2) layer encompassing the metal-containing nanostructure core and a silica (SiO_2) layer encompassing the TiO_2 layer; (b) a porous composite layer comprising a SiO_2 layer with TiO_2 distributed therein, wherein the composite layer has an average aperture diameter of less than 10 nm, preferably less than 5 nm, more preferably less than 2 nm; or (c) a porous SiO_2 layer encompassing the metal-containing nanostructure core having apertures loaded with TiO_2 . Embodiment 2 is the supported catalyst of embodiment 1, wherein the shell is the TiO_2 layer encompassing the metal-containing nanostructure core and the SiO_2 layer encompassing the TiO_2 layer. Embodiment 3 is the supported catalyst of embodiment 2, wherein the TiO_2 layer is a monolayer or submonolayer. Embodiment 4 is the supported catalyst of embodiment 1, wherein the shell is the porous composite layer encompassing the metal-containing nanostructure core comprising the SiO_2 layer with the TiO_2 distributed therein. Embodiment 5 is the supported catalyst of embodiment 1, wherein the shell is the SiO_2 layer encompassing the metal-containing nanostructure core

having apertures loaded with the TiO_2 . Embodiment 6 is the supported catalyst of any one of embodiments 1 to 5, wherein the metal-containing nanostructure core comprises gold or an oxide thereof and has a size of 0.5 nm to 5 nm, preferably 1 nm to 3 nm, or about 2 nm. Embodiment 7 is the supported catalyst of any one of embodiments 1 to 6, wherein the silica layer has an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 50 nm. Embodiment 8 is the supported catalyst of any one of embodiments 1 to 7, wherein the molar ratio of titanium to silicon (Ti:Si) at the inner surface of the shell or in the Si/Ti composite layer is from 1:5 to 1:100, preferably 1:10 to 1:50. Embodiment 9 is the supported catalyst of any one of embodiments 1 to 7, wherein the total shell has an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 100 nm, more preferably 10 to 50 nm.

[0012] Embodiment 10 is a method of producing a core-shell catalyst, the method comprising: (a) obtaining a catalyst precursor material comprising a metal-containing nanostructure core encompassed by a silica (SiO_2) layer; (b) etching the SiO_2 layer to form apertures in the SiO_2 layer; (c) contacting the catalyst precursor material of step (b) with a titania (TiO_2)-precursor solution under conditions sufficient to load the TiO_2 -precursor solution in the apertures of the SiO_2 layer; and (d) calcining the catalyst precursor material of step (c), preferably at 250 °C to 400 °C, to form a catalyst having a metal-containing nanostructure core encompassed by a SiO_2 layer comprising TiO_2 in the apertures of the SiO_2 layer. Embodiment 11 is the method of embodiment 10, wherein catalyst precursor material comprises a surfactant and the etching step (b) comprises: (i) subjecting the catalyst precursor material to acidic conditions to remove the surfactant from the SiO_2 layer; and (ii) heating the catalyst precursor material of step (i) at a temperature of 200 °C to 500 °C, or 225 to 400 °C, or about 300 °C.

[0013] Embodiment 12 is a method of producing a core-shell catalyst, the method comprising: (a) contacting a solution of a metal-containing nanostructure, a cationic surfactant, and a titania (TiO_2)-precursor material with a silica (SiO_2)-precursor material under conditions sufficient to produce a catalyst precursor material having the metal-containing nanostructure encompassed by a TiO_2 layer and a SiO_2 layer, wherein the TiO_2 layer is positioned between the metal-containing nanostructure and the SiO_2 layer; (b) etching the SiO_2 layer to form apertures in the SiO_2 layer; and (c) calcining the catalyst precursor material of step (b), preferably at 250 °C to 500 °C, to form a catalyst having a metal-containing nanostructure having a TiO_2 layer positioned between the core and the SiO_2 layer. Embodiment 13 is the method of embodiment 12, further comprising contacting the catalyst precursor of step (b) with an acid at a temperature of 5 to 95 °C for 1 to 10 hours. Embodiment 14 is the method of any

one of embodiments 12 to 13, wherein the TiO₂-precursor solution is basic and comprises tetraethyl orthotitanate or tetrabutyl orthotitanate, or the TiO₂-precursor solution is acidic and comprises titanium tetrachloride, and the conditions comprise a temperature of 20 to 30 °C. Embodiment 15 is the method of any one of embodiments 12 to 14, wherein the metal-
5 containing nanostructure comprises a gold nanoparticle. Embodiment 16 is the method of any one of embodiments 12 to 15, further comprising drying the catalyst precursor material prior to calcining. Embodiment 17 is the method of any one of embodiments 12 to 16, wherein the titanium to silicon (Ti:Si) molar ratio is 1:10 to 1:50, preferably 1:10 to 1:30 on the inner surface of the shell.

10 **[0014]** Embodiment 18 is a process of oxidizing a hydrocarbon, the process comprising contacting an alkene or an aromatic hydrocarbon and an oxygen source with any one of the catalysts of embodiments 1 to 8 under conditions sufficient to produce an alkene oxide or an aromatic alcohol. Embodiment 19 is the process of embodiment 18, wherein the alkene is propylene and the aromatic hydrocarbon is benzene. Embodiment 20 is the process of any one
15 of embodiments 18 to 19, wherein the alkene is propylene and the conditions comprise a temperature of 100 °C to 400 °C, preferably 200 °C to 300 °C.

[0015] Other embodiments of the invention are discussed throughout this application. Any embodiment discussed with respect to one aspect of the invention applies to other aspects of the invention as well and vice versa. Each embodiment described herein is understood to be
20 embodiments of the invention that are applicable to other aspects of the invention. It is contemplated that any embodiment or aspect discussed herein can be combined with other embodiments or aspects discussed herein and/or implemented with respect to any method or composition of the invention, and vice versa. Furthermore, compositions of the invention can be used to achieve methods of the invention.

25 **[0016]** The following includes definitions of various terms and phrases used throughout this specification.

[0017] The terms “core/shell” or “core-shell” refer to structures having an inner “core” (*i.e.*, a nano- or microstructure, preferably a nanoparticle) and an outer shell that encompasses or encapsulates the core, where the core contacts at least 50% to 100%, preferably 60 to 90%,
30 of the inside surface of the shell. A non-limiting illustration of a core/shell structure is provided in FIG. 2, where the core contacts at least 90% or more of the inside surface of the shell or completely fills a void space that is defined by the inner surface of the shell.

[0018] Determination of whether a given structure is a core-shell structure can be made by persons of ordinary skill in the art. One example is visual inspection of a transition electron microscope (TEM) or a scanning transmission electron microscope (STEM) image of a structure and determining whether the inner core or yolk contacts at least 50 % of the inner surface of the shell.

[0019] An alkene is a linear or branched, substituted or substituted unsaturated hydrocarbon having one or more carbon-carbon double or triple bonds. An alkene can include alkyl groups. An alkyl group is linear or branched, substituted or substituted, saturated hydrocarbon. Non-limiting examples of alkyl group substituents include alkyl, halogen, hydroxyl, alkyloxy, carboxylic acid, ester, amine, amide, nitrile, acyl, thiol and thioether.

[0020] An “aryl” group or an “aromatic” group is a substituted or substituted, mono- or polycyclic hydrocarbon with alternating single and double bonds within each ring structure. Non-limiting examples of aryl group substituents include alkyl, halogen, hydroxyl, alkyloxy, haloalkyl, haloalkoxy, carboxylic acid, ester, amine, amide, nitrile, acyl, thiol and thioether. A non-limiting example of an aromatic group includes benzene.

[0021] “Nanostructure” or “nanomaterial” refer to an object or material in which at least one dimension of the object or material is equal to or less than 1000 nm (*e.g.*, one dimension is 1 to 1000 nm in size). In a particular aspect, the nanostructure includes at least two dimensions that are equal to or less than 1000 nm (*e.g.*, a first dimension is 1 to 1000 nm in size and a second dimension is 1 to 1000 nm in size). In another aspect, the nanostructure includes three dimensions that are equal to or less than 100,000 nm (*e.g.*, a first dimension is 1 to 1000 nm in size, a second dimension is 1 to 1000 nm in size, and a third dimension is 1 to 1000 nm in size). The shape of the nanostructure can be of a wire, a particle (*e.g.*, having a substantially spherical shape), a rod, a tetrapod, a hyper-branched structure, a tube, a cube, or mixtures thereof. “Nanoparticles” include particles having an average diameter size of 1 to 1000 nanometers.

[0022] The terms “about” or “approximately” are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment, the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

[0023] The terms “wt.%”, “vol.%”, or “mol.%” refers to a weight percentage of a component, a volume percentage of a component, or molar percentage of a component,

respectively, based on the total weight, the total volume of material, or total moles, that includes the component. In a non-limiting example, 10 grams of component in 100 grams of the material is 10 wt.% of component.

[0024] The term “substantially” and its variations are defined to include ranges within 10%,
5 within 5%, within 1%, or within 0.5%.

[0025] The terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, when used in the claims and/or the specification includes any measurable decrease or complete inhibition to achieve a desired result.

[0026] The term “effective,” as that term is used in the specification and/or claims, means
10 adequate to accomplish a desired, expected, or intended result.

[0027] The use of the words “a” or “an” when used in conjunction with any of the terms “comprising,” “including,” “containing,” or “having” in the claims, or the specification, may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.”

15 [0028] The words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

20 [0029] The catalysts of the present invention can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, *etc.* disclosed throughout the specification. With respect to the transitional phrase “consisting essentially of,” in one non-limiting aspect, a basic and novel characteristic of the catalysts of the present invention are their abilities to catalyze direct oxidation of alkenes or aromatic hydrocarbons to form
25 oxygenated hydrocarbons such as epoxides or alcohols.

[0030] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant
30 to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. In further embodiments, features from specific embodiments may be combined

with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments. In further embodiments, additional features may be added to the specific embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0031] Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings.

[0032] FIG. 1 is an illustration of an unetched core-shell catalyst.

[0033] FIGS. 2-4 are illustrations of porous core-shell catalysts of the present invention.

10 [0034] FIG. 5 is a transmission electron microscopy (TEM) image of an agglomerated core shell catalyst of the present invention after removing a aperture forming surfactant using an etching process.

[0035] FIG. 6 is graphical representation of hydrogen efficiency (%) of the catalyst of ther present invention, aged catalyst, at 150 °C, with 40% propene, at 4 bar (0.4 MPa) and 12 bar (MPa).
15

[0036] FIG. 7 is a graphical representation of propylene oxide (PO) yield, propene conversion (%) and hydrogen efficiency (%) for a comparative catalyst for cycles 1, 5, 8, 16, 17, 18, 19, and 20 of a 20 cycle experiment (open circles: conversion, closed circles: yield, diamonds: hydrogen efficiency). The vertical lines indicated regeneration at 300 °C.

20 [0037] FIG. 8 is a graphical representation of propylene oxide (PO) yield, propene conversion (%) and hydrogen efficiency (%) for a catalyst of the present invention for cycles 1, 5, 8, 16, 17, 18, 19, and 20 of a 20 cycle experiment (open circles: conversion, closed circles: yield, diamonds: hydrogen efficiency). The vertical lines indicated regeneration at 300 °C.

[0038] While the invention is susceptible to various modifications and alternative forms, 25 specific embodiments thereof are shown by way of example in the drawings. The drawings may not be to scale.

DETAILED DESCRIPTION OF THE INVENTION

[0039] The currently available processes for direct oxidation of alkenes or aromatic hydrocarbons using gold-based catalysts suffer from deactivation or poor stability of the gold
30 catalysts. The present invention provides a solution to this and other problems of catalysts for

direct oxidation of hydrocarbons. The discovery is premised on the structure of a core-shell catalyst that includes a silica and titania containing shell that encompasses a catalytic metal-containing core (*e.g.*, a Au nanoparticle(s)).

[0040] These and other non-limiting aspects of the present invention are discussed in further detail in the following sections with reference to the figures.

A. Catalyst Structure

1. Core-Shell Structure

[0041] The core-shell catalyst of the present invention includes a catalytic core (*e.g.*, metal containing nano- or microstructure) surrounded by a shell that includes TiO₂ and SiO₂ layers or a porous TiO₂/SiO₂ composite. The shell can include a monolayer or submonolayer of TiO₂ positioned between the core and a SiO₂ layer. A submonolayer is an atomic surface coverage of less than one monolayer. In another embodiment, the shell can include TiO₂ dispersed throughout the silica layer, and/or be contained in the apertures of a porous SiO₂ layer. The shell can include aperture (*e.g.*, openings, pores, channels, perforations, *etc.*) that extend through the shell to the catalytic core. FIG. 1 is an illustration of a core-shell catalyst 10 having a core 12 and shell 14. Shell 14 includes TiO₂ layer 16. TiO₂ layer can be a monolayer or a submonolayer. In this embodiment, catalyst 10 does not include apertures and is a representative illustration of a catalyst structure prior to being subjected to an etching process of the present invention. FIGS. 2-4 are illustrations of a core-shell type catalyst with apertures. As illustrated in FIG. 2, the core-shell structure can have a substantially spherical shape. However, other shapes are contemplated (*e.g.*, random shape, cubical shape, pyramidal shape, ellipsoid shape, rod shape, tetrapod shape, hyper-branch shape, *etc.*). FIG. 2A is an illustration of an end view a core-shell catalyst with a solid nano- or microstructure core 12, preferably a nanostructure that is encapsulated by shell 14 that includes TiO₂ layer 16. FIG. 2B is an enlargement of apertures in the shell. FIGS. 3 and 4 are illustrations of a core-shell catalyst having thick and thin shells, respectively. Referring to FIGS. 2-4, catalysts 20 through 40 include catalytic metal-containing core 12, shell 14, and apertures 22. As shown, metal containing core 12 is in full or substantially full contact with the inner surface of shell 26 (*i.e.*, there are few or no voids between the catalytic metal core 12 and the shell 14). In some embodiments, core 12 contacts at least 50% to 100%, 60% to 90% or 70% to 80% of the inner surface of shell 26. Core 12 can include a single metal or can include two, three, four or more metals or metal alloys (*e.g.*, single metal core, bi-metallic core, tri-metallic core, *etc.*). For

example, catalytic metal-containing core 12 can include two metals (bi-metallic) or three metals (tri-metallic). In a preferred embodiment, core 12 includes a single metal, for example, gold particles or a cluster of gold particles. Apertures 22 traverse shell 14 and provide openings in the shell that allow reactants to enter the shell. Depending on the thickness of shell 14, aperture 22 can be an elongated channel (*e.g.*, a channel that can be substantially non-tortuous or can be tortuous/have tortuosity) or a non-elongated hole.

[0042] As discussed in more detail below, the shape and/or size of apertures 22 in shell 14 of the core-shell structure can be tuned to provide a desired shape, flow flux, or porosity for a given application. By way of example, etching of a thicker shell can allow for the formation of elongated channels that can have an overall straighter shape or a more tortuous (*e.g.*, presence of bends or curves) shape (*See*, FIG. 3, element 34). Alternatively, etching of a thinner shell can allow for the formation of holes that are not elongated channels (*See*, FIG. 4, element 44). In FIGS. 3 and 4, apertures 34 and 44 can include TiO₂ (not shown) along the inside walls or on core 12.

2. Core Structure

[0043] The core can be a solid or semi-solid nano- or microstructure. In certain aspects, the nano- or microstructure can have the shape of a wire, a particle (*e.g.*, having a substantially spherical shape), a rod, a tetrapod, a hyper-branched structure, a tube, a cube, or mixtures thereof. In preferred instances, the cores are nanostructures, preferably nanoparticles. Further, the core can include one or more metals, or one or more metal particles. With respect to the core of a core-shell catalyst, the core can fill 50% to 100%, 50% to 99%, 60% to 95%, or 50%, 60%, 70%, 80%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, 99.1%, 99.2%, 99.3%, 99.4%, 99.5%, 99.6%, 99.7%, 99.8%, 99.9%, or any range or value there between of the volume of the void space of the shell, where the void space is defined as the space between the outer surface of the core and the inner surface of the shell. The core can have a size of 0.5 nm to 100 nm, 10 nm to 50 nm, or 20 to 30 nm. In some embodiments, the core is a Au particle and can have a size of 0.5 nm to 10 nm, 1 nm to 3 nm, or about 2 nm.

3. Shell Structures

[0044] The shells (*e.g.*, 14, 32, 42 —see FIGS. 2-4) can have outer surface 24 and inner surface 26 (*e.g.*, FIGS. 2A and 2B). The layers or the shell can have a thickness of 0.5 nm to 1000 nm, 10 nm to 100 nm, 10 nm to 50 nm, or 10 nm, 11 nm, 12 nm, 13 nm, 14 nm, 15 nm, 16 nm, 17 nm, 18 nm, 19 nm, 20 nm, 21 nm, 22 nm, 23 nm, 24 nm, 25 nm, 26 nm, 27 nm, 28

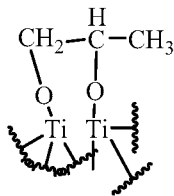
nm, 29 nm, 30 nm, 31 nm, 32 nm, 33 nm, 34 nm, 35 nm, 36 nm, 37 nm, 38 nm, 39 nm, 40 nm, 41 nm, 42 nm, 43 nm, 44 nm, 45 nm, 46 nm, 47 nm, 48 nm, 49 nm, 50 nm, or any range or value there between. The thickness of the TiO₂ layer is less than the thickness of the SiO₂ layer. In some embodiments, the thickness of the TiO₂ layer is 0.1 nm to 10 nm, or 0.1, 0.2, 5 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 nm, 1.5 nm, 2 nm, 2.5 nm, 3 nm, 3.5 nm, 4 nm, 4.5 nm, 5.0 nm, 5.5 nm, 6 nm, 6.5 nm, 7 nm, 7.5 nm, 8 nm, 8.5 nm, 9 nm, 9.5 nm, or 10 nm. In some embodiments, the shell can be considered to be “thin”, “medium” or “thick” as defined below. In FIGS. 3 and 4, the total shell thickness of shell 32 is thicker than the total shell thickness of shell 42. For example, a thin shell or layer (*e.g.*, shell 42 or layer 16) can have a thickness of 10 several nanometers, or 0.5 nm to 10 nm. A thick shell (*e.g.*, shell 32) can have a thickness of 50 nm to 1000 nm. A medium thick shell would have a thickness that overlaps the thin and thick ranges (*i.e.*, 10 nm to 50 nm). The thickness of the shell can be tuned by controlled etching of the shell as described throughout the specification. Such tuning allows for design of a shell thickness and properties needed for a desired chemical reaction.

15 [0045] The shells of the present invention can also have an inner molecular layer (*e.g.*, monolayer) or substantially less than one monolayer (*e.g.*, submonolayer) of one oxide that contacts the core metal particle(s) and an outer coating layer that contacts the inner molecular layer. By way of example, the inner molecular layer can be a single TiO₂ monolayer or a submonolayer, and the outer layer can be a SiO₂ monolayer, or a composite layer having both 20 SiO₂ and TiO₂. The molar ratio of titanium to silicon (Ti:Si) at the inner surface of shell or the composite layer or at the interface between the shell and the catalytic metal nanoparticles can be from 1:5 to 1:100, preferably 1:10 to 1:50, or at least, equal to or between any two of 1:5, 1:10, 1:20, 1:30, 1:40, 1:50, 1:60, 1:70, 1:80, 1:90, and 1:100.

4. Apertures

25 [0046] The apertures (*e.g.*, apertures 22, 34, or 44) can extend from outer surface 24 of the shell to inner surface 26 of the shell (*See*, for example, FIG. 2B). Such an opening allows reactants to traverse the aperture and contact the surface of the catalytic metal core. Without wishing to be bound by theory, it is believed that in core-shell catalysts, the reactant can traverse directly to metal core surface and react on the surface, and then form products, which 30 traverse back to outside of shell. For example, in a direct oxidation reaction, the metal core acts as the oxidation catalyst. Without wishing to be bound by theory it is believed that the catalytic metal core activates the double bond to form a Au-olefin complex, which reacts with

the titania or silica to form a bidentate type intermediate shown below with titania. The intermediate decomposes to an epoxide and water.



[0047] Having the titania dispersed in the silica, as a layer positioned between the silica and metal core, and/or contained within the apertures of the silica layer can promote a Au-Ti interaction, thereby creating an Au-Ti interface that inhibits water formation. The property of shell necessary to perform desired reaction can be designed and the amount of etching to tune the acidity and/or reactivity of the catalyst can be implemented to produce the optimum catalyst for the desired reaction.

[0048] A small void can exist between the inner surface of shell 14 or shell 24 and catalytic metal-containing core 12 at the end of the aperture. A diameter, shape, and tortuosity (*e.g.*, porosity and pore size) of the apertures can be any diameter, shape or length. These dimensions can be tuned through the coating and etching processes described in the specification. For example, based on the chemical reaction conditions, the porosity and aperture (*e.g.*, pore) size of the shell can be tuned to a desired value. By tuning the thickness and the porosity and aperture size of the shell (*e.g.*, by adjusting the etching conditions such as concentration of etching agent, time of etching, temperature, *etc.*) a large surface area, per unit mass of the catalytic metal-containing core, of the catalytic metal-containing core is realized, thereby leading to high catalytic activity.

B. Materials

1. Catalytic Core Materials

[0049] The catalytic cores can be catalytic metal-containing nano- or microstructures and can include one or more metals or alloys thereof. The metals can be noble metals, transition metals, or any combinations or any alloys thereof. Noble metals include silver (Ag), palladium (Pd), platinum (Pt), gold (Au), rhodium (Rh), ruthenium (Ru), rhenium (Re), iridium (Ir) or any combinations or alloys thereof. Transition metals include iron (Fe), copper (Cu), nickel (Ni), zinc (Zn), manganese (Mn), chromium (Cr), molybdenum (Mo), tungsten (W), osmium (Os), or tin (Sn), or any combinations or alloys thereof. In some embodiments, the catalyst includes 1, 2, 3, 4, 5, 6, or more transition metals and/or 1, 2, 3, 4 or more noble metals. In a

preferred embodiment, the catalytic metal core is a gold nanostructure or cluster of gold nanostructures. The metals can be obtained from metal precursor compounds. For example, the metals can be obtained as a metal nitrate, a metal amine, a metal chloride, a metal coordination complex, a metal sulfate, a metal phosphate hydrate, metal complex, or any combination thereof. Examples of metal precursor compounds include, nickel nitrate hexahydrate, nickel chloride, cobalt nitrate hexahydrate, cobalt chloride hexahydrate, cobalt sulfate heptahydrate, cobalt phosphate hydrate, platinum (IV) chloride, ammonium hexachloroplatinate (IV), sodium hexachloroplatinate (IV) hexahydrate, potassium hexachloroplatinate (IV), chloroplatinic acid hexahydrate, or chloroauric acid. These metals or metal compounds can be purchased from any chemical supplier such as MilliporeSigma (St. Louis, Missouri, USA), Alfa-Aeaser (Ward Hill, Massachusetts, USA), and Strem Chemicals (Newburyport, Massachusetts, USA).

[0050] The amount of catalytic metal depends, *inter alia*, on the catalytic activity of the catalyst. In some embodiments, the amount of catalytic metal present in the particle(s) in the core ranges from 0.01 to 20 parts by weight of catalyst per 100 parts by weight of catalyst, from 0.01 to 5 parts by weight of catalyst per 100 parts by weight of catalyst. If more than one catalytic metal is used, the molar percentage of one metal can be 1 to 99 molar % of the total moles of catalytic metals in the catalytic core. In a preferred embodiment, the catalytic metal is present in 0.05 to 5 wt.%, 0.1 to 4 wt.% or 1 to 3 wt.% or at least, equal to, or between any two of 0.05, 0.1, 0.5, 1.0, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 wt.%

[0051] The metal nano- or microstructures can be stabilized with the addition of surfactants (*e.g.*, CTAB, PVP, *etc.*) and/or through controlled surface charge.

2. Shell Materials

[0052] In some embodiments, the shell material is active (*i.e.*, has catalytic activity). In other aspects, the shell is inactive (*i.e.*, non-catalytic). The shell material can be an inorganic oxide or a mixed metal oxide. In preferred aspects, the shell is a silica and TiO₂ shell having a titania layer between the core and silica outer shell, or a composite silica-titania shell with the titania distributed in the silica, or a porous silica layer having titania in the apertures. The shell can include other metal oxides such as alpha, beta or gamma alumina (Al₂O₃), activated Al₂O₃, cerium oxide (CeO₂), titanium dioxide (titania, TiO₂), zirconia (ZrO₂), germania (GeO₂), tin oxide (SnO₂), gallium oxide (Ga₂O₃), zinc oxide (ZnO), hafnium oxide (HfO₂), yttrium oxide (Y₂O₃), lanthanum oxide (La₂O₃), cerium oxide (CeO₂), or any combination thereof. A non-

limiting example of a shell can be a perforated silica-containing shell that includes titania as a monolayer or submonolayer. In another non-limiting example, the shell can be a perforated SiO₂ containing shell with titania in the apertures (*e.g.*, pores or channels). In yet another non-limiting example, the shell can be a perforated SiO₂/TiO₂ containing composite shell. The shell can have a porosity of 20 % to 90% or from 40 % to 70%. The shell can also have a mesoporous or macroporous structure. In a particular instance, the shell has a mesoporous structure. The shell material precursor can be obtained through chemical preparations or purchased through a commercial vendor (*e.g.* MilliporeSigma (St. Louis, Missouri, USA), Alfa-Aeaser (Ward Hill, Massachusetts, USA), and Strem Chemicals (Newburyport, Massachusetts, USA)). In general, the titania and silica sols of the present invention may be prepared by the hydrolysis and peptization of the corresponding organo-metallic compounds in an aqueous medium. Non-limiting organo-metallic compounds are tetraethyl orthotitane, tetrabutyl orthotitane or titanium tetrachloride. The silica sol components may be prepared from the corresponding silanes, such as tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), methyltriethoxysilane (MTES), methyl trimethoxysilane (MTMS), vinyl trimethoxysilane (VTMS), 3-aminopropyl trimethoxysilane (APS), gamma-methacryloxypropyltrimethoxysilane (gamma-MAPTS).

3. Etching Agents

[0053] Etching agents include any material that can selectively remove one metal oxide from the shell in the presence of other metal oxides. Etching agents can be used neat or as a solution (*e.g.*, an aqueous solution). Non-limiting examples of etching materials include hydrofluoric acid (HF), ammonium fluoride (NH₄F), the acid salt of ammonium fluoride (NH₄HF₂), sodium hydroxide (NaOH), nitric acid (HNO₃), hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), boron trifluoride (BF₃), sulfuric acid (H₂SO₄), acetic acid (CH₃COOH), formic acid (HCOOH), or any combination thereof. In certain embodiments, HCL is used to remove any aperture forming agent (*e.g.*, CTAB).

C. Preparation and Use of Core-Shell Catalysts

1. Preparation of a SiO₂/TiO₂ layered shell with a catalytic metal-containing core

[0054] In one non-limiting example, the catalysts of the present invention can be prepared by using the following steps. The catalytic metal-containing core (*e.g.*, particles of Pt, Pd, Au or Ag, or any combination thereof) can be made according to conventional alcohol or other reducing processes or purchased through a commercial vendor. In one non-limiting

embodiment, metal particles can be dispersed in an aqueous solution that has a desired metal concentration. In some embodiments, gold nanoparticles can be made through reduction of chloroauric acid with a reducing agent (*e.g.*, sodium borohydride). The metal nanostructures can be coated with titania source (*e.g.*, tetraethyl orthotitanate) and then coated with a silica source. By way of example, a solvent (*e.g.*, an alcohol such as ethanol) a surfactant (aperture former), and metal nanostructure or metal nanostructure dispersion (*e.g.*, a dispersion of gold colloidal particles having an average diameter of less than 2 nm) can be combined with agitation at 20 °C to 40 °C, or 25 °C to 35 °C. The titania precursor material (*e.g.*, TEOT or titanium tetrachloride (TiCl₄)) can be added over time to metal nanostructure dispersion with agitation. The pH of the dispersion can be adjusted by adding base or acid (*e.g.* NaOH or HCL) depending on the precursor material under agitation to form metal nanostructures having a titania-precursor coating. By way of example, if TEOT is used, the pH can be adjusted to 10 to 11.5 with NaOH. If TiCl₄ is used, acid can be added to the solution to adjust the pH to 1 to 3. To this dispersion a silica source (precursor such as TEOS) can be added (*e.g.*, incrementally) to the dispersion under agitation for a time sufficient to coat the titania-precursor coated metal nanostructures and form a silica precursor coating on the titania-precursor coated metal nanostructures. The silica source, titania source coated metal nanostructure can be isolated (*e.g.*, filtered or centrifuged), washed with deionized water and/or an alcoholic solution. The silica source, titania source coated metal nanostructure can be dried at 100 to 150 °C, 110 to 140 °C, or 115 to 130 °C, or any value or range there between or about 120 °C for a desired amount of time (*e.g.*, 1 to 10 hours, or until the water removed or about 4 hour) to form a dried silica-titania precursor shell encompassing a metal nanostructure core. This core-shell material can be etched with an etching agent (*e.g.*, HCl) to remove the surfactant. For example, the core-shell material can be dispersed in aqueous acid and agitated at 50 to 70 °C for a desired amount of time (*e.g.*, 1 to 10 hours or about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 hours) to form a porous silica-titania precursor shell encompassing the metal nanostructure core. The porous silica-titania precursor shell encompassing the metal nanostructure core can be isolated using known methods (*e.g.*, the catalyst can be centrifuged multiple time at 8000 rpm for 20 minutes each, washed with DI water) and finally dried at 100 to 150 °C, 110 to 140 °C, or 115 to 130 °C, or any value or range there between or about 120 °C for a desired amount of time (*e.g.*, 1 to 10 hours, or until the water is removed or about 4 hour). The dried precursor catalyst can be calcined at 250 to 500 °C, 300 to 450 °C, or 350 to 400 °C in air for a desired amount of time (*e.g.*, 1 to 10 hours, or about 6 hour) to convert the silica precursor and titania precursor material to silica and titania and form a porous core-shell catalyst having a catalytic metal

nanostructure core, a titania layer encompassing the core, and a silica layer encompassing the titania coated catalytic metal nanostructure core.

2. Preparation of a SiO₂ shell TiO₂ loaded in the apertures of the shell with a catalytic metal-containing core

5 [0055] In another non-limiting example, the catalysts of the present invention can be prepared by using the following steps. The catalytic metal-containing core solution as described above can be coated with silica source (*e.g.*, TEOS), etched to form apertures, and then a silica source introduced into the apertures. By way of example, a solvent (*e.g.*, an alcohol such as ethanol) a surfactant (aperture former), metal nanostructure or metal nanostructure
10 dispersion (*e.g.*, an solution of gold colloidal particles having an average diameter of less than 2 nm), and base (*e.g.*, NaOH) can be combined with agitation at 20 °C to 40 °C, or 25 °C to 35 °C. To this dispersion a silica source (precursor such as TEOS) can be added (*e.g.*, incrementally) to the dispersion under agitation for a time sufficient to coat the metal nanostructures and form a silica precursor coated metal nanostructure material. The silica
15 precursor coated metal nanostructure can be isolated (*e.g.*, filtered or centrifuged), washed with deionized water, and/or an alcoholic solution. The silica source (precursor) coated metal nanostructure can be dried at 100 to 150 °C, 110 to 140 °C, or 115 to 130 °C, or any value or range there between or about 120 °C for a desired amount of time (*e.g.*, 1 to 10 hours, or until the water is removed or about 4 hour) to form a dried silica precursor shell encompassing a
20 metal nanostructure core. This core-shell material can be etched with an etching agent (*e.g.*, HCl) to remove the surfactant. For example, the core-shell material can be dispersed in aqueous acid and agitated at 50 to 70 °C for a desired amount of time (*e.g.*, 1 to 10 hours or about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 hours). In some embodiments, the etching can be done at other temperatures for example, 5 °C to 95 °C, 10 °C to 50 °C, 15 °C to 45 °C, *etc.* The etched
25 material can then be heated to 220 to 300 °C, or 230 to 270 °C, or 240 to 260 °C, or about 250 °C for a period of time (*e.g.*, 1 to 10 hours or about 2 hours) to form a porous silica shell encompassing the metal nanostructure core. The porous silica shell/metal nanostructure core can be isolated using known methods (*e.g.*, centrifugation multiple time at 8000 rpm for 20 minutes each, washed with DI water. The heat-treated metal nanostructure core/silica shell can
30 be re-dispersed in a solvent (*e.g.*, an alcohol such as ethanol) and a solution of titanium precursor material (*e.g.*, TEOT in isopropyl alcohol) can be added to the dispersion with agitation for a desired amount of time (*e.g.*, 30 minutes to 1.5 hours or about 60 minutes) to form a core-shell material having a silica shell loaded with titania precursor material and a

metal nanostructure core. This core shell material can be dried at 80 to 130 °C, 85 to 120 °C, or 80 to 100 °C, or any value or range there between or about 90 to 95 °C for a desired amount of time (*e.g.*, 1 to 10 hours, or until the water removed or about 4 hour). The dried precursor catalyst can be calcined at 200 to 500 °C, 300 to 450 °C, or 350 to 400 °C in air for a desired amount of time (*e.g.*, 1 to 10 hours, or about 6 hour) to convert the titania precursor material in the apertures to titania and form a porous core-shell catalyst having a catalytic metal nanostructure core, and a silica layer having titania loaded in its apertures and encompassing the catalytic metal nanostructure core.

3. Preparation of a composite SiO₂ / TiO₂ shell with a catalytic metal-containing core

[0056] A titanium source (*e.g.*, tetraethyl orthotitanate) and a silica source (*e.g.*, tetraethyl orthosilicate (TEOS)) can be added to the solution. In instances where a composite layer having TiO₂ homogenized or dispersed through the SiO₂, a larger amount of the silica source as compared to the titanium source can be used. A surfactant (*e.g.*, CTAB or aperture former) can be added to the metal, titania, silica mixture and the mixture can be heated under conditions sufficient to form a silica (SiO₂)/titania (TiO₂) composite shell that encompasses the catalytic metal-containing particle(s) or alloy thereof. Such conditions can include heating the mixture to a temperature of 70 to 90 °C for about 10 to 20 hours or 16 hours. The resulting core-shell material can be separated from the mixture using known particle separation methods (*e.g.*, filtered, centrifuged or the like) and dried in an oven at 85 to 100 °C, or 90 to 95 °C to remove any solvent and/or remaining catalyst. The dried core-shell material (*e.g.*, a metal-containing core with a SiO₂/TiO₂ composite shell) can be etched with an etching agent to remove a portion of the aperture former and/or to remove at least a portion of a metal oxide (*e.g.*, the SiO₂ and/or TiO₂) from the shell to form perforations in the shell that allow reactants to transverse from outside the shell to the surface(s) of the catalytic metal-containing core. The titania can be dispersed in the SiO₂.

[0057] In the preparations above, the etching step is not preformed. In these cases, the core-shell material is calcined in an inert atmosphere (*e.g.*, a nitrogen atmosphere) at the temperatures described above. At these temperatures the surfactant carbonizes and produces carbonized particles in the shell. During the catalytic reaction with oxygen, the carbon particles can be oxidized and the oxidized carbon particles can be removed from the catalyst by dissolution in the reaction solvent.

[0058] The produced core-shell catalysts of the present invention can be used in a variety of chemical reactions. Non-limiting examples of chemical reactions include a direct oxidation of alkenes or aromatic hydrocarbons reaction. The methods used to prepare the nanoparticle core-shell catalysts can tune the size of the core, the catalytic metal particles, dispersion of the catalytic metal-containing particles in the core, the porosity and aperture size of the shell or the thickness of the shell to produce highly reactive and stable core-shell catalyst for use in a chosen chemical reaction. By way of example, the catalysts of the present invention can be positioned in a reaction zone of a reactor and contacted with oxygen, hydrogen and the alkene or aromatic hydrocarbon at temperatures known to effect oxidation. Propene can be used in an amount of 10 to 40 vol.%, or at least, equal to, or between any two of 10, 15, 20, 25, 30, 35, 40 vol%, preferably 9 to 11 vol.% or about 10 vol.%. Oxygen can be present from 1 to 15 vol.%, or at least, equal to, or between any two of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 vol%, preferably 9 to 11 vol.% or about 10 vol.%. Hydrogen can be present from 1 to 15 vol.%, or at least, equal to, or between any two of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 vol%, preferably 9 to 11 vol.% or about 10 vol.%. In reactions using alkenes, the reaction can take place in the gas phase. Reaction conditions can include temperature, GHSV, pressure, or any combination thereof. The reaction temperature can be 60 °C to 200 °C, 100 to 150 °C or at least, equal to, or between 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, and 200 °C, preferably about 120 °C. The GHSV can be 5 to 20 $\text{Nl}_{\text{gas}}/\text{mL}_{\text{catalyst}}/\text{h}$, or 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 $\text{Nl}_{\text{gas}}/\text{mL}_{\text{catalyst}}/\text{h}$, preferably about 10 $\text{Nl}_{\text{gas}}/\text{mL}_{\text{catalyst}}/\text{h}$. The reaction pressure can be 0.4 MPa to 1.2 MPa (4 to 12 bar), or at least equal to, or between any two of 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 1.0, 1.05, 1.1, 1.15, and 1.2 MPa, preferably about 0.72 MPa. In reactions using heavier alkenes or aromatic hydrocarbons, the reactions can take place in a solvent.

EXAMPLES

[0059] The present invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes only, and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize a variety of noncritical parameters which can be changed or modified to yield essentially the same results.

Example 1

(Synthesis of Gold Nanostructures)

[0060] Unsupported colloidal gold nanoparticles (Au NP) with average particles size of 2

nm were synthesized by reduction of chloroauric acid (HAuCl_4) using sodium borohydride. Au NP were prepared with the following procedure. Polyvinylpyrrolidone (PVP, MW=40,000, 8 grams obtained from MilliporeSigma, U.S.A) was dissolved in DI water (150 mL), and stirred at 600 rpm for 15 min at room temperature. HAuCl_4 solution (20 mL of 10 mM obtained from MilliporeSigma, U.S.A) was added to the PVP solution and the mixture was stirred at 600 rpm for 15 min at room temperature. The resulting solution was immersed into ice-water bath for 1 h at 0 °C (icy-water) while a stirring rate of 600 rpm was maintained. Freshly prepared ice-cooled sodium borohydride solution (NaBH_4 , 10 mL, 0.1 M, obtained from MilliporeSigma, U.S.A) was added to HAuCl_4 solution drop by drop using a syringe while stirring at 800 rpm at 0 °C. The solution turned dark red, due to Au NP formation. After the solution turned dark red, it was stirred at 800 rpm at 0 °C for 15 min. The Au NP solution was stored in refrigerator as a master batch. Au NPs of about 2 nm in diameter obtained with this procedure. The average particle size was determined using transmission electron microscopy (TEM) using a JEOL 2010F (JEOL, USA).

Examples 2A-2E

(Synthesis of Au NP core / Silica Coated Titania Loaded Shell-General Procedure)

[0061] Example 2A. Au NPs from Example 1 were coated with a SiO_2 layer. Hexadecyltrimethylammonium bromide (CTAB, 0.75 gram obtained from Acros Organics, Belgium) was dissolved in DI water (540 mL) by stirring at 600 rpm for at least 30 minutes at room temperature. Au NP stock solution (60 mL) from Example 1 was added to the solution while with agitation at 700 rpm for 5 min. Sodium hydroxide (1.50 mL 2 M NaOH) was subsequently added and the final solution was stirred at 700 rpm for 5 min.

[0062] Tetraethyl orthosilicate (TEOS, 4.80 mL, 0.933 g/mL (obtained from MilliporeSigma) was added drop by drop at 700 rpm, and the solution was stirred for 2-4 hours at room 20 to 25 °C (room temperature). The resulting suspension was centrifuged 3 times at 8000 rpm for 20 minutes each, washed with DI water in first and second rounds, and then with ethanol (EtOH) for the last round. The precipitates were collected and then dried at 90-95 °C overnight. The coating of the particle was confirmed by TEM. The coated silica with aperture former CTAB was etched with hydrochloric acid to remove the CTAB, introduce porosity to the shell expose the titania in the silica surface.

[0063] A portion of the dried precipitates were etched in HCl (0.5 M) at 40 °C in EtOH for 5 hrs at 400 rpm (4 ml solution per 0.1 g solid), was subsequently centrifuged multiple times

at 8000 rpm for 20 min each, re-dispersing and washing with DI water in first two rounds, then with IPA for the last round. The collected solid was dried at 90-95 °C, then heated to 250 °C and held for 2 hrs at the temperature. The dried powder was re-dispersed in 20 ml IPA.

[0064] TEOT (0.126 mL) was dissolved in IPA (1 mL), and was added to the dispersed slurry while being stirred at 400 rpm. The reaction mixture was held for 60 minutes. The resulting slurry was centrifuged, and dried at 90 to 95 °C, then subsequently heated up to 250 °C and held for 2 hrs. FIG. 5 shows the agglomerated core-shell catalyst after removing the CTAB and loading with titania. The bright spots are holes.

[0065] **Example 2B** was prepared using the methodology of Example 2 except that the sample was heated at 250 °C for 2 hour after coating with TEOS and then etched with HCl at 60 °C.

[0066] **Example 2C** was prepared using the methodology of Example 2 except that the sample was etched with HCl at 60 °C.

[0067] **Example 2D** was prepared using the methodology of Example 2 except that the sample was etched with HCl at 60 °C, heated at 250 °C for 2 hour, and then at 320 °C for 2 hour.

[0068] **Example 2E** was prepared using the methodology of Example 2A.

Example 3

(Synthesis of Au NP core / Titania /Silica Shell- General Procedure)

[0069] **Example 3A.** CTAB (0.375 gram) was dissolved in Au NP solution (60 mL, Example 1) and EtOH (10 ml), with agitation 600 rpm for 15 min at room temperature. TEOT (0.063 mL) was added over 5 minutes in the Au NP solution with agitation at 800 rpm. The pH was adjusted to 10-11.5 by adding NaOH (0.5 mL, 2 M) and the solution was continued to be stirred at 800 rpm for 5 minutes. TEOS (2.4 mL) was added dropwise to the solution was stirred for an additional 4 hours at room temperature. The coated catalyst was centrifuged 3 times at 8000 rpm for 20 minutes each, washed with DI water for first two rounds, and then isopropanol (IPA) for the last round. The catalyst was dried at 120 °C for 4 hours, and was then etched at 60 °C with HCl (0.5 M) for 5 hours while being stirred at 400 rpm. The catalyst was centrifuged multiple time at 8000 rpm for 20 minutes each, washed with DI water and finally dried at 120 °C. The catalyst was calcined at 300 °C in air for 6 hours.

[0070] **Example 3B.** CTAB (0.375 gram) was dissolved in Au NP solution (60 mL,

Example 1) and EtOH (10 ml), with agitation 600 rpm for 15 min at room temperature. Tetrabutyl orthotitanate (TBOT, 0.102 mL) was added over 5 minutes in the Au NP solution with agitation at 800 rpm. The pH was adjusted to 10-11.5 by adding NaOH (0.5 mL, 2 M) and the solution was continued to be stirred at 800 rpm for 5 minutes. TEOS (2.4 mL) was added dropwise to the solution, and then stirred for an additional 4 hours at room temperature. The coated catalyst was centrifuged 3 times at 8000 rpm for 20 minutes each, washed with DI water for first two rounds, and isopropanol (IPA) for the last round. The catalyst was dried at 120 °C for 4 hours, and then etched at 60 °C with HCl (0.5 M) for 5 hours while being stirred at 400 rpm. The catalyst was centrifuged multiple time at 8000 rpm for 20 minutes each, washed with DI water, and then dried at 120 °C. The catalyst was calcined at 300 °C in air for 6 hours. Table 1 lists a series of catalyst prepared using the General Procedures of Examples 2A-2E and 3A and 3B

Table 1

Sample	Ti/Si ratio	Gold usage (G or ml)				
	molar	HAuCl ₄ solution	Au NP colloids	CTAB	TEOS	TEOT
		10 mM (mL)	mL	g	mL	mL
Example 2A	4.86:100	12	60	0.75	4.8	0.126
Example 2B	4.86:100	12	60	0.75	4.8	0.126
Example 2C	2.43:100	12	120	0.75	4.8	0.034
Example 2D	2.43:100	12	120	0.75	4.8	0.029
Example 2E	4.86:100	12	120	0.75	4.8	0.126
Example 3A	2.43:100	6	60	0.375	2.4	0.063
Example 3B	2.43:100	6	60	0.375	2.4	0.102

Example 4 (Direct Oxidation of Propylene)

[0071] General Procedure. A mixture of hydrogen, oxygen, propene and nitrogen was prepared. Downstream of each reactor nitrogen was added, a fixed stream for dilution and a controlled stream for pressure regulation. These streams were similarly evenly distributed over 32 parallel reactors by means of sets of barrier capillaries. One reactor could be selected for on-line gas-phase analysis by means of GC-MS.

[0072] The catalysts were tested in catalytic cycles of 8 hours at each experimental condition. In the experiments variations were made in temperature, pressure, and propene concentration. The process conditions are listed in Table 2.

Table 2

Variable	Units	Range	Standard condition
Propene	vol%	10-40	10
Oxygen	vol%		10
Hydrogen	vol%		10
Pressure	bar	4-12	7.2
Temperature	°C	60-200	120
GHSV	Nl _{gas} /ml _{catalyst} /h	10-20	10

[0073] After each catalytic cycle, the catalysts were exposed to a regeneration step in 10% oxygen in nitrogen. During the regeneration, the reactors were heated at 10 °C/min to 300 °C, at which temperature the catalyst was kept for 2 hours to remove any deposited combustible components. After the regeneration, the reactors were cooled to the next reaction temperature, purged with nitrogen and then the next reaction cycle was started. Each catalyst was tested in one single experimental run in about 20-30 reaction cycles, in which the process conditions were varies as described in Table 2. The standard reaction conditions were repeated multiple times throughout these cycles to verify the long term stability of the catalysts.

Catalyst performance parameters

[0074] The performance of the different catalyst was evaluated in the terms of the following key parameters:

$$\text{Propene oxide yield: } Y_{PO} = \frac{F_{PO,out}}{F_{propene,in}} \cong \frac{C_{PO,out}}{C_{propene,in}}$$

This parameter can directly be correlated to the catalyst activity for the desired reaction. Even though the formal calculation of this parameter should be from the molar flows, typically this

parameter can be calculated from the concentrations at the outlet as expansion of the gas can be neglected due to the fact that the system is relatively dilute and the conversion levels are low.

$$\text{Propene oxide selectivity: } S_{PO} = \frac{F_{PO,out}}{F_{propene,in} - F_{propene,out}} \cong \frac{C_{PO,out}}{C_{propene,in} - C_{propene,out}}$$

- 5 This parameter shows the extent in which propene is converted to the desired product, compared to other products. The most common undesired side products are carbon dioxide (at high temperature due to consecutive oxidation), acrolein (for some catalysts a significant co-product, in particular at higher temperature, due to a competing reaction mechanism that is not yet properly understood) and propane (due to propene hydrogenation, typically occurring on
10 catalysts with gold particles smaller than 2 nm, not in contact with Ti)

$$\text{Propene conversion: } X_{PO} \equiv \frac{Y_{PO}}{S_{PO}} = \frac{F_{propene,in} - F_{propene,out}}{F_{propene,in}}$$

- This parameter shows the propene conversion level. This parameter is typically reported as a measure for catalyst activity, but it reflects the combined activity for both desired and undesired reactions. For catalyst selection this parameter is less relevant, but it is provided for
15 completeness and easy comparison with reported works. By definition it is directly correlated to selectivity and yield, in some graphs shown in these report the conversion and yield are shown instead of the selectivity for more convenient plotting (selectivities typically range from 70-100%, while conversion and yield typically range from 0-5 %).

- [0075] In the reaction mechanism, hydrogen is used to create a hydroperoxide species,
20 reacting with an oxygen molecule. This hydroperoxide species is used to epoxidize propene. Ideally, therefore one water molecule is produced per propene oxide. However, the hydroperoxide species can also be hydrogenated or decompose. This parameter indicates how effectively hydrogen is used in the desired reaction route compared to in other routes resulting in direct water production.

$$25 \quad \text{Hydrogen utilization: } U_{H2} = \frac{F_{PO,out}}{F_{H2,in} - F_{H2,out}} \cong \frac{C_{PO,out}}{C_{H2O,out}}$$

Catalyst stability within one cycle (extent of reversible deactivation)

- [0076] Reversible deactivation is commonly assumed to be due to either oligomer formation on Ti sites or due to consecutive oxidation of propene oxide on Ti-agglomerates. Especially for catalysts with non-isolated Ti sites this kind of deactivation is significant and forces one to
30 operate with frequent catalyst regenerations.

Long term catalyst stability (irreversible deactivation)

[0077] This parameter is primarily a measure of the sintering of the gold nanoparticles, the key process for catalyst deactivation which is not reversible.

[0078] **Hydrogen selectivity.** Hydrogen selectivity of the Example 3A catalyst was evaluated by under various testing conditions.

[0079] The Example 3A catalyst showed the highest hydrogen selectivity, indicating good interaction between gold nanoparticles and Ti sites. This catalyst showed exceptionally high hydrogen selectivity under various testing conditions as illustrated in FIG. 6. The aged catalyst showed better selectivity than the fresh catalyst, possibly due to continuously removal of the high content of residue carbon during the reaction/regeneration. High surface area of the catalyst indicated this catalyst has a thick coating of highly porous silica, which limits diffusion of all reactants and products. Within the Knudsen diffusion zone, hydrogen diffuses 4 times as fast as oxygen, 4.5 times as fast as propylene. It was noted that when the propylene concentration increased to 40%, hydrogen and propylene were near stoichiometric values at the catalyst surface. Thus, the reaction can be operated at best compositional conditions.

[0080] **Activity and Regeneration of Core-Shell Catalysts.** FIG. 7 shows consecutive experiments conducted at the standard condition a comparative sample (triangles with closed being PO yield, open being propylene conversion and triangles being hydrogen efficient) prepared according to Chen *et al.*, *Chem. Cat. Chem.*, 2013, Vol. 5. FIG. 8 shows consecutive experiments conducted at the standard condition for Example 3A catalyst for a total 20 cycles (data shown are for cycles 1, 5, 8, 16, 17, 18, 19 and 20) with closed circles being propene oxide yield, open circles being propene conversion and diamonds being hydrogen efficiency. The vertical lines indicating regenerations at 300 °C, which is a high temperature treatment for PO catalyst. The regenerations were conducted in a 10% O₂/90% N₂ flow at 300 °C. As shown in FIGS. 7 and 8, in a typical PO reaction cycle, PO reaction rate and yield decrease along with time, indicating PO product further oligomerized into heavy molecules (*e.g.*, dimers, trimers, *etc*). Without wishing to be bound by theory, it is believed that these heavy molecules do not desorb, consequently they blocked the catalyst surface, and caused propylene conversion and PO yield to decline. Compared to the comparative catalyst, the catalyst of the present invention showed substantial catalytic performance improvements over many regeneration cycles. After 20 cycles, the maximum performance was achieved. Without wishing to be bound by theory, it is believed that the comparative catalyst had a significant amount of residue carbon even with

extended calcination in air.

[0081] Although embodiments of the present application and their advantages have been described in detail, it should be understood that various changes, substitutions and alterations
5 can be made herein without departing from the spirit and scope of the embodiments as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the above disclosure, processes, machines, manufacture,
10 compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein can be utilized. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

CLAIMS

1. A supported catalyst having a core-shell structure comprising a catalytic metal-containing nanostructure core and a metal oxide support shell encompassing the catalytic metal-containing nanostructure core, wherein the shell comprises:
 - (a) a titania (TiO_2) layer encompassing the metal-containing nanostructure core and a silica (SiO_2) layer encompassing the TiO_2 layer;
 - (b) a porous composite layer comprising a SiO_2 layer with TiO_2 distributed therein, wherein the composite layer has an average aperture diameter of less than 10 nm, preferably less than 5 nm, more preferably less than 2 nm; or
 - (c) a porous SiO_2 layer encompassing the metal-containing nanostructure core having apertures loaded with TiO_2 .
2. The supported catalyst of claim 1, wherein the shell is the TiO_2 layer encompassing the metal-containing nanostructure core and the SiO_2 layer encompassing the TiO_2 layer.
3. The supported catalyst of claim 2, wherein the TiO_2 layer is a monolayer or submonolayer.
4. The supported catalyst of claim 1, wherein the shell is the porous composite layer encompassing the metal-containing nanostructure core comprising the SiO_2 layer with the TiO_2 distributed therein.
5. The supported catalyst of claim 1, wherein the shell is the SiO_2 layer encompassing the metal-containing nanostructure core having apertures loaded with the TiO_2 .
6. The supported catalyst of claim 1, wherein the metal-containing nanostructure core comprises gold or an oxide thereof and has a size of 0.5 nm to 5 nm, preferably 1 nm to 3 nm, or about 2 nm.
7. The supported catalyst of claim 1 wherein the silica layer has an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 50 nm.
8. The supported catalyst of claim 1, wherein the molar ratio of titanium to silicon (Ti:Si) at the inner surface of the shell or in the Si/Ti composite layer is from 1:5 to 1:100, preferably 1:10 to 1:50.

9. The supported catalyst of claim 1, wherein the total shell has an average thickness of 0.5 nm to 1000 nm, preferably 5 nm to 100 nm, more preferably 10 to 50 nm.
10. A method of producing a core-shell catalyst, the method comprising:
 - (a) obtaining a catalyst precursor material comprising a metal-containing nanostructure core encompassed by a silica (SiO_2) layer;
 - (b) etching the SiO_2 layer to form apertures in the SiO_2 layer;
 - (c) contacting the catalyst precursor material of step (b) with a titania (TiO_2)-precursor solution under conditions sufficient to load the TiO_2 -precursor solution in the apertures of the SiO_2 layer; and
 - (d) calcining the catalyst precursor material of step (c), preferably at 250 °C to 400 °C, to form a catalyst having a metal-containing nanostructure core encompassed by a SiO_2 layer comprising TiO_2 in the apertures of the SiO_2 layer.
11. The method of claim 10, wherein catalyst precursor material comprises a surfactant and the etching step (b) comprises:
 - (i) subjecting the catalyst precursor material to acidic conditions to remove the surfactant from the SiO_2 layer; and
 - (ii) heating the catalyst precursor material of step (i) at a temperature of 200 °C to 500 °C, or 225 to 400 °C, or about 300 °C.
12. A method of producing a core-shell catalyst, the method comprising:
 - (a) contacting a solution of a metal-containing nanostructure, a cationic surfactant, and a titania (TiO_2)-precursor material with a silica (SiO_2)-precursor material under conditions sufficient to produce a catalyst precursor material having the metal-containing nanostructure encompassed by a TiO_2 layer and a SiO_2 layer, wherein the TiO_2 layer is positioned between the metal-containing nanostructure and the SiO_2 layer;
 - (b) etching the SiO_2 layer to form apertures in the SiO_2 layer; and
 - (c) calcining the catalyst precursor material of step (b), preferably at 250 °C to 500 °C, to form a catalyst having a metal-containing nanostructure having a TiO_2 layer positioned between the core and the SiO_2 layer.

13. The method of claim 12, further comprising contacting the catalyst precursor of step (b) with an acid at a temperature of 5 to 95 °C for 1 to 10 hours.
14. The method of claim 12, wherein the TiO₂-precursor solution is basic and comprises tetraethyl orthotitanate or tetrabutyl orthotitanate, or the TiO₂-precursor solution is acidic and comprises titanium tetrachloride, and the conditions comprise a temperature of 20 to 30 °C.
15. The method of claim 12, wherein the metal-containing nanostructure comprises a gold nanoparticle.
16. The method of claim 12, further comprising drying the catalyst precursor material prior to calcining.
17. The method of claim 12, wherein the titanium to silicon (Ti:Si) molar ratio is 1:10 to 1:50, preferably 1:10 to 1:30 on the inner surface of the shell.
18. A process of oxidizing a hydrocarbon, the process comprising contacting an alkene or an aromatic hydrocarbon and an oxygen source with the catalyst of claim 1 under conditions sufficient to produce an alkene oxide or an aromatic alcohol.
19. The process of claim 18, wherein the alkene is propylene and the aromatic hydrocarbon is benzene.
20. The process of claim 18, wherein the alkene is propylene and the conditions comprise a temperature of 100 °C to 400 °C, preferably 200 °C to 300 °C.

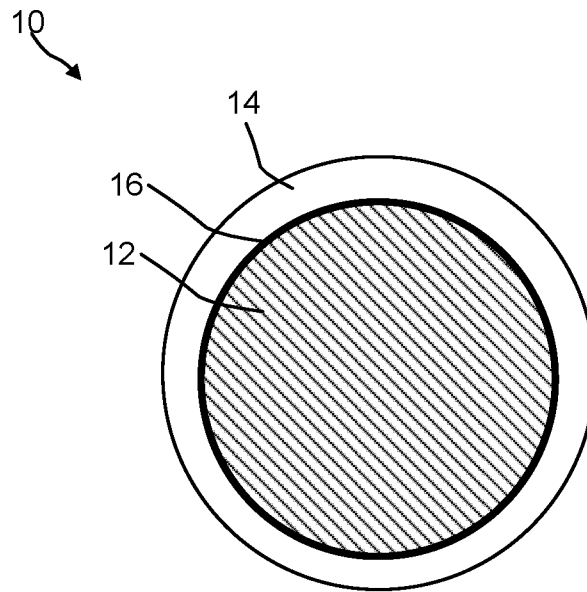
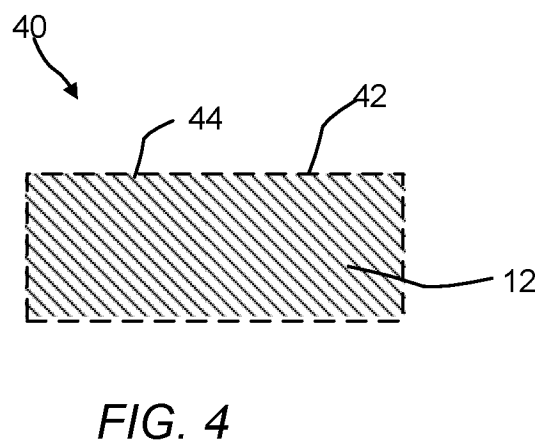
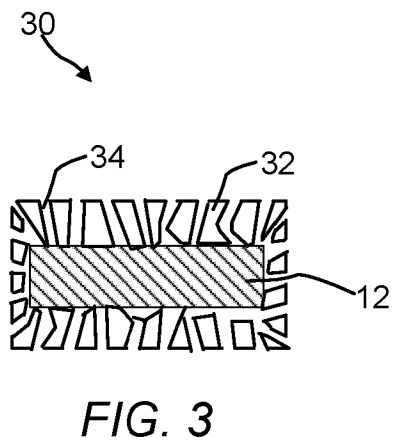
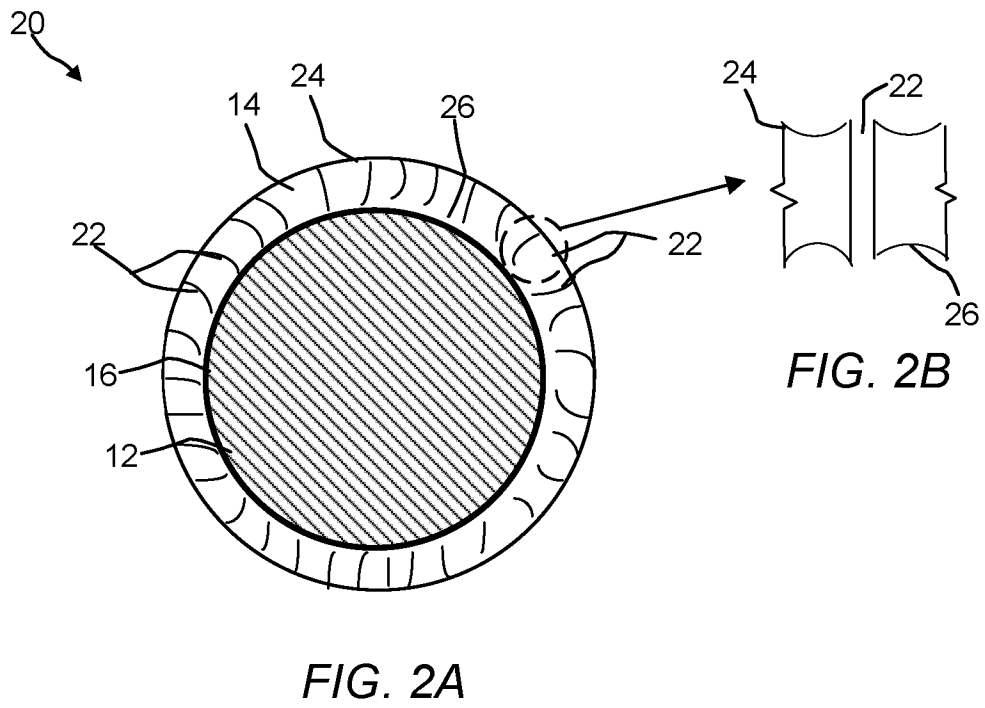
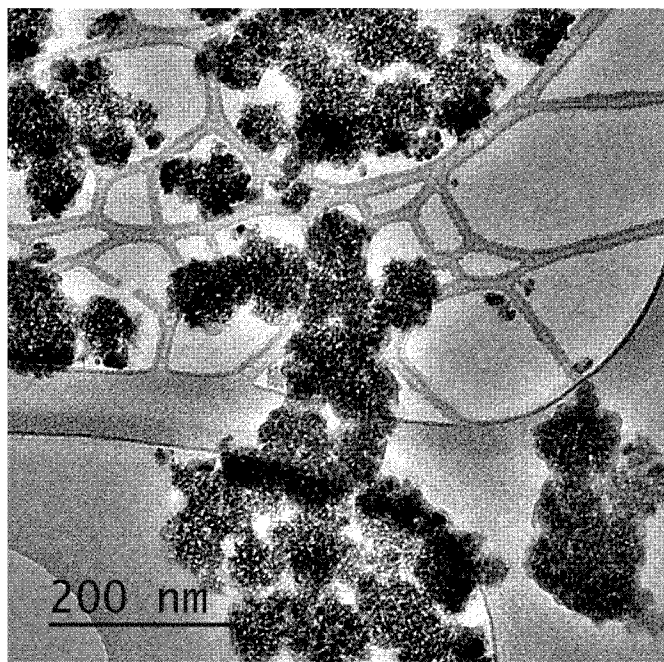
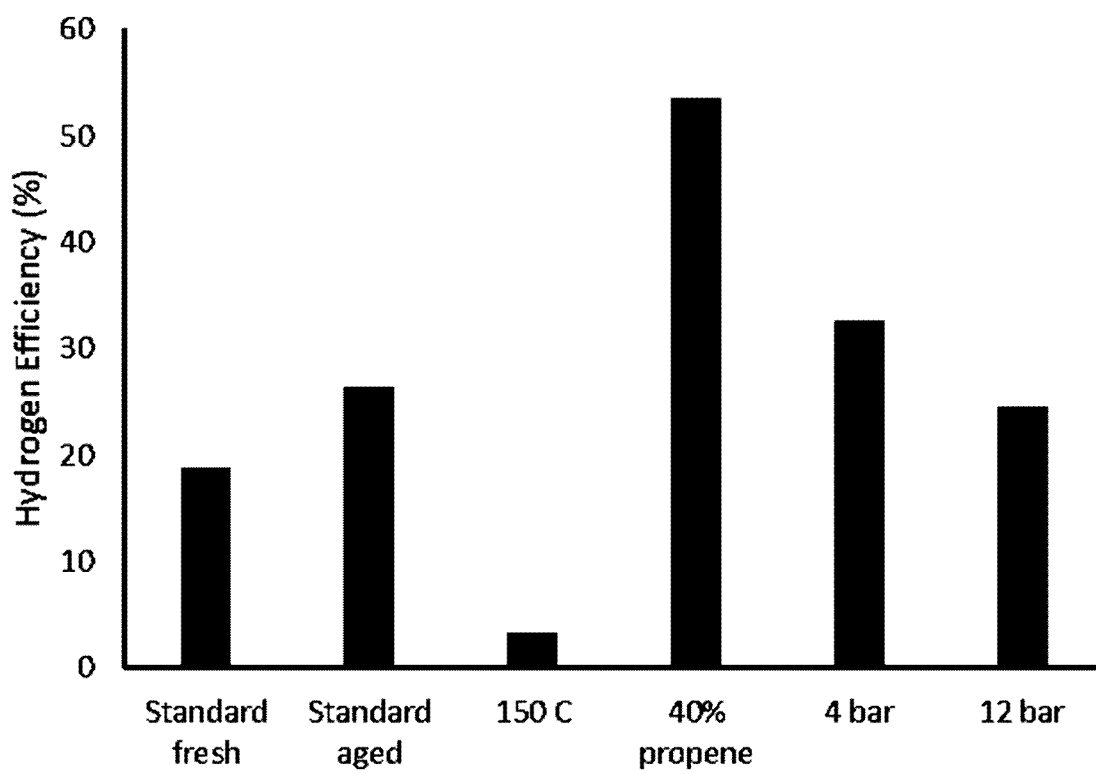


FIG. 1



*FIG. 5**FIG. 6*

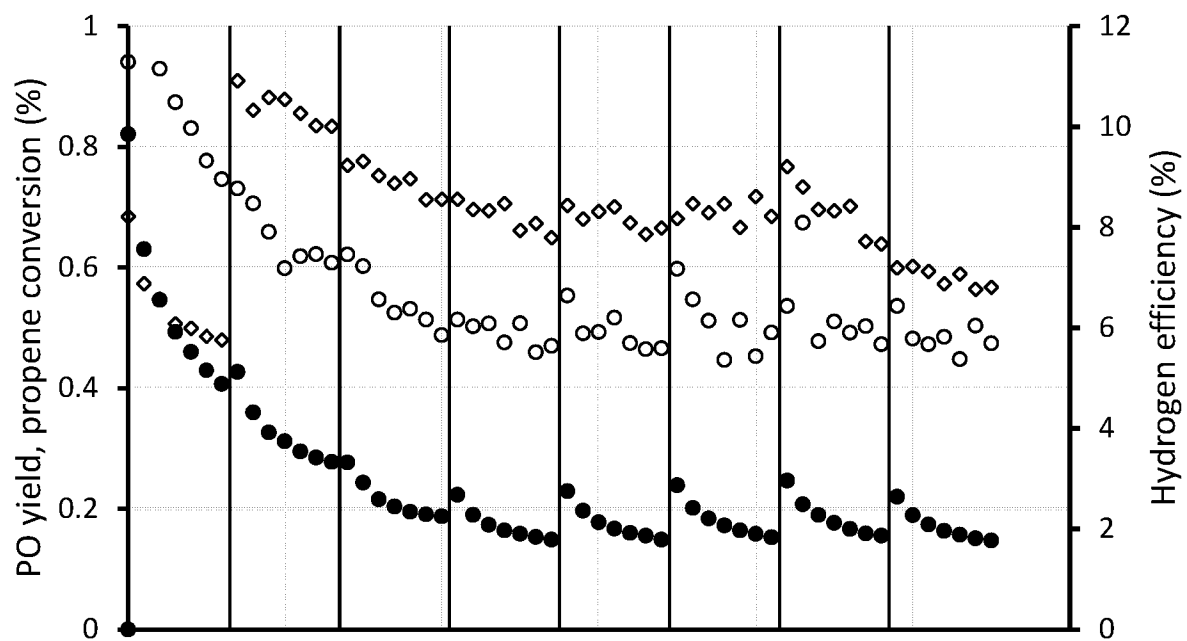


FIG. 7

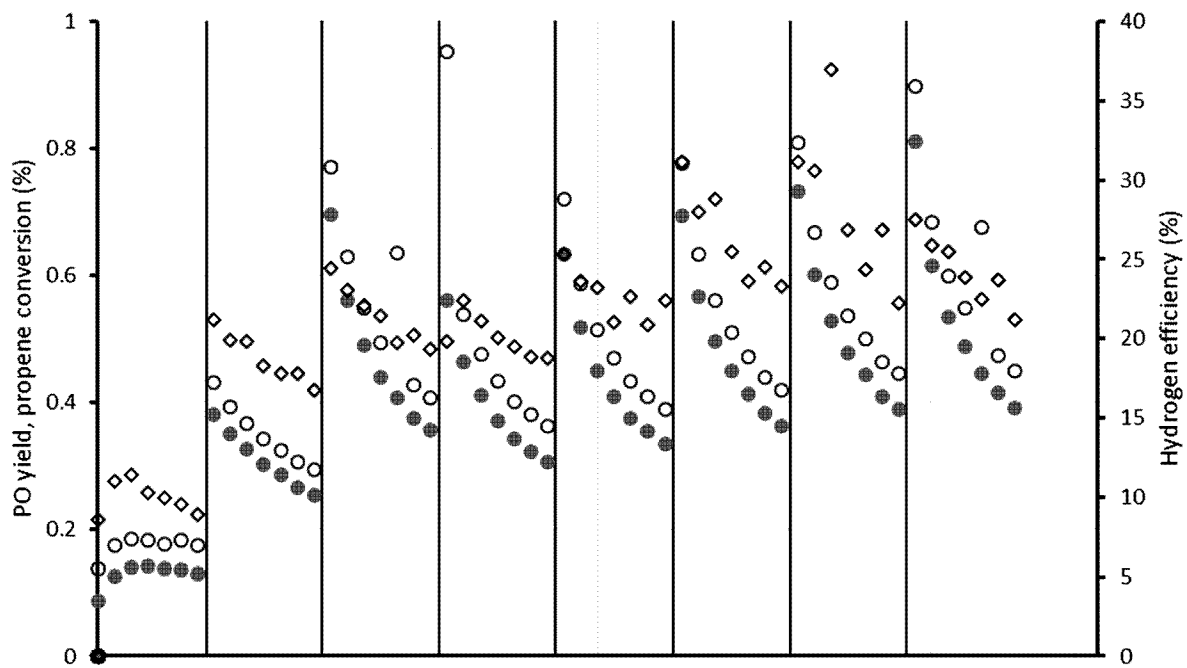


FIG. 8

A. CLASSIFICATION OF SUBJECT MATTER**B01J 35/00(2006.01)i, B01J 23/52(2006.01)i, B01J 21/06(2006.01)i, B01J 21/08(2006.01)i, C07C 5/48(2006.01)i, C07C 11/06(2006.01)i**

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)

B01J 35/00; B01J 21/08; B01J 23/52; B01J 23/89; C07C 213/02; B01J 21/06; C07C 5/48; C07C 11/06

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: core, shell, catalyst, metal, silica, titania, SiO₂, TiO₂**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104307514 A (DALIAN UNIVERSITY OF TECHNOLOGY) 28 January 2015 See paragraph [0005]; examples 1-2, 6; claims 1, 2; and table 2.	1,4,6-9,18-20
Y		2,3,12-17
A		5,10,11
Y	US 2012-0238442 A1 (LEE, KWANGYEOL) 20 September 2012 See paragraphs [0013]-[0014], [0036], [0054]-[0055]; claim 1; and figure 2.	2,3,12-17
A	WO 2017-062226 A1 (SABIC GLOBAL TECHNOLOGIES B.V. et al.) 13 April 2017 See the whole document.	1-20
A	US 2014-0171290 A1 (UMICORE AG & CO. KG) 19 June 2014 See the whole document.	1-20
A	LEKEUFACK, D. DJOUMESSI et al., "Core-shell Au@(TiO ₂ , SiO ₂) nanoparticles with tunable morphology", Chemical Communications, 2010, Vol.46, pp.4544-4546 See the whole document.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

14 June 2019 (14.06.2019)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2019/051394

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