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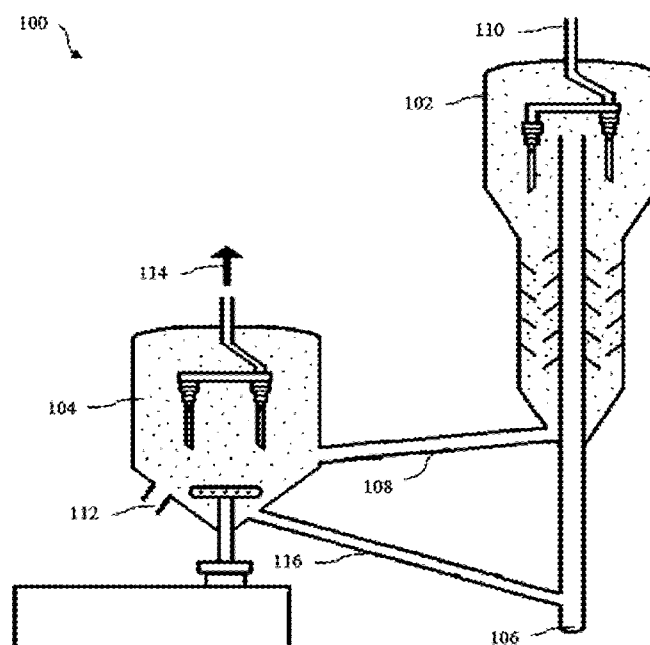


FIG. 2

(57) Abstract: Process and systems for the independent production of hydrogen ( $H_2$ ) and carbon monoxide (CO), the process comprising: (a) decomposing a hydrocarbon by (i) introducing a gaseous light hydrocarbon feed stream into a decomposition reactor having a hydrocarbon decomposition catalyst under non-oxidizing conditions, (ii) contacting gaseous light hydrocarbon feed stream with the decomposition catalyst at a temperature of 500 to 800 °C, forming  $H_2$  and a carbonized catalyst, and (iii) collecting the  $H_2$  product; and (b) contacting the carbonized decomposition catalyst with carbon dioxide ( $CO_2$ ) gas, producing CO gas and regenerating the hydrocarbon decomposition catalyst.



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TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
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**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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# THERMOCATALYTIC PROCESS FOR GENERATING HYDROGEN AND CARBON MONOXIDE FROM HYDROCARBONS

## CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent  
Application No. 62/535,525 filed July 21, 2017, which is hereby incorporated by reference  
in its entirety.

## BACKGROUND OF THE INVENTION

### A. Field of the Invention

[0002] The invention generally concerns compositions, methods, or catalysts for production  
of hydrogen (H<sub>2</sub>) and carbon monoxide (CO). In particular the compositions, methods, or  
catalysts include a bimetallic or trimetallic nanoparticle and a hollow zeolite support.

### B. Description of Related Art

[0003] The demand for hydrogen is increasing because it is being used in hydro-treating  
processes in the petroleum industry and also for hydrogen fuel cells. Since hydrogen is a non-  
polluting fuel, its use as a fuel has been increasing rapidly, particularly for fuel cells.

[0004] The main natural sources of hydrogen are hydrocarbons and water. Among the  
hydrocarbons, methane has the highest hydrogen to carbon ratio. Conventional processes for  
the production of hydrogen are based on steam reforming of hydrocarbons, such as naphtha  
and methane or natural gas, and auto thermal reforming of hydrocarbons, particularly heavier  
hydrocarbons. These processes can use nickel, cobalt or iron metal particles impregnated on  
silica. Peña *et al.* (*Applied Catalysis A: General*, 1996, 144:7-57) provides a review of  
hydrogen production using steam reforming and auto thermal reforming. Both the hydrocarbon  
steam reforming and auto thermal reforming processes are typically operated at high  
temperatures, above about 900 °C, and the product stream of these processes contains  
appreciable amounts of carbon monoxide along with hydrogen. These processes suffer in that  
removal of carbon monoxide at low concentrations from hydrogen has a high economic impact.  
Hence, the hydrocarbon steam reforming and auto thermal reforming processes are not  
economical for the production of carbon monoxide-free hydrogen. Thus, there is a practical  
need to develop a process for the production of hydrogen from methane at temperatures lower  
than that used in the conventional hydrocarbon steam reforming and auto thermal reforming  
processes.

[0005] A few processes are known for the production of carbon monoxide-free hydrogen from methane. Kikuchi (*CATTECH*, 1997, March 67-74) describes a process based on steam reforming of methane in a membrane reactor to produce hydrogen free of carbon monoxide. By applying a Pd/ceramic composite membrane to steam reforming of methane over a commercial supported nickel catalyst, methane conversion up to 100 percent can be accomplished in a Pd-membrane reactor at temperatures as low as 500 °C to produce carbon monoxide-free hydrogen. In this process, the hydrogen produced in the steam reforming of methane is continuously removed from the reaction system by the selective permeation of hydrogen through the Pd-membrane. However, this process has the following drawbacks/limitations: (1) the capital cost of this process is economically undesirable due to the use of a number of Pd-membrane tubes; (2) deactivation of the Pd-membrane due to deposition of carbonaceous matter; and (3) membrane stability and/or a possibility of membrane failure due to formation of pinholes in the membrane.

[0006] U.S. Patent No. 6,509,000 to Choudhary *et al.* describes a process for the continuous production of hydrogen from methane and/or natural gas and/or methane-rich hydrocarbons and steam at low temperature, using a solid transition metal catalyst without deactivation of the catalyst by carbon deposition or coking using a two reactor system. The catalyst in both reactors are reduced. The reduced catalyst in the first reactor is contacted with a hydrocarbon stream and the reduced catalyst in the second reactor is contacted with a stream that include water. No carbon monoxide is produced in this reaction

[0007] Choudhary *et al.* (*Catalysis Letter*, 1999, 59:93-94) reported a process for the production of carbon monoxide-free hydrogen involving stepwise methane steam reforming. In this process, a methane pulse and a water pulse are alternately passed over a pre-reduced nickel-based catalyst at 375 °C. When the methane pulse is passed over the catalyst, the methane from the pulse is decomposed to hydrogen and carbon, leaving the carbon deposited on the catalyst. When the water pulse is passed over the catalyst with the carbon deposited on it, the carbon on the catalyst reacts with steam to form carbon dioxide and hydrogen. In some cases, the products of the above reaction are also accompanied by an amount of unreacted methane. In this process, although the carbon monoxide-free hydrogen is produced by catalytic cracking of methane and the carbon deposited on the catalyst is removed by the cyclic operation of the methane and water pulses in the same reactor, the process is not operated in the steady state and the hydrogen produced is not continuous. Hence, it is not practical and also not

economical to produce carbon monoxide-free hydrogen on a large scale by this transient process involving cyclic operation of methane and water pulses.

[0008] U.S. Patent No. 7,001,586 to Wang *et al.* describes a method for decomposing methane to hydrogen and carbon with substantially no carbon oxides produced at a temperature of 425 °C to 625 °C using a  $\text{Ni}_x\text{Mg}_y\text{O}$  catalyst. This process suffers in that the methane conversion was below 40%.

[0009] Because of the above-mentioned drawbacks and limitations of the prior art processes, there is a need for developing a process for the continuous production of carbon monoxide-free hydrogen by catalytic decomposition of methane or natural gas at a temperature while addressing the carbon build-up on the catalyst.

### **SUMMARY OF THE INVENTION**

[0010] The catalyst, systems, and methods of the current invention provide a solution to the efficiency and reaction condition problems associated with the prior art methods for production of hydrogen. The discovery is premised on a process to continuously produce hydrogen and carbon monoxide independently, which results in a process that reduces the carbon dioxide emission during the production of hydrogen and produces carbon monoxide from hydrocarbons. Other aspects of the invention are directed to, or include, a catalyst that includes a bimetallic ( $\text{M1M2}$ ) or trimetallic ( $\text{M1M2M3}$ ) nanoparticle, or oxides thereof, in a hollow zeolite support.

[0011] In certain aspects of the invention processes, incorporating independent production of hydrogen ( $\text{H}_2$ ) and carbon monoxide ( $\text{CO}$ ) are described. The process can include a hydrocarbon decomposition step and a catalyst regeneration step. The hydrocarbon decomposition step can include (i) introducing a light hydrocarbon/nitrogen gas feed source into a decomposition reactor having a decomposition catalyst under non-oxidizing conditions, (ii) contacting light hydrocarbon with the decomposition catalyst at a temperature of 500 to 800 °C forming  $\text{H}_2$  and a carbonized catalyst, and (iii) collecting the  $\text{H}_2$  product. The catalyst regeneration step can include contacting the carbonized catalyst with carbon dioxide ( $\text{CO}_2$ ) gas producing carbon monoxide ( $\text{CO}$ ) gas and regenerating the catalyst.

[0012] The light hydrocarbon gas feed can include  $\text{C1}$  to  $\text{C5}$  gaseous hydrocarbons. In certain aspects, the light hydrocarbon gas is natural gas. In particular aspects, the light hydrocarbon in the gaseous hydrocarbon feed is 50 vol.% to 100 vol.% methane. In some embodiments, the gaseous light hydrocarbon feed can include an inert gas (*e.g.*, nitrogen, argon, helium, *etc.*). When an inert gas is included, the gaseous light hydrocarbon feed can have a

hydrocarbon to nitrogen volume ratio of 1000:1 to 10:1, including all values and ranges there between. In certain aspects, light hydrocarbon/nitrogen gas feed can have a hydrocarbon to nitrogen volume ratio of 200:1 to 50:1, including all values and ranges there between. In particular aspects, the light hydrocarbon/nitrogen gas feed can have a hydrocarbon to nitrogen volume ratio of 90:10 to 95:5, including all values and ranges there between.

**[0013]** In certain aspects the decomposition catalyst can include a metal. The decomposition catalyst can include two or more metals from Columns 7-12 of the Periodic Table or alloys thereof. Non-limiting examples of catalytic metals can include iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), and platinum (Pt). In certain aspects, the decomposition catalyst includes at least two of Ni, Fe, or Co or alloys thereof. In a preferred aspect, the decomposition catalyst includes Ni. The decomposition catalyst can be a hollow zeolite catalyst. In certain aspects, the catalyst can include a bimetallic or trimetallic nanoparticle. The Ni nanoparticles can be encapsulated in the hollow portion of a hollow silicate-1 support. In some embodiments, the decomposition catalyst is a hollow zeolite catalyst, pyrochlore catalyst, a spinel catalyst, an olivine catalyst, or a combination thereof

**[0014]** Certain embodiments of the invention are directed to a single reactor system for independent production of H<sub>2</sub> and CO. The single reactor system can include a reactor having (a) at least one inlet that is configurable as a gaseous light hydrocarbon inlet or a carbon dioxide (CO<sub>2</sub>) inlet; (b) at least one outlet that is configurable as (i) an H<sub>2</sub> outlet or (ii) a CO outlet; and (c) a decomposition catalyst contained within the reactor. The reactor can be configured for hydrocarbon decomposition producing H<sub>2</sub> or catalyst regeneration producing CO. The reactor can be cycled from a hydrogen decomposition configuration to a carbon monoxide generation configuration. The decomposition catalyst can be a decomposition catalyst as described herein. In a preferred embodiment, the catalyst is a Ni metal nanoparticle positioned in a hollow portion of a hollow zeolite.

**[0015]** Certain embodiments are directed to a two reactor system configured for independent production of hydrogen and carbon monoxide. The two reactor system can include a methane decomposition reactor having a feed source inlet, a decomposition catalyst capable of catalyzing the production of hydrogen, a carbonized decomposition catalyst outlet, and a fresh catalyst inlet. The carbonized decomposition catalyst outlet can be connected to a carbon monoxide generating reactor. A carbon monoxide generating reactor can have a carbon dioxide inlet, a carbonized decomposition catalyst inlet, and a fresh catalyst outlet, where the

carbon monoxide generating unit is connected to the decomposition reactor and configured to receive carbonized decomposition catalyst from the decomposition reactor and to provide fresh catalyst to the decomposition reactor. The decomposition catalyst can be as described herein and in particular can be a Ni, Fe, and/or Co hollow zeolite catalyst. In some embodiments, the catalyst can be a pyrochlore catalyst, olivine catalyst, or a spinel catalyst. The catalyst can include a metallic, bimetallic or trimetallic component or nanoparticle metals, where the nanoparticles is encapsulated in a hollow zeolite support. In certain aspects, the decomposition catalyst is a Ni, Fe, and/or Co hollow zeolite catalyst, a Ni, Fe, and/or Co pyrochlore catalyst, a Ni, Fe, and/or Co olivine catalyst, a Ni, Fe, and/or Co spinel catalyst, or a combination thereof

**[0016]** 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 embodiments of the invention that are applicable to all aspects of the invention. It is contemplated that any embodiment discussed herein can be 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.

**[0017]** The following includes definitions of various terms and phrases used throughout this specification.

**[0018]** 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%.

**[0019]** 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.

**[0020]** The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

**[0021]** 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.

[0022] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0023] 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.”

[0024] 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.

[0025] The methods, systems, and 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 methods, systems, and catalysts the present invention are their abilities to produce CO free hydrogen stream from the reforming of light hydrocarbons.

[0026] Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0027] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of the specification embodiments presented herein.

[0028] **FIG. 1** is an illustration of one embodiment of a system and process for H<sub>2</sub> and CO production.



[0029] FIG. 2 is a schematic diagram for a double bed fluidized reactor system for hydrocarbon decomposition and catalyst regeneration.

[0030] FIG. 3 is an illustration of CH<sub>4</sub> in contact with active Ni metal on the surface of a support and the coking of the active Ni metal during the process of reaction.

5 [0031] FIG. 4 is an illustration of a hollow zeolite encapsulated Ni catalyst. During the reaction carbon can be trapped in hollow zeolite.

[0032] FIGS. 5A-B are composition plots versus time on stream (TOS) as determined by mass spectrometry for (5A) composition of the outlet gas during H<sub>2</sub> production in 3 cyclic injection of CH<sub>4</sub>, and (5B) composition of the outlet gas during CO production in 3 cyclic  
10 injection of CH<sub>4</sub>.

[0033] FIGS. 6A-C are transmission electron microscopy (TEM) images of a hollow zeolite (HZ-1) at different magnifications: a (50 nm), b (100 nm), and c (200 nm).

[0034] FIG. 7 are nitrogen isothermal plots of the HZ-1 and silicate-1.

### **DETAILED DESCRIPTION OF THE INVENTION**

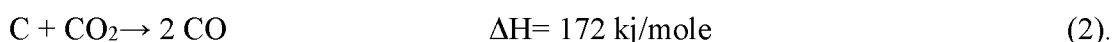
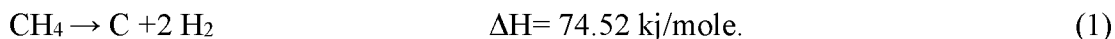
15 [0035] The present invention provides systems, processes, and catalysts for production of hydrogen and carbon monoxide from a hydrocarbon feed stream. The processes described herein are efficient and streamlined processes that reduce carbon dioxide emissions during production of hydrogen and produce carbon monoxide from a carbonized catalyst. This alternative to the conventional processes of hydrocarbon decomposition is a two-step thermo-  
20 catalytic decomposition and regeneration process (TCD) for decomposing hydrocarbons into hydrogen and carbon monoxide. Due to the absence of oxidants (*e.g.*, H<sub>2</sub>O, CO<sub>2</sub>, and/or O<sub>2</sub>) during the methane decomposition process, no carbon oxides are formed, thus obviating the need for water gas shift and CO<sub>2</sub> removal stages, which significantly simplifies the process.

[0036] These and other non-limiting aspects of the present invention are discussed in further  
25 detail in the following sections with reference to various figures. The systems and methods described can also include various equipment that is not shown and is known to one of skill in the art of chemical processing. For example, controllers, piping, computers, valves, pumps, heaters, thermocouples, and/or pressure indicators may not be shown.

#### **A. Generation of Hydrogen and Carbon Monoxide**

30 [0037] The production of carbon oxides free hydrogen can be advantageous in terms of environmental and economic aspects. Furthermore, the conventional methods used for

hydrogen production involve multistep operations and are not commercially viable; in contrast to the methods described herein. The systems and processes described herein result in production of graphitic or filamentous carbon along with hydrogen. The carbon can be independently gasified with CO<sub>2</sub> to form further value added CO which ultimately can be used in the synthesis of chemicals like methanol, acetic acid, or formic acid. The catalytic decomposition of methane is shown in reaction equation 1 and the carbon regeneration is shown in reaction equation 2.



**[0038]** A non-limiting example of a hydrocarbon decomposition system and process is illustrated in FIG. 1. System 100 can include a decomposition reactor (DR) 102 and catalyst regeneration reactor 104. Feed stream 106 that includes light C1 to C5 hydrocarbons (*e.g.*, methane, propane, butane, pentane, preferably methane) can enter DR 102, which contains a hydrocarbon decomposition catalyst of the present invention (*e.g.*, a methane decomposition catalyst). In DR 102, the gaseous light hydrocarbons in feed stream 106 can be contacted with the hydrocarbon decomposition catalyst and be decomposed into H<sub>2</sub> and elemental carbon (C), where the carbon is deposited on the decomposition catalyst forming a carbonized catalyst and hydrogen stream 110. Hydrogen stream 110 can include less than 1 mol.% of CO or substantially no CO. Hydrogen stream 110 can exit DR 102 and be collected or transported to other processing units. The H<sub>2</sub> produced can have a H<sub>2</sub> purity of at least 90 mol.% with the balance being inert gases. Carbonized catalyst stream 108 can exit DR 102 and enter catalyst regeneration reactor 104. Carbon dioxide stream 114 can enter catalyst regeneration reactor 104. In catalyst regeneration reactor 104, the carbonized catalyst in carbonized catalyst stream 108 can be contacted with carbon dioxide stream 110 under conditions that generate a CO stream 114 and a regenerated catalyst. Regenerated catalyst 116 stream can exit catalyst regeneration reactor 104 and enter DR 102 to continue the cycle. CO stream 114 can exit catalytic regeneration reactor 104 and be collected or transported to other processing units. Conditions sufficient to generate H<sub>2</sub> and/or CO can include temperature, pressure, flow rates, and time. Temperatures in DR 102, catalyst regeneration reactor 104, or both can be equal to, or between any two of, 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, 775 °C, 800 °C, 825 °C, 850 °C, 875 °C, 900 °C, 925 °C, 950 °C, 975 °C, 1000 °C, 1025 °C, 1050 °C, 1100 °C. Pressure of DR 102, catalytic regeneration reactor 104 or both can be equal to, or between any two of, 0.5 MPa, 1 MPa, 1.5 MPa, 2 MPa,

2.5 MPa, 3 MPa, 3.5 MPa, 4 MPa, 4.5 MPa, 5 MPa, 5.5 MPa, 6 MPa, 6.5 MPa, 7 MPa, 7.5 MPa, 8 MPa, 8.5 MPa. As depicted in FIG. 1, one embodiment is a two reactor system with the catalytic material being fluidized and transferred between reactors.

**[0039]** In certain aspects, the catalytic conversion systems include two separate reaction zones allowing for separations in two separate reactions that are connected by a stream of solid catalytic material, whereby the gas streams can be essentially prevented from mixing. The chamber(s) can be defined as individual chambers where one chamber produces a first gas and a physically separate chamber produces a second gas. In some embodiments, the system can be a single chamber system where a chamber is time demarcated, that is a single chamber produces a first gas under a first set conditions over a first time period and the same chamber produces a second gas under a second set conditions over a second time period. Certain aspects include a fluidized or moving bed catalytic conversion system(s), *i.e.*, the solid phase includes the decomposition catalyst. A “fluidized bed system” refers to a system that is configured to transport solids, *e.g.*, the catalyst. The system can include devices for separating solids from an outflowing gas stream (such as a centrifugal or gravity separator assembly). Such systems, single or two chamber systems, can be configured and used for decomposing a light hydrocarbon stream, such as a methane containing stream, and regenerating a carbonized catalyst producing carbon oxides free hydrogen product stream and a carbon monoxide product stream. The two step decomposition and catalyst regeneration process can be performed in a system designed to generate a continuous supply of H<sub>2</sub> and CO.

**[0040]** Embodiments of the present invention provide methods for continuous production of H<sub>2</sub> and CO, an example of which is illustrated in FIG. 2, which is a more detailed version of FIG. 1. Referring to FIG. 2, the decomposition catalyst of the present invention (*e.g.*, a metal encapsulated hollow silicate catalyst or bulk form active metal catalyst) can be loaded into catalyst regeneration reactor 104. A mixture of nitrogen and hydrogen at a gas hourly space velocity (GHSV) of 5000, 7500, 10000, 12500 to 15000 h<sup>-1</sup> (including all values and ranges there between) can be provided to the reactor at 500, 525, 550, 575, 600, 625, 650, 675, 700, 725, 750, 775 to 800 °C, including all values and ranges there between, to produce an active decomposition catalyst. The pressure of the catalyst regeneration unit 104 can be equal to, or be between two of, 0.1 MPa, 1 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa, 25 MPa, 30 MPa, 40 MPa, to 50 MPa. In some embodiments, the pressure can be 0.1 MPa to 40 MPa. In particular aspects, the pressure can be 0.1 MPa to 30 MPa. The active catalyst can be provided to DR 102. In some embodiments, catalyst is positioned in both reactors and activated as described

above. A mixture of gaseous hydrocarbon feed stream 102 that includes hydrocarbon (*e.g.*, methane) gas and optionally inert gas (*e.g.*, nitrogen) can enter DR 102 at 500, 525, 550, 575, 600, 625, 650, 675, 700, 725, 750, 775 to 800 °C, including all values and ranges there between and GHSV of 5000, 7500, 10000, 12500 to 15000 h<sup>-1</sup>. The molar ratio of hydrocarbon to optionally inert gas (nitrogen) being from 0.5, 0.6, 0.7, 0.8, 0.9, to 1 including all values and ranges there between. In DR 102, contact of the hydrocarbon with the decomposition catalyst can produce H<sub>2</sub> and carbonized or coked catalyst. The pressure of the DR 102 can be equal to, or be between two of, 0.1 MPa, 1 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa, 25 MPa, 30 MPa, 40 MPa, to 50 MPa. In some embodiments, the pressure can be 0.1 MPa to 40 MPa. In particular aspects the pressure can be 0.1 MPa to 30 MPa.

**[0041]** FIG. 3 and FIG. 4 illustrate the coking of a surface metal catalyst and a hollow silicate catalyst, respectively. Referring to FIG. 3, a schematic for deactivation of a conventional catalyst having the metal impregnated on a support surface (SiO<sub>2</sub>) due to coking. During the decomposition process, metal particles may be lifted up from the catalyst surface and taken away on top of the growing carbon fibers by process called “tip growth” mode. Alternatively, the metal particles may stay on the surface, leading to the “base growth” mode. Using a metal@hollow zeolite catalyst as shown in FIG. 4, the metal particles within the hollow cavity are bigger than the pore size of the zeolite, thus, the particle can be trapped and the deactivation process can be inhibited or prevented. Furthermore, In other hand, the coke which surrounds the active site, is confined within the hollow portion, and the regeneration is facilitated by such confinement. When a bulk metal catalyst (*e.g.*, a catalyst formed by incorporating the metal in the crystal lattice) is used, incorporation of the catalytic metal in the crystal lattice can inhibit leaching or removal of the metal.

**[0042]** The hydrogen product stream 110 can exit MDR 102 during the process and can be collected and/or stored. The product stream of the MDR can include at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, H<sub>2</sub>, or be greater than, equal to or between two of 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100 mol%.

**[0043]** Coked catalyst 108 can enter regeneration or CO-generation reactor, *e.g.*, by fluidization using a carrier gas, or the decomposition reactor conditions can be changed to regeneration conditions. Any fresh catalyst in the CO generation reactor can be directed to, or transferred into, the decomposition reactor. In certain aspects, the transfer of the catalyst is a continuous process with reactions occurring while the regenerated catalyst is transiting to the DR 102 unit and/or the coked catalyst is transiting to the regeneration unit 104. Transfer of the

catalyst can be aided with a carrier gas such as an N<sub>2</sub> carrier gas. CO<sub>2</sub> feed stream 112 can be introduced to the CO generator reactor oxidizing the coke in the catalyst to CO. In some embodiments, CO<sub>2</sub> containing feed 112 can be introduced into the CO generation reactor, the reactor being at a temperature of 500, 525, 550, 575, 600, 625, 650, 675, 700, 725, 750, 775 to 800 °C, including all values and ranges there between, producing CO and regenerated catalyst. The pressure of the CO generation unit 104 can equal to, or be between any two of 0.1 MPa, 1 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa, 25 MPa, 30 MPa, 40 MPa, to 50 MPa. In some embodiments, the pressure can be 0.1 MPa to 40 MPa. In particular aspects, the pressure can be 0.1 MPa to 30 MPa. CO stream 114 can be exit reactor 104 and collected separately and/or stored. A continuous flow of H<sub>2</sub> and CO can be generated by running simultaneously the decomposition reaction and carbon regeneration reaction. The product stream of the CO-generation reactor can include at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, CO, or be greater than, equal to or between two of 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100 mol%.

**[0044]** Conditions sufficient to generate H<sub>2</sub> or CO can include temperature, pressure, flow rates, and time. Temperatures in the H<sub>2</sub> or CO production zone can be equal to, or between any two of, 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, 775 °C, 800 °C, 825 °C, 850 °C, 875 °C, 900 °C, 925 °C, 950 °C, 975 °C, 1000 °C, 1025 °C, 1050 °C, 1100 °C. Pressure of reactor(s) or chamber(s) can be equal to, or between any two of, 0.5 MPa, 1 MPa, 1.5 MPa, 2 MPa, 2.5 MPa, 3 MPa, 3.5 MPa, 4 MPa, 4.5 MPa, 5 MPa, 5.5 MPa, 6 MPa, 6.5 MPa, 7 MPa, 7.5 MPa, 8 MPa, and 8.5 MPa. Regenerated hydrocarbon decomposition catalyst can exit CO generation unit *via* a regenerated catalyst outlet and enter the hydrocarbon decomposition unit *via* regenerated/catalyst inlet. In some embodiments, regenerated hydrocarbon decomposition catalyst can be mixed with a stream of fresh hydrocarbon decomposition catalyst prior to entering the hydrocarbon decomposition unit.

## **B. Reactants**

### **1. Catalyst**

**[0045]** Certain embodiments of the invention address problems involving catalyst deactivation. Methods are directed to a process for preparation of a catalyst composition for the decomposition of lower hydrocarbons or a light hydrocarbon stream.

**[0046]** The hydrocarbon decomposition catalyst used in a hydrocarbon decomposition reactor or chamber can be a hollow zeolite catalyst, a bulk-metal catalyst, or mixtures thereof.

Non-limiting examples of a bulk-metal hydrocarbon decomposition catalyst include a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof. The catalyst can include two or more catalytic metals from Columns 7-12 of the Periodic Table. Non-limiting examples of the metals include manganese (Mn), palladium (Pd), platinum (Pt), gold (Au), rhodium (Rh), ruthenium (Ru), rhenium (Re), osmium (Os), iridium (Ir), iron (Fe) silver (Ag), copper (Cu), nickel (Ni), zinc (Zn), or any combinations or alloys thereof. In some embodiments, the catalytic metals can include 1, 2, 3, 4, 5, 6, or more metals. In a preferred embodiment, the catalyst is a Ni/hollow zeolite catalyst. In another embodiment, the catalyst is a Ni-Mn-Si oxide olivine catalyst. In some embodiments, the invention can include a catalyst that includes a M1, a M1M2, or a M1M2M3 nanoparticle, oxides, or alloy thereof, and a hollow zeolite support. The hollow space in the zeolite support can include the catalytic metal nanoparticle, or oxides, or alloy thereof. As previously described, the catalyst of the present invention used in the hydrocarbon decomposition reaction can overcome the deactivation problems suffered by conventional hydrocarbon decomposition reactions and be easily regenerated.

**[0047]** 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, metal oxide 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), or chloroplatinic acid hexahydrate. Metal oxides include silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ), zirconia ( $\text{ZrO}_2$ ), germania ( $\text{GeO}_2$ ), stannic oxide ( $\text{SnO}_2$ ), gallium oxide ( $\text{Ga}_2\text{O}_3$ ), zinc oxide ( $\text{ZnO}$ ), hafnia ( $\text{HfO}_2$ ), yttria ( $\text{Y}_2\text{O}_3$ ), lanthana ( $\text{La}_2\text{O}_3$ ), ceria ( $\text{CeO}_2$ ), manganese oxide ( $\text{MnO}$ ), nickel oxide ( $\text{NiO}$ ), or any combinations or alloys thereof. The metal or metal oxide nano- or microstructures can be stabilized with the addition of surfactants or templating agents (*e.g.*, tetrapropylammonium hydroxide (TPA(OH)), cetyl trimethyl ammonium bromide (CTAB), polyvinylpyrrolidone (PVP), *etc.*) and/or through controlled surface charge. These metals or metal compounds can be purchased from any chemical supplier such as Sigma-Aldrich (St. Louis, Missouri, USA), Alfa-Aeaser (Ward Hill, Massachusetts, USA), and Strem Chemicals (Newburyport, Massachusetts, USA).

**[0048]** The hollow zeolite catalyst of the present invention can have a Si to Al (Si:Al) ratio of great than, equal to, or between two of: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100. In a preferred embodiment, the hollow zeolite material is an MFI zeolite such as silicalite-1 (Si:Al = infinity).

5 **[0049]** The catalysts can be prepared by processes known to those having ordinary skill in the art, for example the catalyst can be prepared by any one of the methods comprising liquid-liquid blending, solid-solid blending, or liquid-solid blending (*e.g.*, any of precipitation, co-precipitation, impregnation, complexation, gelation, crystallization, microemulsion, sol-gel, solvothermal, hydrothermal, sonochemical, or combinations thereof).

10 **[0050]** In embodiments when the metal hollow zeolite catalysts of the present invention is used, it can be prepared by impregnation of any of the above mentioned metals, metal oxides, or mixtures thereof, followed by drying and further heating in the presence of a quaternary ammonium salt or amines. Non-limiting examples of quaternary ammonium salts include tetrapropylammonium hydroxide (TPAOH), tetraethylammonium hydroxide (TEAOH),  
15 tetramethylammonium hydroxide (TMAOH), hexadecyltrimethylammonium hydroxide, dibenzyltrimethylammonium hydroxide, benzyltriethylammonium hydroxide, and cetyltrimethylammonium hydroxide or alkyl derivatives thereof. Non-limiting examples of amines include, diisopropylamine (DIPA), diisopropylethylamine (DIPEA), morpholine, piperidine, pyrrolidine, diethylamine (DEA), triethylamine (TEA), or alkyl derivatives thereof.

20 Heating the metal loaded zeolite in the presence of a quaternary ammonium salts and/or amines can affect the resultant crystal morphology (size, shape, dispersion, surface area, distribution), and thus the activity of the zeolite catalyst formed. The pH of the solution can be adjusted to assist in the dissociation of the counter ion (*e.g.*, nitrate, oxalate, chloride, sulfide, *etc.*) from the metal oxide. Without wishing to be bound by theory, it is believed that the heating the  
25 metal loaded zeolite in the presence of the hydroxide salt can preferentially dissolve the silica in the zeolite structure. The treated zeolite and/or hollow zeolite can have an increased surface area, increased micropore surface area, an increased surface Si/Al ratio, and an increased amount of strong acid sites, all of which facilitating hydrogen transfer reactions. The quaternary ammonium salts and/or amines can be mixed or suspended with the metal  
30 impregnated zeolite catalyst from 1 ml/g zeolite to 6 ml/g zeolite, or from 3 ml/g zeolite to 5 ml/g zeolite and all value there between including about 3.1 ml/g zeolite, about 3.2 ml/g zeolite, about 3.3 ml/g zeolite, about 3.4 ml/g zeolite, about 3.5 ml/g zeolite, about 3.6 ml/g zeolite, about 3.7 ml/g zeolite, about 3.8 ml/g zeolite, about 3.9 ml/g zeolite, about 4 ml/g zeolite, about

4.1 ml/g zeolite, about 4.2 ml/g zeolite, about 4.3 ml/g zeolite, about 4.4 ml/g zeolite, about 4.5 ml/g zeolite, about 4.6 ml/g zeolite, about 4.7 ml/g zeolite, about 4.8 ml/g zeolite, about 4.9 ml/g zeolite, and in a specific embodiment 4.15 ml/g zeolite. The metals used to prepare the hollow zeolite catalyst of the present invention can be provided in varying oxidation states as metallic, oxide, hydrate, or salt forms typically depending on the propensity of each metals stability and/or physical/chemical properties. The metals in the catalyst can also exist in one or more oxidation states. By way of example, a metal precursor solution (*e.g.*,  $\text{Ni}(\text{NO}_3)_3$ ) can be impregnated into the silicate-1 zeolite and the Ni impregnated zeolite can be suspended with an aqueous templating solution (*e.g.*,  $\text{TPA}(\text{OH})$ ), followed by drying of the solution. The dried mixture can be heat treated under static conditions (*e.g.*, heated under autogenous pressure) to produce a Ni particle encapsulated in a silicate-1 zeolite. A surface area of the hollow zeolite catalyst can be  $220 \text{ m}^2\text{g}^{-1}$  to  $300 \text{ m}^2\text{g}^{-1}$ , or equal to, or between any two of 220, 225, 230, 235, 240, 245, 250, 255, 260, 265, 270, 275, 280, 285, 290, 295, 300  $\text{m}^2\text{g}^{-1}$ . A pore volume of the hollow zeolite catalyst can be  $0.1 \text{ cm}^3\text{g}^{-1}$  to  $0.3 \text{ cm}^3\text{g}^{-1}$  or equal to, or between any two of 0.1, 0.15, 0.2, 0.25, 0.3  $\text{cm}^3\text{g}^{-1}$ . In a preferred instance, a Ni-silicate-1 hollow zeolite catalyst has a surface area of about  $237 \text{ m}^2\text{g}^{-1}$  and a pore volume of  $0.25 \text{ cm}^3\text{g}^{-1}$ . A particle size of the catalyst can be from 100 to 300 nm, or equal to, or between any two of, 100, 125, 150, 175, 200, 225, 250, 275, and 300.

**[0051]** In embodiments when a bulk metal catalyst is used (*e.g.*, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst), the catalyst can be prepared by solid-solid mixing. By way of example, a M2 metal precursor (*e.g.*,  $\text{MnO}$ ) can be mixed with non-catalytic metal oxide (*e.g.*,  $\text{SiO}_2$ ) under agitation to form a homogeneous mixture (*e.g.*, a powder). M1 metal precursor (*e.g.*,  $\text{NiO}$ ) can be added under agitation to the homogeneous mixture to form a M1/M2/non-catalytic metal oxide composition. The M1/M2/non-catalytic metal oxide composition can be dried (*e.g.*, 100 to 150 °C for 8 to 12 h, or about 120 °C for 10 h) to remove any residual water. The dried composition can be ground and shaped under pressure using known catalyst shaping techniques (*e.g.*, pelletized using a hydraulic press at an operating pressure of 8 tons-force/sq. inch), and then calcined at a temperature greater than, equal to, or between two of 1000 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C for 20 to 30 hour, or about 24 hours. The calcination temperature can be ramped at 1 to 5 °C per minute until the final temperature is obtained. The grinding, shaping and calcination can be repeated at least 2 times (*e.g.*, 2, 3, 4, 5, *etc.*).



[0052] The amount of catalytic metal to be used can depend, *inter alia*, on the catalytic activity of the catalyst. In some embodiments, the total amount of catalytic metal present in the catalyst can range from 0.01 to 100 parts by weight of catalytic metal per 100 parts by weight of catalyst, from 0.01 to 5 parts by weight of catalytic metal 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 catalyst. The catalyst of the present invention (e.g., metal/hollow zeolite, or bulk catalyst) can include up to 20 wt. % of the total catalytic metal and/or metal oxide, from 0.1 wt.% to 20 wt. %, from 1 wt. % to 10 wt. %, or from 3 wt. % to 7 wt. % or all wt.% equal to, or between two of, 0.1 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.%, 3.0 wt.%, 3.5 wt.%, 4.0 wt.%, 4.5 wt.%, 5 wt.%, 5.5 wt.%, 6 wt.%, 6.5 wt.%, 7 wt.%, 7.5 wt.%, 8 wt.%, 9 wt.%, 10 wt.%, 15 wt.%, 20 wt.%. In a specific embodiment, the zeolite catalyst includes about 1 to 6 wt. %, or about 1.8 wt.% of total catalytic metal. In some embodiments, a molar ratio of M1 to M2 can range from 0:0.1 to 0:1, or 0.1:0.9, 0.2:0.8, or about 0.5. In some embodiments, M1 is nickel and M2 is manganese.

[0053] In certain aspects the active site is separated from the silica by encapsulation of active site with the coke within a hollow zeolite (FIG. 4). Indeed, if the metal particles within the hollow cavity are bigger than the pore size of the zeolite, the particle will be trapped and the deactivation process will be prevented. On other hand, the coke surrounding the active site, will be confine within the hollow as well and regeneration should be facilitate. Another possibility to overcome the deactivation problems is to use a bulk catalyst without metal supported. Indeed, if a bulk catalyst is used, the active site could not be separated from the support and the material will be resistant to the experimental conditions involved in this reaction.

## 2. Hydrocarbon feed source

[0054] The light hydrocarbon gas feed can include hydrocarbons having 1, 2, 3, 4, or 5 carbon atoms. Non-limiting examples of C1 to C5 hydrocarbons include methane, ethane, ethylene, propane, propylene, butane, isobutene, butylene, isobutylene, methyl substituted butanes, pentane, pentene, and combinations thereof. The light hydrocarbon gas feed can be obtained from known sources, or known chemical or production processes.

## EXAMPLES

[0055] The following examples as well as the figures are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the

techniques disclosed in the examples or figures represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

### Example 1

#### (Methane Decomposition and Carbon Regeneration)

[0056] The activity of catalysts for methane conversion, and hydrogen and carbon monoxide yield was compared in a fixed-bed quartz reactor (i.d. = 9 mm and length= 50 cm) in a conventional down flow mode. The Ni/HZ catalyst of Example 2 (0.4 g) was loaded in the reactor, and then packed with small amount of inert to prevent the channeling. An N- type thermocouple was placed into the annular space between the reactor and the furnace to minimize the temperature difference between the catalyst bed and the thermocouple. The feed was introduced through a mass flow controller (Bronkhorst High-Tech, Netherlands) by passing the reactant gas mixture of CH<sub>4</sub> and N<sub>2</sub> over the catalyst bed. Once the coke formation predominates the H<sub>2</sub> production the CH<sub>4</sub> feed was switch off and CO<sub>2</sub> mass flow was switched on to oxidize the carbon formed. Prior to activity tests, all calcined samples in the oxidized state were reduced *in-situ* with a total volumetric flow rate of 60 ml/min in a mixture N<sub>2</sub> and H<sub>2</sub> (1: 1 ratio) at 750 °C for 5 h. Initially, pure nitrogen was allowed into the reactor, to create an inert atmosphere in the reactor. Catalytic CH<sub>4</sub> decomposition was performed at atmospheric pressure by passing a flow of methane along with N<sub>2</sub> or H<sub>2</sub> in the range of 10-100 ml/min and reaction temperature at 550-800 °C. The composition of the outlet gas from the reactor was determined by mass spectrometry. FIGS. 5A and 5B show graphs of the H<sub>2</sub> and CO production for a 3 cyclic injection of CH<sub>4</sub>.

### Example 2

#### (Catalyst Synthesis)

[0057] *Ni-Hollow zeolite*. Silicalite-1 is obtained by mixing tetraethylorthosilicate (TEOS, 98% purity, Sigma-Aldrich®, USA) and tetrapropylammonium hydroxide (TPA(OH), 1.0 M, in H<sub>2</sub>O, Sigma-Aldrich®, USA) with water. The gel composition is: SiO<sub>2</sub>:0.4 TPA(OH):35 H<sub>2</sub>O. Then, the mixture is transferred into a Teflon-lined autoclave and heated at 170 °C under static condition for 3 days. The solid produced by the reaction was recovered by centrifugation

and washed with water, this operation was repeated 3 times. The resulting solid was dried overnight at 110 °C and then calcined at 525 °C in air for 12 h. The calcined silicalite-1 was impregnated with aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich®, USA) to produce 1.8 wt% of Ni on the silicalite-1. The suspension was dried at 50 °C under air over the night.

5 The impregnated silicalite-1 (1 g) was suspended with an aqueous TPA(OH) solution (4.15 in 3.33 mL of  $\text{H}_2\text{O}$ ). The mixture was transferred into a Teflon-lined autoclave and heated at 170 °C under static conditions for 24 h to form a nickel encapsulated in the hollow portion of the silicate-1 (Ni/HZ). Finally, the 1.8 wt.% Ni/HZ was calcined in air at 450 °C for 6 h to produce the catalyst of the present invention.

10 **[0058]** *Olivine synthesis.* General Procedure. All the reactants were dried at 110 °C under air overnight. Then, the mixtures of Mn:Si in a molar ratio of 2:1 were prepared. Manganese oxide ( $\text{MnO}$ , 2.3 g) and silicon dioxide ( $\text{SiO}_2$ , 1.2 g) were mixed together thoroughly in a mortar to form a homogeneous powder.  $\text{NiO}$  was added with different molar ratio, ranging from 0 to 0.5 mole, with respect to the mole of manganese. Then the mixture was transferred  
15 to a crucible and dried at 120 °C for 10 h. After this, the material was ground to a fine powder in a mortar, and pelletized with a hydraulic press at an operating pressure of 8 tons-force/(sq. inch) to form cylindrical pellets. The formed pellets were then transferred into a crucible and calcined to 1250 °C at a ramp rate of 1 °C per minute, held at that temperature for 24 h and finally cooled down slowly to room temperature. The grinding and calcination procedure were  
20 repeated twice.

### Example 3

#### (Characterization of Hollow Zeolite Catalyst of Example 2)

**[0059]** *Isothermal Analysis.* Nitrogen Isotherms of the HZ-1 and silicate-1 using an ASAP 2010 micromeritics instrument were obtained. FIG. 7 are isothermal graphs of the silicate-1  
25 and HZ-1 catalyst. The surface area for the HZ-1 catalyst was lower than the surface area for silicate-1 ( $237 \text{ m}^2\text{g}^{-1}$  vs.  $326 \text{ m}^2\text{g}^{-1}$ ). The pore volume for the HZ-1 sample was greater than the pore volume of the silicate-1 sample ( $0.25 \text{ cm}^3\text{g}^{-1}$  vs.  $36 \text{ cm}^3\text{g}^{-1}$ ). Without wishing to be bound by theory, it is believed that the lower BET surface area was due to the dissolution of the silicate-1 core, while the higher pore volume was due to the formation of the hollow.

30 **[0060]** *Transmission Electron Microscopy (TEM).* TEM analysis was performed on the HZ-1 sample. FIG. 6 are TEM images of the Ni/HZ-1. FIG. 6A, FIG 6B, and FIG. 6C are images of the Ni/HZ-1. From the image in FIG. 4A a particle size of the Ni/HZ-1 was about

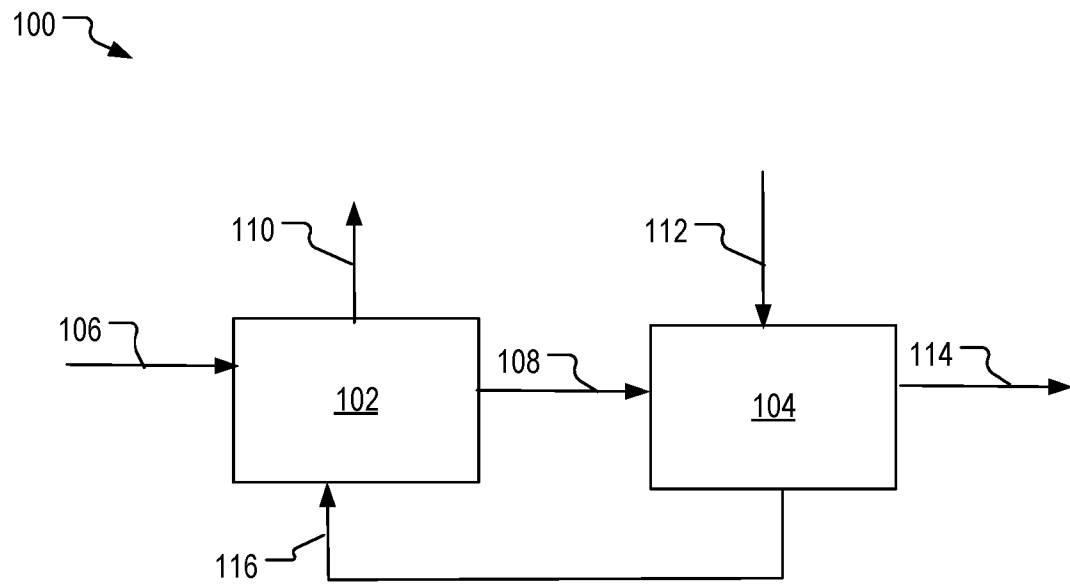
150 x 150 x 200 nm. FIG. 4B and FIG. 4C show the homogeneity of the hollow formation in the MFI zeolite structure.

### CLAIMS

1. A process for independent production of hydrogen ( $H_2$ ) and carbon monoxide (CO) comprising:
  - (a) decomposing a hydrocarbon by (i) introducing a gaseous light hydrocarbon feed stream into a decomposition reactor having a hydrocarbon decomposition catalyst under non-oxidizing conditions, (ii) contacting gaseous light hydrocarbon feed stream with the decomposition catalyst at a temperature of 500 to 800 °C, forming  $H_2$  and a carbonized catalyst, and (iii) collecting the  $H_2$  product; and
  - (b) contacting the carbonized decomposition catalyst with carbon dioxide ( $CO_2$ ) gas, producing CO gas and regenerating the hydrocarbon decomposition catalyst.
2. The process of claim 1, wherein the decomposition catalyst is a metal based catalyst.
3. The process of claim 1, wherein the decomposition catalyst comprises two or more metals from Columns 7-12 of the Periodic Table.
4. The process of claim 1, wherein the decomposition catalyst comprises two or more of Ni, Fe, or Co.
5. The process of claim 1, wherein the decomposition catalyst comprises Ni.
6. The process of claim 4, wherein the decomposition catalyst is a hollow zeolite catalyst, pyrochlore catalyst, a spinal catalyst, an olivine catalyst, or a combination thereof.
7. The process of claim 4, wherein the catalyst comprises metallic, bimetallic, or trimetallic nanoparticles.
8. The process of claim 7, wherein the nanoparticles are Ni nanoparticles encapsulated in a hollow silicate-1 support.
9. The process of claim 1, wherein the gaseous light hydrocarbon feed stream comprises methane ( $CH_4$ ).
10. A single reactor system for independent production of hydrogen ( $H_2$ ) and carbon monoxide (CO) comprising a reactor having:
  - (a) at least one inlet that is configurable as (i) a gaseous light hydrocarbon feed inlet or (ii) a carbon dioxide feed ( $CO_2$ ) inlet;

- (b) at least one outlet that is configurable as (i) an H<sub>2</sub> outlet or (ii) a CO outlet;  
and
  - (c) a decomposition catalyst contained within the reactor,  
wherein the reactor can be configured for hydrocarbon decomposition producing H<sub>2</sub> or catalyst regeneration producing CO.
11. The system of claim 10, wherein the reactor is cycled from a hydrocarbon decomposition configuration to a carbon monoxide generation configuration.
  12. The system of claim 10, wherein the decomposition catalyst is a metal based catalyst.
  13. The system of claim 12, wherein the decomposition catalyst comprises two or more metals from Columns 7-12 of the Periodic Table.
  14. The system of claim 13, wherein the decomposition catalyst comprises two or more of Ni, Fe, or Co metals.
  15. The system of claim 10, wherein the decomposition catalyst is a hollow zeolite catalyst, pyrochlore catalyst, a spinal catalyst, an olivine catalyst, or a combination thereof.
  16. The system of claim 10, wherein the decomposition catalyst comprises metallic, bimetallic or trimetallic nanoparticles.
  17. The system of claim 16, wherein the nanoparticles are Ni nanoparticles encapsulated in a hollow silicate-1 support.
  18. A two reactor system configured for independent production of hydrogen and carbon monoxide comprising:
    - a methane decomposition reactor having a feed source inlet, a decomposition catalyst configured to catalyze the production of hydrogen, a carbonized decomposition catalyst outlet, and a fresh catalyst inlet, wherein the carbonized decomposition catalyst outlet is connected to a carbon monoxide generating reactor; and
    - a carbon monoxide generating reactor having a carbon dioxide inlet, a carbonized catalyst inlet, and a fresh catalyst outlet, wherein the carbon monoxide generating unit is connected to the decomposition reactor and configured to receive carbonized decomposition catalyst from the decomposition reactor and to provide fresh catalyst to the decomposition reactor.

19. The system of claim 18, wherein the decomposition catalyst comprises a Ni, Fe, and/or Co hollow zeolite catalyst, a Ni, Fe, and/or Co pyrochlore catalyst, a Ni, Fe, and/or Co olivine catalyst, a Ni, Fe, and/or Co spinel catalyst, or a combination thereof.
20. The system of claim 19, wherein decomposition catalyst comprises bimetallic or trimetallic Ni nanoparticle metals encapsulated in a hollow zeolite support.

*FIG. 1*



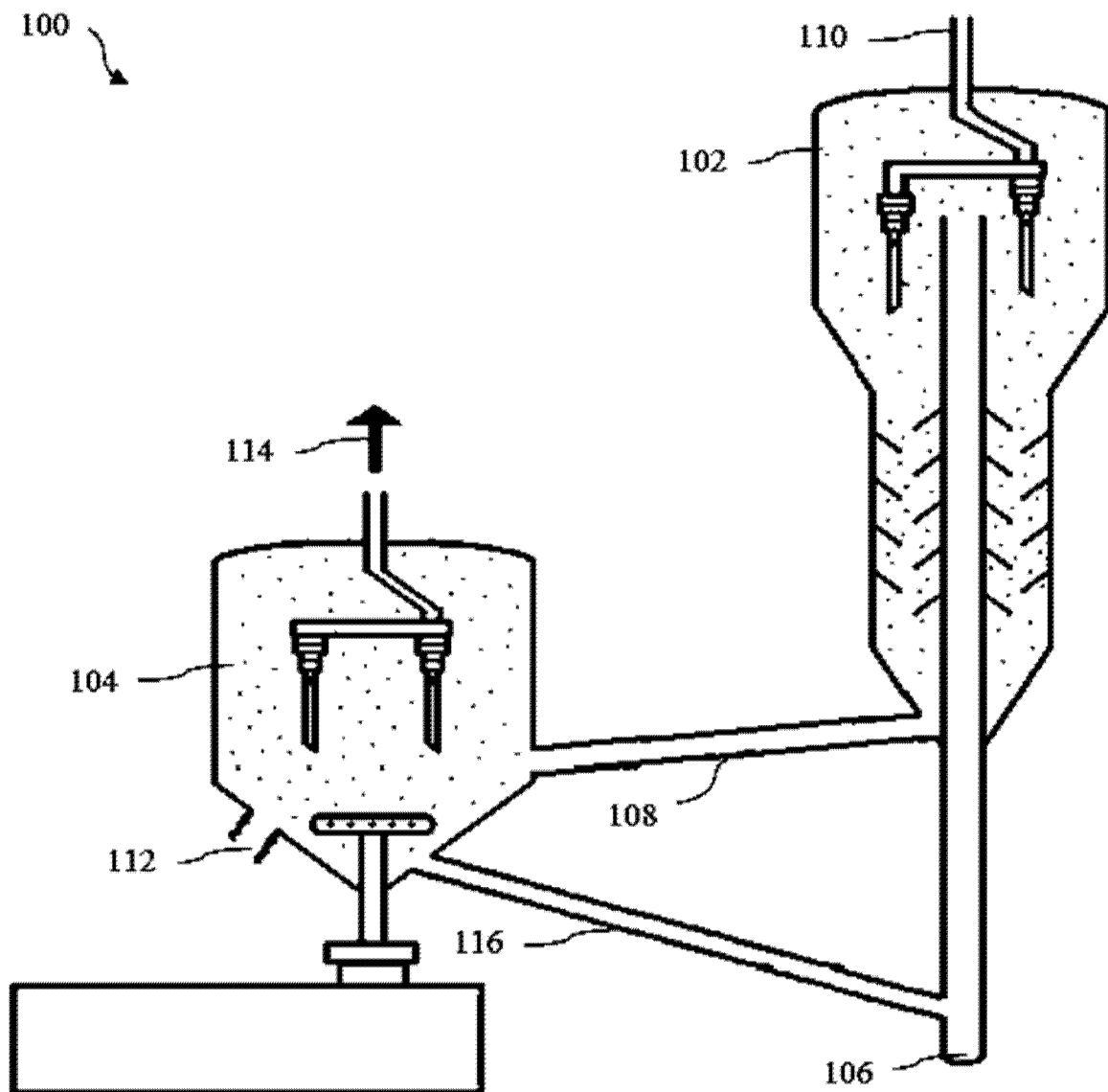


FIG. 2

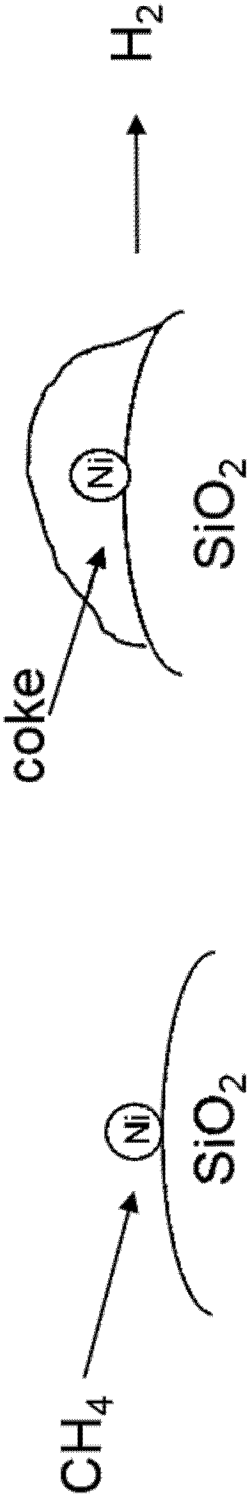


FIG. 3

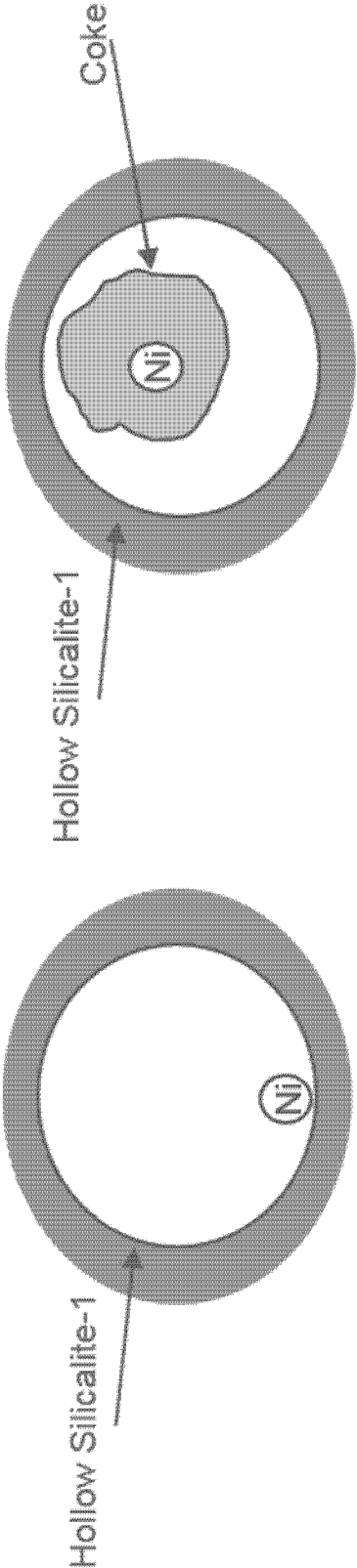


FIG. 4

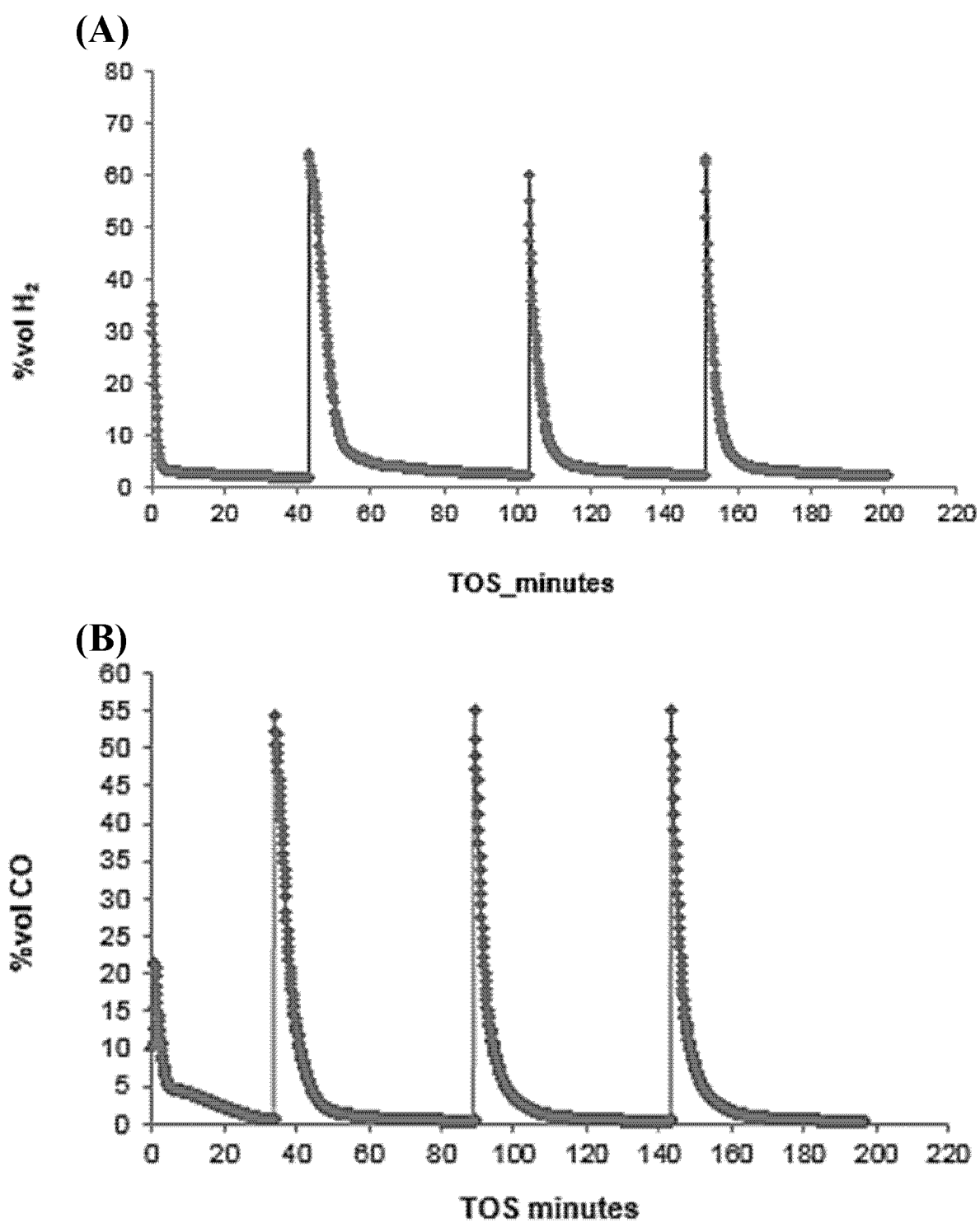


FIG. 5A-B

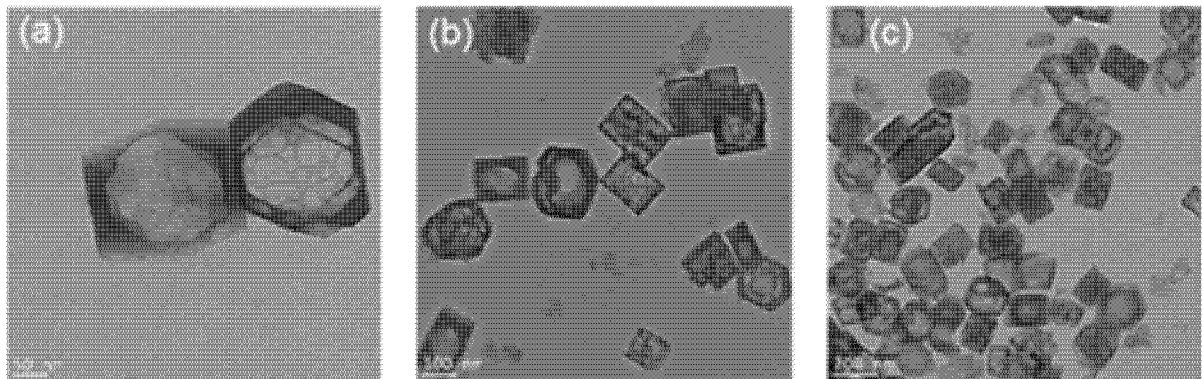


FIG. 6A-C

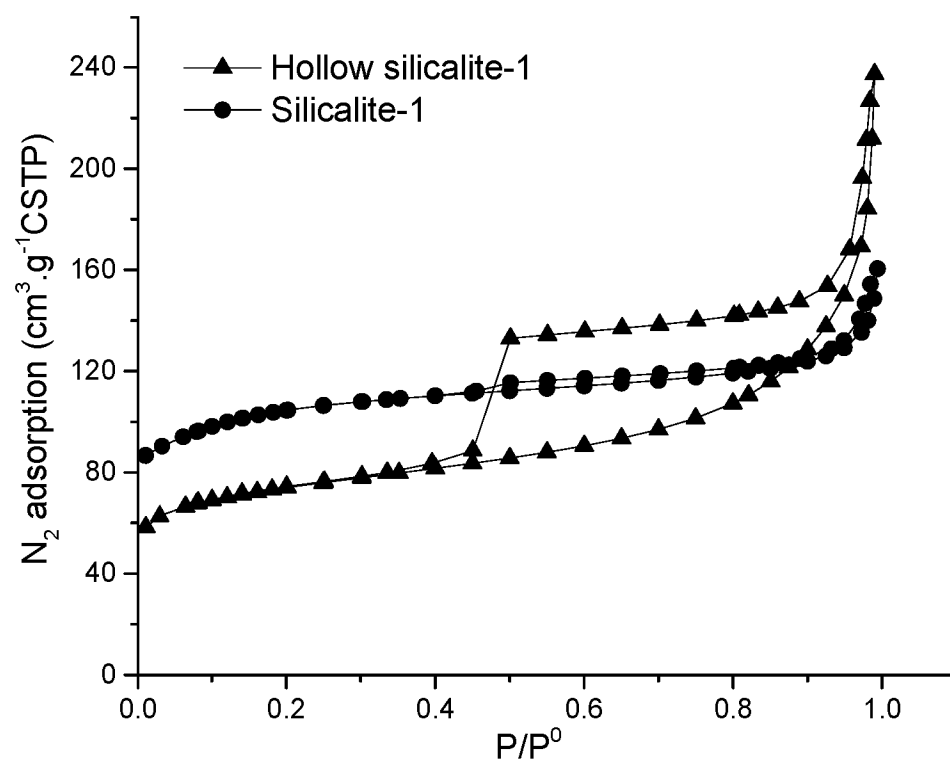


FIG. 7

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2018/055403

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>INV. C01B3/26 C10J3/48 B01J23/00 B01J29/00<br>ADD.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                               |                         |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|-------------------------|
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                               |                         |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>C01B C10J B01J                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                               |                         |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                               |                         |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>EPO-Internal, WPI Data                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                               |                         |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                               |                         |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Citation of document, with indication, where appropriate, of the relevant passages                                            | Relevant to claim No.   |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | FR 3 020 356 A1 (UNIV LILLE SCIENCES TECH [FR]; CENTRE NAT RECH SCIENT [FR])<br>30 October 2015 (2015-10-30)                  | 1-5,<br>9-14, 18,<br>19 |
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| <div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</span> <span><input checked="" type="checkbox"/> See patent family annex.</span> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                               |                         |
| <div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |                                                                                                                               |                         |
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