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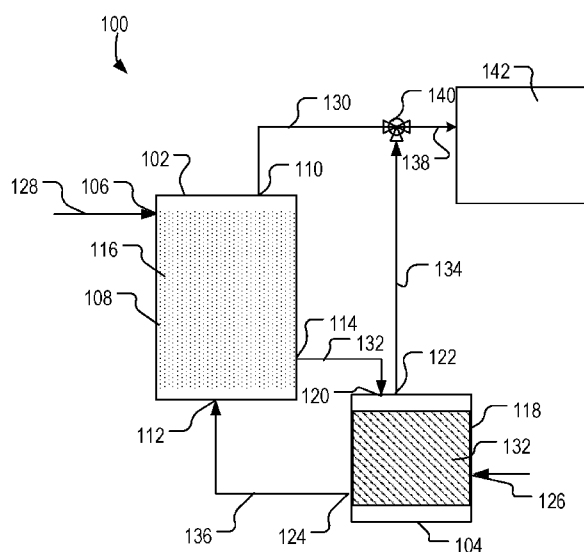


FIG. 1

(57) **Abstract:** Processes, systems, and catalysts for the production of a gaseous hydrogen (H_2) stream and a synthesis gas stream comprising H_2 and carbon monoxide (CO) are described. A process can include contacting a gaseous mixture of hydrocarbons having 1 to 5 carbon atoms (C_{1-5}) with a hydrocarbon decomposition catalyst under non-oxidizing conditions suitable to produce a gaseous H_2 stream and a carbon coated hydrocarbon decomposition catalyst, and contacting the carbon coated hydrocarbon decomposition catalyst with water under conditions suitable to produce a synthesis gaseous stream comprising H_2 and CO in a H_2 :CO molar ratio of about 1 : 1 and a regenerated hydrocarbon decomposition catalyst. The hydrocarbon decomposition catalyst can be a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof.



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COMBINED GASIFICATION AND CATALYTIC DECOMPOSITION FOR THE
PRODUCTION OF HYDROGEN AND SYNTHESIS GAS FROM
HYDROCARBONS**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application
5 No. 62/520,309 filed June 15, 2017, which is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION**A. Field of the Invention**

[0002] The invention generally concerns a process for the production of gaseous hydrogen
(H₂) and a H₂/carbon monoxide (CO) synthesis gas. Specifically, the invention concerns
10 producing H₂ and a carbon coated hydrocarbon decomposition catalyst from C₁₋₅ hydrocarbons
and a non-carbon coated or regenerated hydrocarbon decomposition catalyst. The produced
carbon coated hydrocarbon decomposition catalyst can then be used to produce synthesis gas
from water and from carbon present on the catalyst. The H₂:CO molar ratio of the synthesis
gas stream can be adjusted with H₂ from the H₂ generated stream to produce a synthesis gas
15 stream having a H₂:CO molar ratio suitable for methanol production.

B. Description of Related Art

[0003] Methanol is a major chemical raw material, ranking third in volume behind
ammonia and ethylene. Methanol can be produced by hydrogenating carbon dioxide as shown
in Equation (1):



Methanol can be produced using the CAMRE process (carbon dioxide hydrogenation to form
methanol *via* a reverse-water gas shift reaction (RWGSR)) as shown in reaction schemes (2)
and (3).



First carbon dioxide is hydrogenated to produce CO and H₂O (reaction scheme (2)). In the
second step, water and unreacted carbon dioxide can be removed to form a stream rich in
carbon monoxide. In the final step, the enriched carbon monoxide stream can be used to
produce methanol under catalytic conditions (*See*, reaction scheme (3)).

[0004] A source of the H₂, CO, and CO₂ reactants in the methanol synthesis can be synthesis gas (syngas). Syngas can be generated using steam methane reforming, partial oxidation or gasification of methane, autothermal reforming, a combined reforming or autothermal methane reforming process, coal gasification, or the like (See, Abbas *et al.*,
5 “Hydrogen production by methane decomposition: A review”, *International Journal of Hydrogen Energy* 2010, Vol. 35, pp. 1160-1190). Steam methane reforming is the catalytic reaction of methane-containing gas with steam to produce a synthesis gas that can include H₂, CO₂, CO, CH₄, and H₂O with a H₂:CO ratio of about 3:1 or higher. The steam methane reformation reaction is endothermic, therefore, external heat is required. A portion of the
10 reactant natural gas can be used as fuel to provide the heat required for the reaction. Drawbacks to steam methane reforming is its limitation to low pressure applications (*e.g.*, (0.5 MPa to 2.8 MPa) and production of syngas with a high CH₄ impurity content (*e.g.*, 3 to 15 vol.%), which requires an external supply of CO₂ to convert the methane to methanol.

[0005] Partial oxidation or gasification of methane is a non-catalytic reaction of methane-
15 containing gas (*e.g.*, natural gas) with oxygen under controlled oxygen conditions. The reaction is exothermic and is shown in the reaction scheme (4):



The partial oxidation process can be operated at high pressure to minimize or eliminate the synthesis gas compression needed to reach the desired elevated pressure suitable for methanol
20 production (*e.g.*, 1.38 MPa to 13.8 MPa). However, this process suffers in that the syngas produced can have a lower H₂:CO molar ratio (*e.g.*, 1.5 to 2.0). Thus, an external H₂ source is required to meet the methanol syngas requirements.

[0006] Various attempts to produce synthesis gas having an acceptable H₂:CO ratio for the production of methanol have been described. By way of example, U.S. Patent No. 5,767,165
25 to Steinberg *et al.* describes thermally decomposing methane to produce elemental carbon and hydrogen gas. The elemental carbon can then be gasified with carbon dioxide to produce carbon monoxide. The H₂ and CO obtained from the two reactions can be used to produce methanol. In another example, International Application Publication No. WO 2016/005317 to Schoonebeek *et al.* describes contacting a hydrocarbon stream with heated mass of solids at
30 1000 °C to thermally crack the hydrocarbons and produce solid carbon and H₂. The obtained carbon is contacted with water and carbon dioxide to obtain a CO/H₂ stream having a H₂:CO vol.% ratio of 0.0005 to 1.04. This stream is then combined with the produced H₂ to produce

a H₂/CO stream with a H₂:CO vol.% ratio of 0.5 to 5.0. This process suffers in that the ratio of H₂:CO is not reproducible under the reaction conditions.

[0007] Despite the various attempts to produce syngas suitable for the production of methanol, these processes are energy inefficient, costly, require complex processing steps, and suffer from catalyst deactivation.

SUMMARY OF THE INVENTION

[0008] A solution that addresses the problems associated with producing a synthesis gas stream suitable for use in methanol production has been discovered. The solution is premised on a catalytic decomposition of hydrocarbons process that produces gaseous H₂ and a carbon coated hydrocarbon decomposition catalyst. The carbon coated hydrocarbon decomposition catalyst can then be contacted with water to produce a synthesis gas stream that includes H₂ and CO in a H₂:CO molar ratio of about 1:1 and a regenerated hydrocarbon decomposition catalyst that can be reused in the catalytic hydrocarbon decomposition process. Thus, providing a continuous catalytic process. A portion of the generated H₂ can be used to adjust the H₂:CO molar ratio in the generated synthesis gas stream to form a combined synthesis gas, which can be referred to as a “stoichiometric ratioed synthesis gas” having a H₂:CO molar ratio of 1.5:1 to 2.1:1. The stoichiometric ratioed synthesis gas stream can be used for the production of methanol. The respective generation of the synthesis gas stream and the gaseous H₂ stream can be performed under pressure conditions ranging from 1 MPa to 8.5 MPa, providing the advantage of minimal external compression before entering a methanol processing unit. Furthermore, the process can be performed using fluidized or moving bed catalytic conversion systems for decomposing a light hydrocarbon stream, such as methane, which can utilize substantially different operating conditions than those encountered in the conventional reforming reactions to produce syngas. The decomposition catalyst can be a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof. In particular, the invention concerns a catalyst that includes a metallic (M¹), bimetallic (M¹M²), or trimetallic (M¹M²M³) nanoparticle, or oxides thereof, and a hollow zeolite support. The hollow space in the zeolite support can include the M¹, M¹M², or M¹M²M³ nanoparticle, or oxides thereof. The catalyst of the present invention used in the hydrocarbon decomposition reaction can overcome the deactivation problems suffered by conventional hydrocarbon decomposition reactions and can be easily regenerated. Deactivation of conventional surface deposited catalysts can occur when coke deposits on the surface of the catalyst and encapsulates the active metal. In this process, the coke separates the active metal from the surface and can

cause leaching or removal of the active metal from the catalyst. Without wishing to be bound by theory, it is believed that when 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. If the active site does become encapsulated with carbon, removal of the carbon is facilitated in the regeneration process, as the carbon is not attached to the zeolite.

[0009] In one aspect of the present invention, processes for the production of a gaseous (H_2) stream and a synthesis gas stream that can include H_2 and carbon monoxide (CO) are described. A process can include (a) contacting a gaseous mixture of hydrocarbons having 1 to 5 carbon atoms (C_{1-5}) with a hydrocarbon decomposition catalyst under non-oxidizing conditions suitable to produce a gaseous H_2 stream and a carbon coated hydrocarbon decomposition catalyst, and (b) contacting the carbon coated catalyst with water under conditions suitable to produce a synthesis gas stream that can include H_2 and CO in a H_2 :CO molar ratio of about 1:1 and a regenerated hydrocarbon decomposition catalyst. In one embodiment, the gaseous H_2 stream generated in step (a) can include at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, H_2 , preferably 80 mol.% H_2 , and/or the synthesis gas stream generated in step (b) is absent carbon dioxide (CO_2) and/or methane. The decomposition non-oxidizing conditions in step (a) can include a temperature of 500 to 800 °C and/or a pressure of 1 MPa to 8.5 MPa, preferably 1.4 MPa to 8.3 MPa. The C_{1-5} hydrocarbons can include at least 80 vol.% , at least 90 vol.% or at least 95 vol.% C_1 hydrocarbons. Conditions suitable to produce synthesis gas in step (b) can include a temperature of 650 to 1100 °C and/or a pressure of 0.5 MPa to 8.5 MPa. In some embodiments, the decomposition of hydrocarbons and production of synthesis gas can be performed in a single reactor having a decomposition zone and a syngas production zone. The process can further include adjusting the H_2 :CO molar ratio of the generated synthesis gaseous stream in step (b) with H_2 from the generated gaseous H_2 stream in step (a) to produce a second synthesis gaseous stream enriched in hydrogen. In some embodiments, the second synthesis gaseous stream has a H_2 :CO molar ratio of 1.5:1 to 2.5:1, 1.9 to 2.1:1, or about 2:1. The second synthesis gaseous stream can also be used to produce methanol.

[0010] In another aspect of the present invention, multiple bed fluidized reactor systems are described. The fluidized reactor systems can be used to perform the methods of the present invention. A multiple bed fluidized reactor system can include a fluidized hydrocarbon decomposition reaction zone and a fluidized synthesis gas zone. The fluidized hydrocarbon decomposition reaction zone can be configured to contact the gaseous hydrocarbon stream with

a hydrocarbon decomposition catalyst to produce a gaseous hydrogen stream and a coked hydrocarbon decomposition catalyst. The fluidized synthesis gas zone can be configured to receive the coked hydrocarbon decomposition catalyst and regenerate the carbon coated hydrocarbon decomposition catalyst under conditions sufficient to produce a synthesis gas stream that can include H₂ and carbon monoxide (CO), and a regenerated hydrocarbon decomposition catalyst. The system can also be configured to combine the produced synthesis gas stream with at least a portion of the H₂ from the gaseous hydrogen stream to produce a synthesis gas stream having H₂:CO molar ratio of about 2:1. In some embodiments, the system can be coupled to a methanol synthesis unit and is capable of transferring the synthesis gas stream having a H₂:CO molar ratio of about 2:1 to the methanol synthesis unit. In another aspect, the system can include a conduit coupled to the fluidized hydrocarbon decomposition reaction zone and to the fluidized synthesis gas zone and configured to provide the carbon coated hydrocarbon decomposition catalyst to the fluidized synthesis gas zone.

[0011] The decomposition catalyst used in the methods and systems of the present invention can include a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof. Such a catalyst can include metals from Columns 8-11 of the Periodic Table (*e.g.*, nickel (Ni), iron (Fe), palladium (Pd), platinum (Pt), iridium (Ir), copper (Cu) or cobalt (Co)). The catalytic metals can be metallic (M¹), bimetallic (M¹M²) or trimetallic (M¹M²M³) nanoparticle, or oxides, alloys thereof. In a preferred aspect of the present invention, the decomposition catalyst is a hollow zeolite catalyst and a catalytic metal nanoparticle is encapsulated in the hollow zeolite support. The hollow zeolite support can be a MFI zeolite, preferably a pure silicate-1 zeolite.

[0012] In the context of the present invention 20 embodiments are described. Embodiment 1 is a process for production of a gaseous hydrogen (H₂) stream and a synthesis gas stream comprising H₂ and carbon monoxide (CO), the process comprising: (a) contacting a gaseous mixture of hydrocarbons having 1 to 5 carbon atoms (C₁₋₅) with a hydrocarbon decomposition catalyst under non-oxidizing conditions suitable to produce a gaseous H₂ stream and a carbon coated hydrocarbon decomposition catalyst, wherein the hydrocarbon decomposition catalyst comprises a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof; and (b) contacting the carbon coated hydrocarbon decomposition catalyst with water under conditions suitable to produce a synthesis gaseous stream comprising H₂ and CO in a H₂:CO molar ratio of about 1:1 and a regenerated hydrocarbon decomposition catalyst. Embodiment 2 is the process of embodiment 1, comprising adjusting the H₂:CO molar ratio of

the step (b) synthesis gaseous stream with H₂ from the gaseous H₂ stream of step (a) to produce a second synthesis gaseous stream enriched in hydrogen. Embodiment 3 is the process of embodiment 2, wherein the H₂:CO molar ratio of the second synthesis gaseous stream is 1.5:1 to 2.5:1, 1.9 to 2.1:1, or about 2:1. Embodiment 4 is the process of any one of embodiments 1 to 3, further comprising producing methanol from the synthesis gaseous stream and/or the second synthesis gaseous stream. Embodiment 5 is the process of any one of embodiments 1 to 4, wherein the hydrocarbon decomposition catalyst comprises at least a metal from Columns 8-11 of the Periodic Table. Embodiment 6 is the process of embodiment 5, wherein the Columns 8-11 metals comprise nickel (Ni), iron (Fe), palladium (Pd), platinum (Pt), iridium (Ir), copper (Cu), or cobalt (Co). Embodiment 7 is the process of any one of embodiments 5 to 6, wherein the metals are metallic (M1), bimetallic (M1M2), or trimetallic (M1M2M3) nanoparticles. Embodiment 8 is the process of embodiment 7, wherein the hydrocarbon decomposition catalyst is a hollow zeolite catalyst and the nanoparticles are encapsulated in a hollow zeolite support. Embodiment 9 is the process of embodiment 8, wherein the hollow zeolite support is a MFI zeolite, preferably a pure silicate-1 zeolite. Embodiment 10 is the process of any one of embodiments 1 to 9, wherein the step (a) conditions comprise a temperature of 500 °C to 800 °C. Embodiment 11 is the process of any one of embodiments 1 to 10, wherein the step (a) conditions comprise a pressure of 1 MPa to 8.5 MPa, preferably 1.4 MPa to 8.3 MPa. Embodiment 12 is the process of any one of embodiments 1 to 11, wherein the C₁₋₅ hydrocarbons comprise at least 80 vol.% , at least 90 vol.% or at least 95 vol.% C₁ hydrocarbons. Embodiment 13 is the process of any one of embodiments 1 to 12, wherein the synthesis gaseous stream of step (b) is absent carbon dioxide (CO₂). Embodiment 14 is the process of any one of embodiments 1 to 13, wherein the gaseous H₂ stream of step (a) comprises at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, H₂, preferably about 80 mol.% H₂. Embodiment 15 is the process of any one of embodiments 1 to 14, wherein the conditions of step (b) comprise a temperature of 650 °C to 1100 °C. Embodiment 16 is the process of any one of embodiments 1 to 15, wherein the conditions of step (b) comprise a pressure of 0.5 MPa to 8.5 MPa.

[0013] Embodiment 17 is a multiple bed fluidized reactor system comprising: (a) a fluidized hydrocarbon decomposition reaction zone configured to contact a gaseous hydrocarbon stream with a hydrocarbon decomposition catalyst to produce a gaseous hydrogen (H₂) stream and a carbon coated hydrocarbon decomposition catalyst, wherein the hydrocarbon decomposition catalyst is a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a

spinel catalyst, or mixtures thereof; and (b) a fluidized synthesis gas production zone configured to receive the coked hydrocarbon decomposition catalyst and regenerate the carbon coated hydrocarbon decomposition catalyst under conditions sufficient to produce a synthesis gas stream comprising H₂ and carbon monoxide (CO) and a regenerated hydrocarbon decomposition catalyst. Embodiment 18 is the fluidized reactor system of embodiment 17, wherein the system is configured to combine the produced synthesis gas stream with at least a portion of the H₂ from the gaseous hydrogen stream to produce a synthesis gas stream having a H₂:CO molar ratio of about 2:1. Embodiment 19 is the fluidized reactor system of embodiment 17, wherein the system is coupled to a methanol synthesis unit and is capable of transferring the synthesis gas stream having a H₂:CO molar ratio of about 2:1 to the methanol synthesis unit. Embodiment 20 is the fluidized reactor system any one of embodiments 17 to 19, further comprising a conduit coupled to the fluidized hydrocarbon decomposition reaction zone and to the fluidized synthesis gas production zone and configured to provide the carbon coated hydrocarbon decomposition catalyst to the fluidized synthesis gas production zone.

[0014] The following includes definitions of various terms and phrases used throughout this specification.

[0015] 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%.

[0016] The terms “wt.%,” “vol.%,” or “mol.%” refers to a weight, volume, 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.

[0017] The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0018] The terms “inhibiting,” “reducing,” “preventing,” “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.

[0019] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0020] 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.”

5 [0021] 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.

10 [0022] The processes and systems 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 phase “consisting essentially of,” in one non-limiting aspect, a basic and novel characteristic of the processes and systems of the present invention is the ability to produce a gaseous H₂ stream and a synthesis gas stream that
15 includes H₂ and CO in a single reactor system while also being able to continuously regenerate carbon coated catalyst by using carbon from the carbon coated catalyst and water to produce the synthesis gas.

[0023] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be
20 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 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
25 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

[0024] Advantages of the present invention may become apparent to those skilled in the
30 art with the benefit of the following detailed description and upon reference to the accompanying drawings.

[0025] FIG. 1 is a schematic of a system of the invention to produce a gaseous H₂ stream and a synthesis gas stream that includes H₂ and CO.

[0026] FIG. 2 depicts isothermal graphs of a comparative Ni impregnated zeolite and a Ni hollow zeolite catalyst of the present invention.

5 [0027] FIG. 3A depicts transmission electron microscopy (TEM) images of the metallic Ni encapsulated inside the hollow zeolite catalyst of the present invention. FIG. 3B shows the energy dispersive spectra.

[0028] FIG. 4 shows is the thermogravimetric curve for carbon coated catalysts of the present invention.

10 [0029] FIG. 5A and FIG. 5B depict the experimental data for the methane decomposition (FIG. 5A) and the steam regeneration of the catalyst (FIG. 5B) to produce H₂ and CO.

[0030] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings. The drawings may not be to scale.

15

DETAILED DESCRIPTION OF THE INVENTION

[0031] A discovery has been made that provides at least a solution to the reactant feed used in methanol synthesis. The solution is premised on a process that catalytically decomposes a hydrocarbon stream to produce a gaseous H₂ stream and a carbon coated hydrocarbon decomposition catalyst. The carbon coated hydrocarbon decomposition catalyst can be
20 contacted with water to produce a synthesis gas stream that has a H₂:CO molar ratio of about 1:1 and a regenerated hydrocarbon decomposition catalyst. The H₂:CO molar ratio of the synthesis gas stream can be adjusted using a portion of the H₂ generated from the decomposition of hydrocarbons. This can provide for an elegant continuous process for the production of a reactant stream suitable for methanol production as well as an excess of H₂,
25 which could be effectively utilized as an energy source or reactant in other processes.

[0032] The hydrocarbon decomposition catalyst can be a hollow zeolite catalyst, a bulk-metal catalyst, or mixtures thereof. Non-limiting examples of the hydrocarbon decomposition catalyst include a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof. In one non-limiting particular aspect, the invention can concern
30 a catalyst that includes a metallic (M1), bimetallic (M1M2) or trimetallic (M1M2M3) nanoparticle, or oxides thereof, and a hollow zeolite support. The hollow space in the zeolite

support can include the M1, M1M2, or M1M2M3 nanoparticle, or oxides, or alloys thereof. By way of example, such a catalyst of the present invention can overcome the problems of conventional catalysts, as the catalysts of the present invention are capable of separating the active site from the metal oxide support (*e.g.*, silica) by positioning a catalytic metal structure(s) within a hollow cavity of the zeolite. Without wishing to be bound by theory it is believed that because the catalytic metal structure is bigger than the pore size of the zeolite, the catalytic metal can be trapped, thereby inhibiting deactivation of the catalyst. Use of a hollow zeolite type catalyst can facilitate regeneration of the catalyst as the carbon, which surrounds the active site, can be confined within the hollow void. Use of a bulk-metal catalyst can provide the advantage of not having a support, thus, no support-metal separation can occur.

[0033] These and other non-limiting aspects of the present invention are discussed in further detail in the following sections with reference to FIG. 1. The system and methods described in FIG. 1 can also include various equipment that is not shown and is known to one of skill in the art of chemical processing. For example, some controllers, piping, computers, valves, pumps, heaters, thermocouples, and/or pressure indicators may not be shown.

A. Process to Produce a Gaseous H₂ Stream and a H₂/CO Synthesis Gas Stream

[0034] FIG. 1 depicts a system 100 used to perform the process for production of a gaseous H₂ stream and a synthesis gas stream that can include H₂ and CO. System 100 can include H₂ generating unit 102 and synthesis gas generating unit 104. H₂ generating unit 102 can include hydrocarbon inlet 106, hydrocarbon decomposition reaction zone 108, H₂ product stream outlet 110, and catalyst inlet 112, and deactivated catalyst outlet 114. Reaction zone 108 can include hydrocarbon decomposition catalyst 116. Synthesis gas generating unit 104 can include a fluidized synthesis gas production zone 118, deactivated catalyst inlet 120, synthesis gas product outlet 122, regenerated catalyst outlet 124, and water inlet 126. Deactivated catalyst inlet 120 can be coupled to deactivated catalyst outlet 114 *via* piping, flexible hose or other known equipment such that the carbon coated decomposition catalyst can flow in a continuous manner from H₂ generating unit 102 to synthesis gas generation unit 104. Similarly, regenerated catalyst outlet 124 can be coupled to catalyst inlet 112 such that the regenerated hydrocarbon decomposition catalyst 116 can flow from synthesis gas generation unit 104 to H₂ generation unit 102 in a continuous manner. H₂ generation unit 102 and synthesis gas generation unit 104 can be any known fluidized bed catalytic reactor that can include one or more cyclone separator systems (not shown) and be capable of fluidizing the catalyst or deactivated catalyst in the reaction zones. Cyclone separator systems can separate the gas from

the fluidized catalyst particles and return the catalyst to the reactor. A non-limiting example of a fluidized reactor is a double fluidized bed reactor.

[0035] In the process to produce H₂ and a synthesis gas stream, gaseous hydrocarbon reactant mixture 128 can enter H₂ generating unit 102 *via* inlet 106. The gaseous hydrocarbon mixture can include hydrocarbons having 1, 2, 3, 4, or 5 carbon atoms. Non-limiting examples of C₁₋₅ hydrocarbons include methane, ethane, ethylene, propane, propylene, butane, isobutene, butylene, isobutylene, methyl substituted butanes, pentane, pentene, and mixtures thereof. The reactant mixture can be obtained from known chemical or production processes. Non-limiting examples of such processes include a refinery process, oil and gas production, natural gas feed, or the like. In some embodiments, the hydrocarbon reactant mixture can include at least, equal to, or between two of 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100 vol.% of C₁ hydrocarbons (*i.e.*, methane). In some embodiments, a chemically inert carrier gas (*e.g.*, nitrogen, argon, helium) is combined with the gaseous hydrocarbon mixture. The inert carrier gas and/or gaseous hydrocarbon mixture can be used to fluidize the catalyst in the H₂ generating unit 102.

[0036] In H₂ generating unit 102, gaseous C₁₋₅ hydrocarbon stream 128 can contact hydrocarbon decomposition catalyst 116 (discussed below) in hydrocarbon decomposition zone 108 under conditions suitable to produce a carbon coated decomposition catalyst and product stream 130 that includes H₂. Hydrocarbon decomposition conditions can include temperature, pressure, time, gaseous hourly space velocity, flow rates, and the like. Hydrocarbon decomposition zone 108 can be heated to a temperature at least, equal to, or between two of 500 °C, 525 °C, 550 °C, 600 °C, 625 °C, 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, 775 °C, 800 °C using known heating equipment and methods (*e.g.*, heaters, heat exchange units, heating fluid, steam, and the like). A pressure of H₂ generating unit 102 can be at least, equal to, or between two of 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. In some embodiments, the pressure can be 1.4 MPa to 8.3 MPa. H₂ containing product stream 130 can exit H₂ generation unit *via* H₂ product outlet 110. H₂ containing product stream 130 can include at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, H₂, or be greater than, equal to, or between two of 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100 mol%. Product stream 130 can include less than, equal to or between two of 50 mol.%, 40 mol.%, 30 mol.%, 20 mol.%, 10 mol.%, and 5 mol.% of hydrocarbons. In a preferred embodiment, H₂ containing product stream 130 includes about 80 mol.% of H₂ with the balance being hydrocarbons. In

some embodiments, product stream 130 is passed through a gas/gas separation unit (not shown) to produce a product stream having at least 100 mol.% H₂. A non-limiting example of a gas/gas separation unit includes one or more membrane units.

[0037] Contact of hydrocarbons 128 with hydrocarbon decomposition catalyst 116 also produces elemental carbon, which can, coat the active metal of the hydrocarbon deactivation catalyst and produce carbon coated hydrocarbon decomposition catalyst 132. By “carbon coated hydrocarbon decomposition catalyst,” it is meant that the surface of the active metal has been partially or completely coated with carbon. Optionally, the surface(s) of the non-catalytically active portion of the catalyst may or may not also be partially or completely coated with carbon. As carbon coated hydrocarbon decomposition catalyst 132 is produced, a portion of the carbon coated hydrocarbon decomposition catalyst can exit H₂ generation unit 102 *via* deactivated catalyst outlet 114 and enter synthesis gas generation unit 104 *via* deactivated catalyst inlet 120. In some embodiments, an inert carrier gas (*e.g.*, nitrogen, helium, argon, or the like) can be used to move the catalyst from one unit to another.

[0038] In synthesis generation unit 104, carbon coated hydrocarbon decomposition catalyst 132 can be contacted with water under conditions sufficient to oxidize the carbon and generate synthesis gas stream 134 and regenerated hydrocarbon decomposition catalyst 136. The water can be provided to synthesis gas generation unit 104 *via* water inlet 126 at a rate or amount sufficient to fluidize carbon coated hydrocarbon decomposition catalyst 136. Generated synthesis gas stream 134 can include H₂, CO, and optional CO₂, with a molar ratio of H₂:CO being about 1:1. In a preferred embodiment, little to substantially no CO₂ is generated. Conditions sufficient to generate synthesis gas stream 134 and regenerated hydrocarbon decomposition catalyst 136 can include temperature, pressure, flow rates, and time. Temperatures in synthesis gas production zone 118 can be at least, equal to, or between any two of 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, and 1100 °C. Pressure of synthesis gas generation unit 104 can be at least, 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 136 can exit synthesis gas generation unit 104 *via* regenerated catalyst outlet 124 and enter H₂ generation unit 102 *via* regenerated catalyst inlet 112. In some embodiments, regenerated hydrocarbon decompositions catalyst 136 can be mixed with a stream of fresh hydrocarbon decomposition catalyst 116 prior to entering H₂ generation unit 102 (not shown).

In some embodiments, H₂ generation zone 108 and synthesis gas production/generation zone 118 are in one reactor.

[0039] Synthesis gas stream 134 can exit synthesis gas generation unit 104 *via* synthesis gas outlet 122 and be mixed with H₂ product stream 130 to produce a second synthesis gas stream 138. Second synthesis gas stream 138 can have a H₂:CO molar ratio of 1.5:1 to 2.5:1, 1.9 to 2.1:1, or about 2:1, or 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, or any value or range there between. The amount of H₂ added to synthesis gas stream 134 can be adjusted using mixing unit 140. Mixing unit 140 can be a three-way valve, a computer operated valve, a gas-gas mixing unit, a compressor, or the like. Second synthesis gas stream 138 can enter methanol unit 142 and be contacted with a catalyst under conditions sufficient to produce methanol. Since the H₂ generation unit 104 and synthesis gas generation unit 102 operate at a pressure range of 0.5 to 8.5 MPa, minimal to no compression of second synthesis gas stream 138 is necessary before being converted to methanol.

B. Catalyst

[0040] The hydrocarbon decomposition catalyst used in H₂ generating unit 102 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 8-11 of the Periodic Table. Non-limiting examples of metals include noble metals, transition metals, or any combinations or any alloys thereof. Noble metals include palladium (Pd), platinum (Pt), gold (Au), rhodium (Rh), ruthenium (Ru), rhenium (Re), osmium (Os), iridium (Ir) or any combinations or alloys thereof. Transition metals include iron (Fe), silver (Ag), copper (Cu), nickel (Ni), zinc (Zn), manganese (Mn), chromium (Cr), molybdenum (Mo), tungsten (W), or tin (Sn), or any combinations or alloys thereof. In some embodiments, the catalytic metals can include 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 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.

[0041] 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 (SiO_2), alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), germania (GeO_2), stannic oxide (SnO_2), gallium oxide (Ga_2O_3), zinc oxide (ZnO), hafnia (HfO_2), yttria (Y_2O_3), lanthana (La_2O_3), ceria (CeO_2), manganese oxide (MnO), nickel oxide (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 SigmaMillipore (St. Louis, Missouri, USA), Alfa-Aeaser (Ward Hill, Massachusetts, USA), and Strem Chemicals (Newburyport, Massachusetts, USA).

[0042] 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, and 100. In a preferred embodiment, the hollow zeolite material is an MFI zeolite such as silicalite-1 (Si:Al = infinity).

[0043] 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, coprecipitation, impregnation, complexation, gelation, crystallization, microemulsion, sol-gel, solvothermal, hydrothermal, sonochemical, or combinations thereof).

[0044] 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, or metal precursors, 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), 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. 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 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 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 3.1 mL/g zeolite, 3.2 mL/g zeolite, 3.3 mL/g zeolite, 3.4 mL/g zeolite, 3.5 mL/g zeolite, 3.6 mL/g zeolite, 3.7 mL/g zeolite, about 3.8 mL/g zeolite, 3.9 mL/g zeolite, 4 mL/g zeolite, 4.1 mL/g zeolite, 4.2 mL/g zeolite, 4.3 mL/g zeolite, 4.4 mL/g zeolite, 4.5 mL/g zeolite, 4.6 mL/g zeolite, 4.7 mL/g zeolite, 4.8 mL/g zeolite, 4.9 mL/g zeolite, and in a specific embodiment about 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.*, $\text{Ni}(\text{NO}_3)_2$) can be impregnated into the silicate-1 zeolite and the Ni impregnated zeolite can be suspended with an aqueous templating solution (*e.g.*, TPA(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 at least, equal to, or between any two of 220, 225, 230, 235, 240, 245, 250, 255, 260, 265, 270, 275, 280, 285, 290, 295, and 300 m^2g^{-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 at least, equal to, or between any two of 0.1, 0.15, 0.2, 0.25, and 0.3 cm^3g^{-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 at least, equal to, or between any two of 100, 125, 150, 175, 200, 225, 250, 275, and 300.

[0045] 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., MnO) can be mixed with non-catalytic metal oxide (e.g., SiO₂) under agitation to form a homogeneous mixture (e.g., a powder). M1 metal precursor (e.g., 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.).

[0046] 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.

EXAMPLES

[0047] 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 Bimetallic Olivine Bulk Metal Catalyst)

5 [0048] MnO (Powder, -60 mesh, 99% Aldrich), SiO₂ (silica gel, 70-230 mesh, Sigma-Millipore, U.S.A.), and NiO (Black, Ni 76% Alfa Aesar, U.S.A.) are used in this protocol. All reactants were dried at 110 °C under air overnight. Manganese oxide (MnO, 2.3 g) and silicon dioxide (SiO₂, 1.2 g) in a Mn:Si molar ratio of 2:1, were mixed together thoroughly in a mortar to form a homogeneous powder. NiO was added in a molar ratio of 0 to 0.5 mole, with respect
10 to the mole of manganese was added to the powder. Then resulting mixture was transferred to a crucible and dried at 120 °C for 10 h. The dried material was grounded to 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 transferred to a crucible, calcined to 1250 °C at a ramp rate of 1 °C per minute, held at that temperature for 24 h, and then cooled
15 down slowly to room temperature. The grinding and calcination procedures were repeated twice.

Example 2

(Synthesis of Silicalite-1 Zeolite Catalyst)

[0049] Silicalite-1 was obtained by mixing tetraethylorthosilicate (TEOS, 98% purity, SigmaMillipore, USA) and tetrapropylammonium hydroxide (TPA(OH), 1.0 M, in H₂O, SigmaMillipore, USA) with water. The gel composition was: SiO₂: 0.4 TPA(OH): 35 H₂O. The resulting mixture was transferred into a Teflon-lined autoclave and heated at 170 °C under static condition for 3 days. The solid 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
25 calcined at 525 °C in air for 12 h.

Example 3

(Synthesis of Ni / Hollow Zeolite (NiHZ) Catalyst)

[0050] Silicalite-1 from Example 2 was impregnated with aqueous solution of Ni(NO₃)₂·6H₂O (SigmaMillipore, USA) to produce 1.8 wt.% of Ni on the silicalite-1. The
30 suspension was dried at 50 °C under air over the night. The impregnated silicalite-1(1 g) was suspended with an aqueous TPA(OH) solution (4.15 in 3.33 mL of H₂O). The mixture was

transferred into a Teflon-lined autoclave and heated at 170 °C under static conditions for 24 h. Finally, the 1.8 NiHZ was calcined in air at 450 °C for 6 h.

Example 4

(Synthesis of Comparative Metal Impregnated Zeolite Catalyst)

- 5 [0051] Silicalite-1 from Example 2 was impregnated with aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (SigmaMillipore, USA) to produce a 5.5 wt.% of Ni on the silicalite-1. The suspension was dried at 50 °C under air over the night. The dried material was calcined at 450 °C in air.

Example 5

(Characterization of the Catalyst)

10

- [0052] **Isothermal Analysis.** Nitrogen Isotherms of the HZ and silicate-1 using a Micromeritics® ASAP 2010 instrument (Micromeritics®, U.S.A.) were obtained. FIG. 2 depicts isothermal graphs of the silicate-1 and HZ. The surface area for the HZ 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 sample was greater than the pore volume of the silicate-1 sample ($0.36 \text{ cm}^3\text{g}^{-1}$ vs. $0.25 \text{ cm}^3\text{g}^{-1}$). 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.

- 20 [0053] **Transmission Electron Microscopy (TEM) and EDAX.** Imaging was performed using a Titan G2 80–300 kV transmission electron microscope operating at 300 kV (FEI Company, U.S.A.) equipped with a $4 \text{ k} \times 4 \text{ k}$ CCD camera, a GIF Tridiem (Gatan, Inc., U.S.A.) and an EDS detector (EDAX, Inc., U.S.A.). FIG. 3A shows the homogeneity of the hollow formation on the MFI zeolite structure and the metallic Ni encapsulated inside the hollow zeolite. FIG. 3B shows the EDS spectrum.

- 25 [0054] **Thermogravimetric Analysis.** The quantity of carbon coating the catalysts was estimated by thermo-gravimetric analysis (TGA) in air atmosphere using STA 449 F3 Jupiter® TGA Thermo-gravimetric analyzer. For this analysis 20-30 mg of spent catalyst, was heated from room temperature to 1000 °C at a heating rate of 20 °C/min. FIG. 4 shows the TGA data. From the data in FIG. 4, it was determined that the weight loss of sample due to carbon gasification with air and that the amount of carbon present on the catalyst was approximately 30 around 31.82 wt.% after methane decomposition step.

Example 6

(Production of H₂ and a Synthesis Gas Stream)

[0055] Catalytic activity measurements were carried out in a tubular fixed-bed continuous-flow reactor. The reactor was loaded with of the NiHZ (0.342 g, Example 4). As a startup of the experiment, the catalyst was reduced with 10 mol.% H₂ in Ar at 750 °C for 6 hours. After the completion of reduction, the reactant gas feed consisted of CH₄, and Ar with 1:1 molar ratios, was been introduced into the reactor. After 10 mins of CH₄ flow at 25 mL/min, the CH₄ gas was stopped and flushed for 60 minutes with Ar gas at 10 mL/min. The reaction temperature was 800 °C, the pressure was 1.5 MPa (15 bar), and the gas hourly space velocity was 5000 h⁻¹. Followed by introduction of steam gas at 0.5 mL /min for 15 minutes to regenerate the coked catalyst. The reaction temperature was 800 °C, the pressure was 1.5 MPa (15 bar), and the gas hourly space velocity was 1000 h⁻¹. After 15 minutes of steam flow the steam flow was stopped and the Ar gas was flowed to flush out left over CO₂ gas and other gaseous products. Thereafter, the methane decomposition and regeneration step with steam was repeated for several cycles. FIG. 5A and FIG. 5B depict the experimental data for the methane decomposition (FIG. 5A) and the steam regeneration of the catalyst (FIG. 5B) to produce H₂ and CO. Hydrogen was produced in 40 vol.% from the methane decomposition. H₂ was produced at 30 to 35 vol% and about 5 vol.% of CO was produced from regeneration of the catalyst. Gas composition of reactants and products is been analyzed using an online Mass spectrometer.

Example 7

(Prophetic Simultaneous Production of H₂ and a Synthesis Gas Stream)

[0056] NiMnSi oxide olivine bulk metal catalyst (0.345 g, Example 1) or Example 4 catalyst will be loaded into the methane CH₄ decomposition reactor and a synthesis gas generation reactor and the catalyst will be reduced at 750 °C for 6 hours using a flow of H₂ in Ar. A mixture of methane gas and nitrogen will be provided to the CH₄ decomposition reactor at temperature of 800° C at a pressure range of 1.5 MPa, and a GHSV of 5000 h⁻¹. The H₂ product will be kept in a light-phase fluidization state, and as a result, H₂ gas will be released out of the reactor during the process and stored separately. As the accumulation of carbon starts, the carbon coated catalyst will be directed into the synthesis gas-generation reactor and the fresh catalyst in the synthesis gas generation reactor will be directed into the CH₄ decomposition reactor with the aid of N₂ carrier gas.

[0057] In the synthesis gas generator reactor the carbon coated catalyst will be fluidized with a steam (H_2O) feed at 0.5 mL/ min at 800°C at a pressure range of 1.5 MPa, and a GHSV of 1000 h^{-1} . The carbon will be oxidized to hydrogen and CO at a $\text{H}_2:\text{CO}$ molar ratio of 1. The synthesis gas stream will be removed from the reactor, collected, and stored.

5 [0058] A continuous flow of H_2 and synthesis gas will be obtained when the CH_4 decomposition reaction and synthesis gas reaction will be run simultaneously. The resulting synthesis gas generated will be mixed with 1 mole of H_2 separated from the 2 mole of H_2 produced in the CH_4 decomposition reactor to provide a synthesis gas $\text{H}_2:\text{CO}$ molar ratio of 2, which will be supplied to methanol synthesis plant to produce methanol.

10 [0059] Although embodiments of the present application and their advantages have been described in detail, it should be understood that various changes, substitutions and alterations 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
15 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, 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
20 claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

CLAIMS

1. A process for production of a gaseous hydrogen (H_2) stream and a synthesis gas stream comprising H_2 and carbon monoxide (CO), the process comprising:
 - (a) contacting a gaseous mixture of hydrocarbons having 1 to 5 carbon atoms (C_{1-5}) with a hydrocarbon decomposition catalyst under non-oxidizing conditions suitable to produce a gaseous H_2 stream and a carbon coated hydrocarbon decomposition catalyst, wherein the hydrocarbon decomposition catalyst comprises a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof; and
 - (b) contacting the carbon coated hydrocarbon decomposition catalyst with water under conditions suitable to produce a synthesis gaseous stream comprising H_2 and CO in a H_2 :CO molar ratio of about 1:1 and a regenerated hydrocarbon decomposition catalyst.
2. The process of claim 1, comprising adjusting the H_2 :CO molar ratio of the step (b) synthesis gaseous stream with H_2 from the gaseous H_2 stream of step (a) to produce a second synthesis gaseous stream enriched in hydrogen.
3. The process of claim 2, wherein the H_2 :CO molar ratio of the second synthesis gaseous stream is 1.5:1 to 2.5:1, 1.9 to 2.1:1, or about 2:1.
4. The process of claim 1, further comprising producing methanol from the synthesis gaseous stream and/or the second synthesis gaseous stream.
5. The process of claim 1, wherein the hydrocarbon decomposition catalyst comprises at least a metal from Columns 8-11 of the Periodic Table.
6. The process of claim 5, wherein the Columns 8-11 metals comprise nickel (Ni), iron (Fe), palladium (Pd), platinum (Pt), iridium (Ir), copper (Cu), or cobalt (Co).
7. The process of any one of claims 5 to 6, wherein the metals are metallic (M1), bimetallic (M1M2), or trimetallic (M1M2M3) nanoparticles.
8. The process of claim 7, wherein the hydrocarbon decomposition catalyst is a hollow zeolite catalyst and the nanoparticles are encapsulated in a hollow zeolite support.
9. The process of claim 8, wherein the hollow zeolite support is a MFI zeolite, preferably a pure silicate-1 zeolite.

10. The process of claim 1, wherein the step (a) conditions comprise a temperature of 500 °C to 800 °C.
11. The process of claim 1, wherein the step (a) conditions comprise a pressure of 1 MPa to 8.5 MPa, preferably 1.4 MPa to 8.3 MPa.
12. The process of claim 1, wherein the C₁₋₅ hydrocarbons comprise at least 80 vol.% , at least 90 vol.% or at least 95 vol.% C₁ hydrocarbons.
13. The process of claim 1, wherein the synthesis gaseous stream of step (b) is absent carbon dioxide (CO₂).
14. The process of claim 1, wherein the gaseous H₂ stream of step (a) comprises at least 50 mol.%, at least 60 mol.%, at least 75 mol.%, at least 80 mol.%, H₂, preferably about 80 mol.% H₂.
15. The process of claim 1, wherein the conditions of step (b) comprise a temperature of 650 °C to 1100 °C.
16. The process of claim 1, wherein the conditions of step (b) comprise a pressure of 0.5 MPa to 8.5 MPa.
17. A multiple bed fluidized reactor system comprising:
 - (a) a fluidized hydrocarbon decomposition reaction zone configured to contact a gaseous hydrocarbon stream with a hydrocarbon decomposition catalyst to produce a gaseous hydrogen (H₂) stream and a carbon coated hydrocarbon decomposition catalyst, wherein the hydrocarbon decomposition catalyst is a hollow zeolite catalyst, a pyrochlore catalyst, an olivine catalyst, a spinel catalyst, or mixtures thereof; and
 - (b) a fluidized synthesis gas production zone configured to receive the coked hydrocarbon decomposition catalyst and regenerate the carbon coated hydrocarbon decomposition catalyst under conditions sufficient to produce a synthesis gas stream comprising H₂ and carbon monoxide (CO) and a regenerated hydrocarbon decomposition catalyst.
18. The fluidized reactor system of claim 17, wherein the system is configured to combine the produced synthesis gas stream with at least a portion of the H₂ from the gaseous hydrogen stream to produce a synthesis gas stream having a:H₂:CO molar ratio of about 2:1.

19. The fluidized reactor system of claim 17, wherein the system is coupled to a methanol synthesis unit and is capable of transferring the synthesis gas stream having a H₂:CO molar ratio of about 2:1 to the methanol synthesis unit.
20. The fluidized reactor system of claim 17, further comprising a conduit coupled to the fluidized hydrocarbon decomposition reaction zone and to the fluidized synthesis gas production zone and configured to provide the carbon coated hydrocarbon decomposition catalyst to the fluidized synthesis gas production zone.

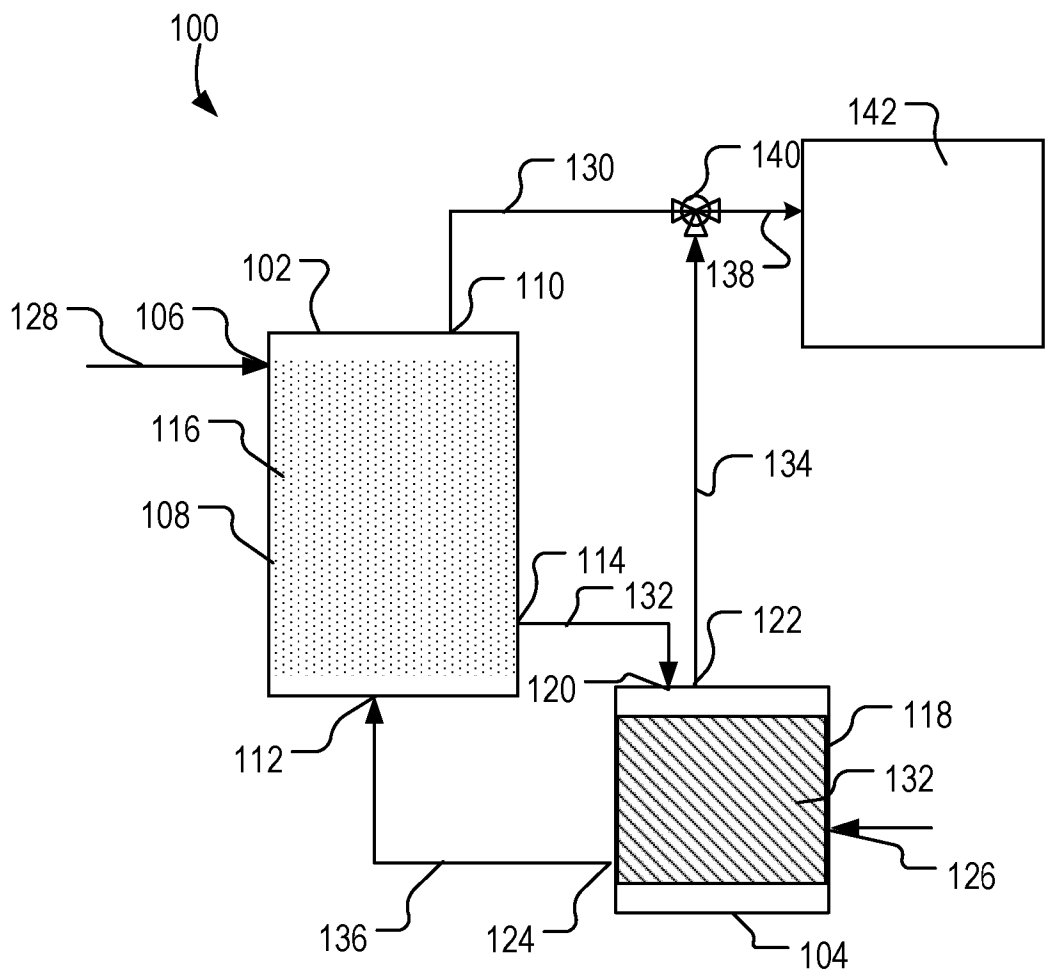
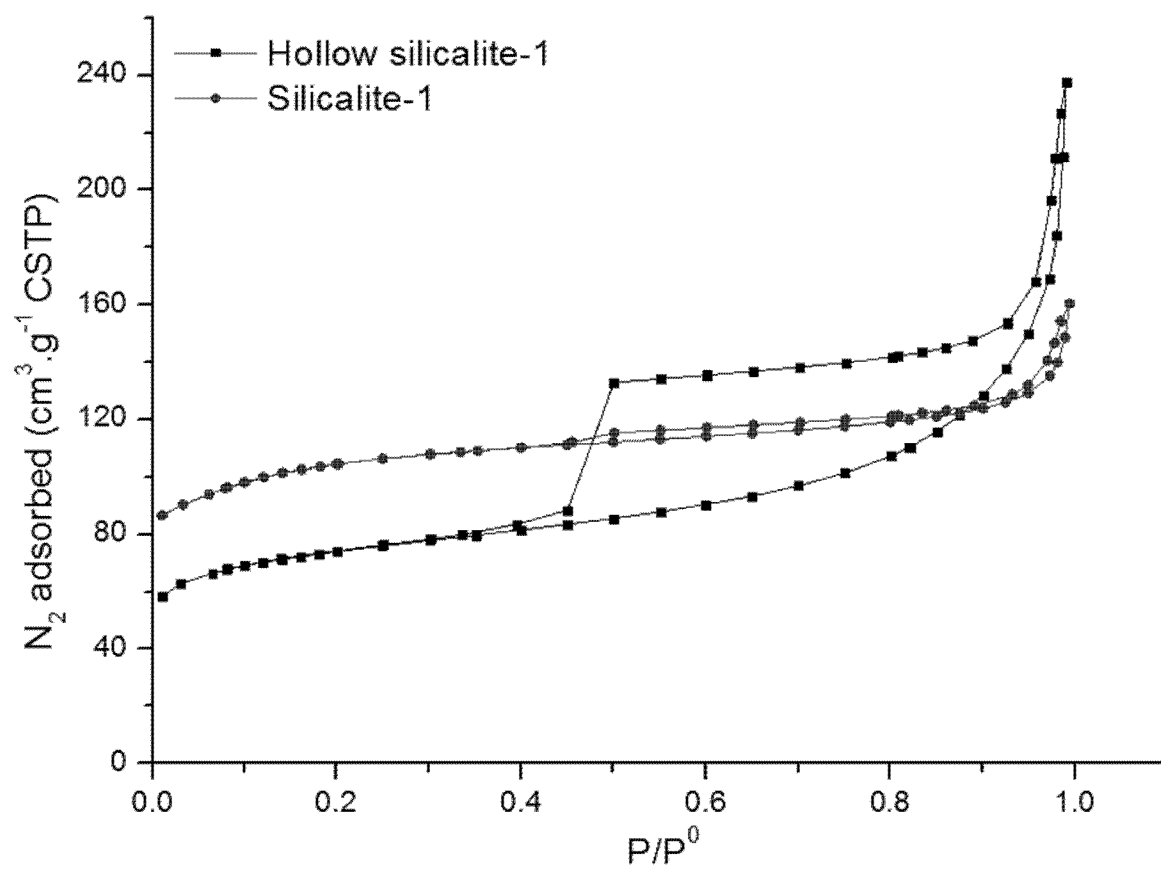
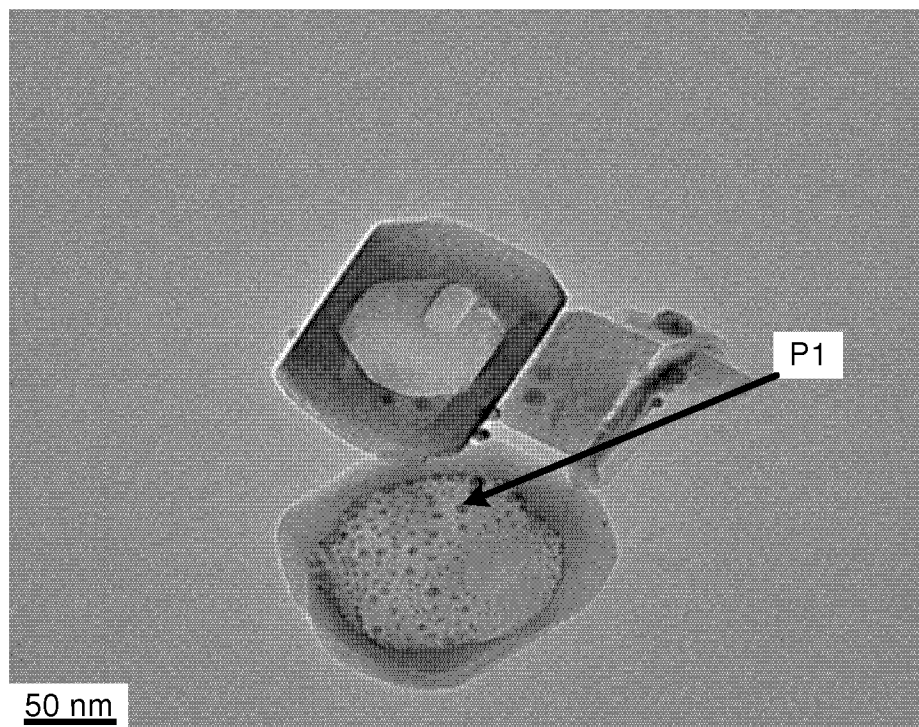
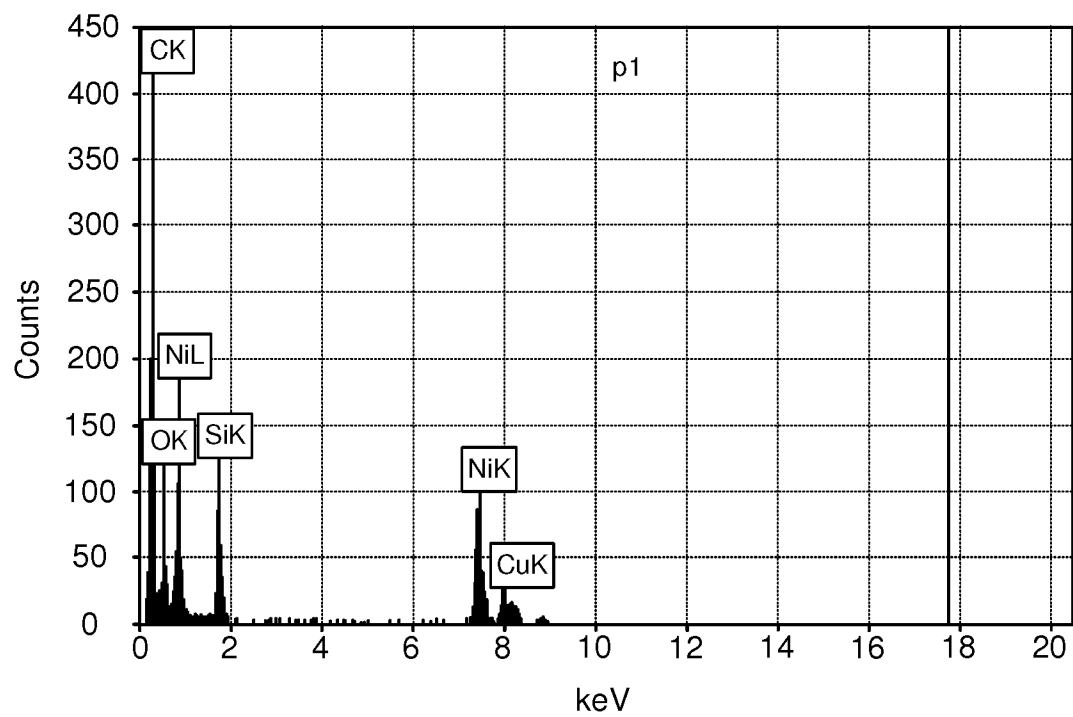
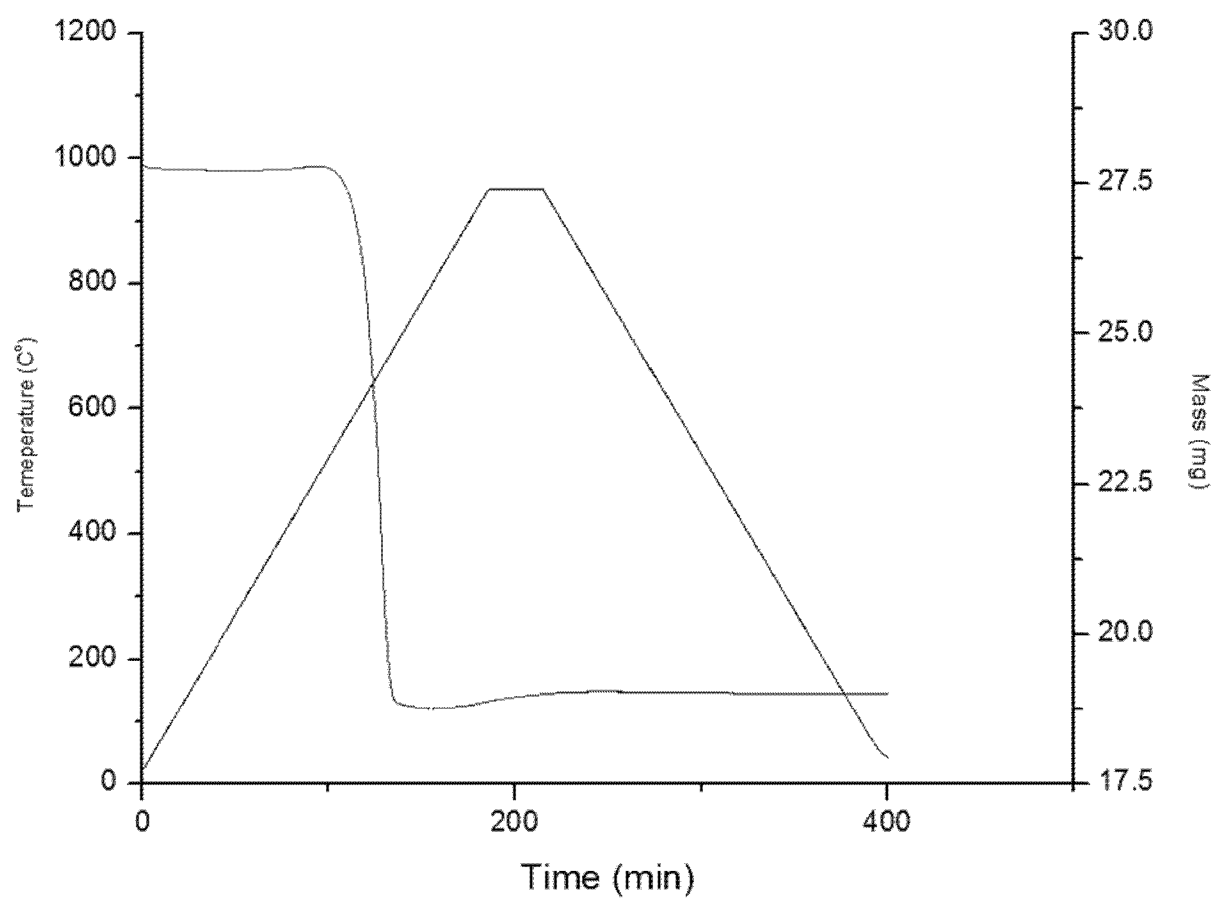
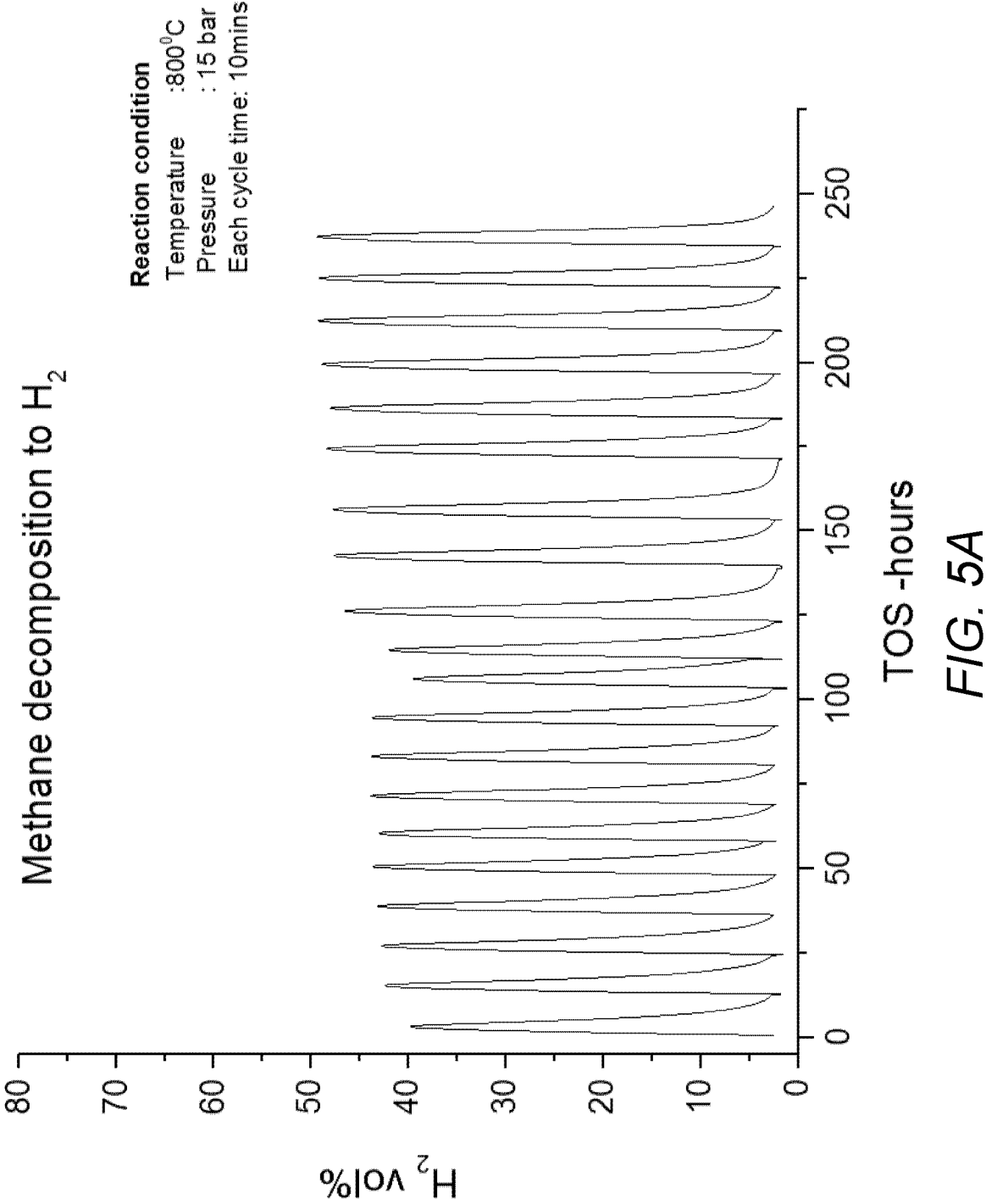


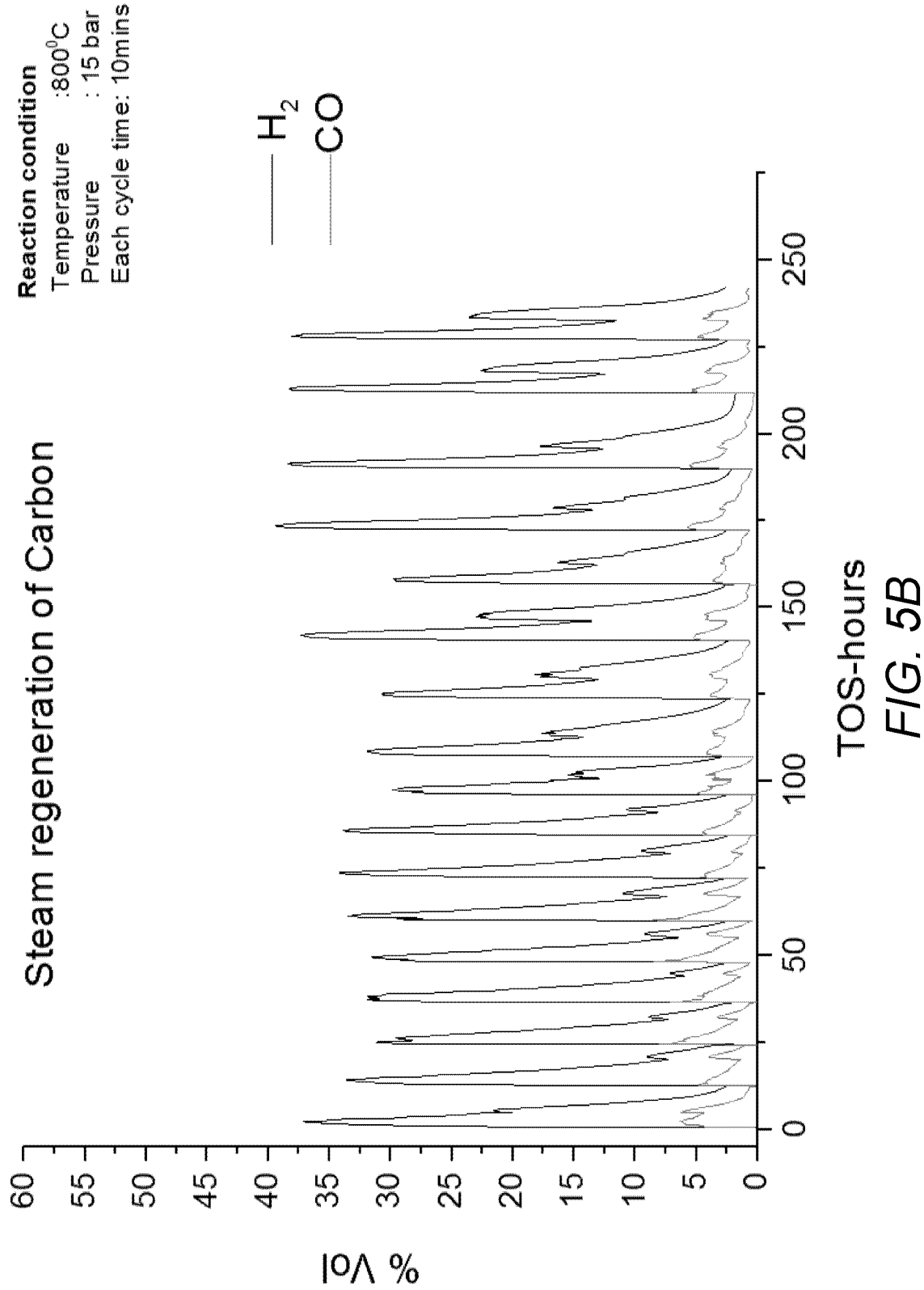
FIG. 1

*FIG. 2*

*FIG. 3A**FIG. 3B*

**FIG. 4**





INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054439

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B3/26 C01B3/28 C10J3/56 C10J3/46 C07C29/151 B01J23/00 B01J29/00 ADD. 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) C01B C10J C07C B01J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 60%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 30%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top;">X</td> <td style="vertical-align: top;">US 2004/118047 A1 (CHOUDHARY VASANT RAMCHANDRA [IN] ET AL) 24 June 2004 (2004-06-24)</td> <td style="vertical-align: top;">1-3,5,6, 8,10-18</td> </tr> <tr> <td style="vertical-align: top;">Y A</td> <td style="vertical-align: top;">paragraphs [0023] - [0033] paragraphs [0071] - [0073] figure claims</td> <td style="vertical-align: top;">7-9 20</td> </tr> <tr> <td style="vertical-align: top;">Y</td> <td style="vertical-align: top;">----- EP 0 219 163 A2 (SHELL INT RESEARCH [NL]) 22 April 1987 (1987-04-22) column 2, line 15 - column 3, line 21 column 3, line 40 - line 55 column 4, line 35 - line 37 claims 1-12 ----- -/--</td> <td style="vertical-align: top;">1-4, 10-16</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2004/118047 A1 (CHOUDHARY VASANT RAMCHANDRA [IN] ET AL) 24 June 2004 (2004-06-24)	1-3,5,6, 8,10-18	Y A	paragraphs [0023] - [0033] paragraphs [0071] - [0073] figure claims	7-9 20	Y	----- EP 0 219 163 A2 (SHELL INT RESEARCH [NL]) 22 April 1987 (1987-04-22) column 2, line 15 - column 3, line 21 column 3, line 40 - line 55 column 4, line 35 - line 37 claims 1-12 ----- -/--	1-4, 10-16
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 2004/118047 A1 (CHOUDHARY VASANT RAMCHANDRA [IN] ET AL) 24 June 2004 (2004-06-24)	1-3,5,6, 8,10-18												
Y A	paragraphs [0023] - [0033] paragraphs [0071] - [0073] figure claims	7-9 20												
Y	----- EP 0 219 163 A2 (SHELL INT RESEARCH [NL]) 22 April 1987 (1987-04-22) column 2, line 15 - column 3, line 21 column 3, line 40 - line 55 column 4, line 35 - line 37 claims 1-12 ----- -/--	1-4, 10-16												
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.														
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family														
Date of the actual completion of the international search 26 September 2018		Date of mailing of the international search report 09/10/2018												
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Harf-Bapin, E												

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Y	DEVI L ET AL: "Olivine as tar removal catalyst for biomass gasifiers: Catalyst characterization", APPLIED CATALYSIS A: GENERAL, ELSEVIER, AMSTERDAM, NL, vol. 294, no. 1, 4 October 2005 (2005-10-04), pages 68-79, XP027814782, ISSN: 0926-860X [retrieved on 2005-10-04] page 69, left-hand column, line 43 - page 69, right-hand column, line 22 -----	1-3, 10-16
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