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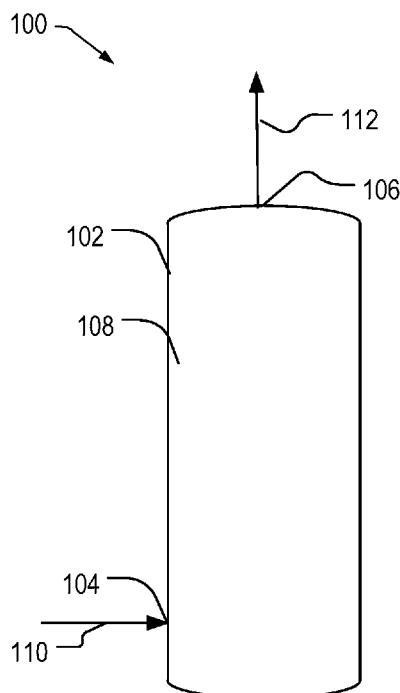


FIG. 1

(57) Abstract: Systems and processes for producing hydrogen gas (H_2) from water (H_2O) are described. A process can include contacting H_2O with a catalyst that includes iron sulfide at a reaction temperature of 500 °C to 800 °C to produce a product stream that includes H_2 and optionally hydrogen sulfide gas (H_2S).

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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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HYDROGEN PRODUCTION FROM WATER USING METAL SULFIDE CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/678,349 filed May 31, 2018, which is hereby incorporated by reference in its entirety.

5

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns processes for producing hydrogen gas (H_2) from water (H_2O). In particular, the invention concerns a self-sustaining reaction that includes contacting H_2O with a metal sulfide catalyst at a reaction temperature of less than 600 °C to
10 convert the metal sulfide to a metal oxide and produce a gaseous product stream that includes H_2 , optional hydrogen sulfide (H_2S), and optional hydrogen sulfide (SO_2).

B. Description of Related Art

[0003] H_2 can be produced using diverse resources including fossil fuels (*e.g.*, such as natural gas and coal, nuclear energy, or the like) and renewable energy sources (*e.g.*, biomass,
15 wind, solar, geothermal, and hydroelectric power) through a wide range of technologies. Currently, a majority of H_2 is produced through steam reforming of hydrocarbons (*e.g.*, natural gas), and the produced H_2 is then used in oil refining, ammonia production, and/or methanol production. However, a problem with using fossil fuels is their inevitable depletion, which necessitates finding alternative feedstocks to meet the growing demand for hydrogen
20 production globally. Another problem associated with using renewable energy sources is the costs and technical difficulties associated with the storage and/or transportation of the produced H_2 .

[0004] Alternative processes for hydrogen production have been proposed. By way of example, H_2 can be produced from splitting of H_2O using photocatalysts or Z-scheme catalysts.
25 However, these types of technologies suffer from low efficiencies and high economic costs. Other efforts to split H_2O include using an inorganic shuttle or carrier. By way of example, German Patent Application DE2541824 to Kluas describes producing hydrogen from water using a thermochemical cycle to split sulfuric acid into water, elemental sulfur, sulfur dioxide, hydrogen and oxygen. In another example, Bhosale *et al.* (*International Journal of Hydrogen
30 Energy*, 2015, 40, 1639-1650) describes solar hydrogen production *via* thermochemical iron oxide-iron sulfate water-splitting. European Patent Application No. 0016644 to Fujimori *et*

al., describes regenerating iron catalysts for heavy oil cracking applications by contacting the spent catalyst containing hydrogen sulfides with water to generate hydrogen sulfide with some hydrogen produced. This process suffers in that production of the metal sulfide is a multi-step synthesis, dependent on the feed stream containing sulfur, and the generation of hydrogen and hydrogen sulfide requires temperatures of 600 to 850 °C.

[0005] Although various methods to obtain H₂ from H₂O are known, the methods can be complicated or be inefficient for commercial production.

SUMMARY OF THE INVENTION

[0006] A discovery has been made that provides a solution to at least some of the aforementioned problems associated with producing H₂ from H₂O. The solution is premised on a self-sustaining process that contacts water with a catalyst that includes a metal sulfide at high temperatures (*e.g.*, greater than 300 °C, but less than 600 °C) to produce a metal oxide material and a gaseous product stream that includes H₂, optional H₂S, and optional SO₂. The produced metal oxide material can then be converted back to a metal sulfide by contact with a sulfur source (*e.g.*, H₂S, elemental sulfur or the like), which can also produce additional water. The generated water can be contacted with the generated metal sulfide to continue the reaction cycle. Reaction conditions (*e.g.*, temperature and/or pressures) can be adjusted to control the amount of elemental sulfur formed during the process. By way of example, the temperature can be greater than 300 °C, but less than 600 °C during the production of H₂ from water to inhibit the production of elemental sulfur. After the H₂ production decreases, the temperature can be raised to above 600 °C to convert the produced iron oxide to FeS. Notably, little to no (*e.g.*, less than 0.001 wt.%) sulfuric acid (H₂SO₄) and/or SO₂ is produced during the reaction when iron-containing catalysts are used, and neither of these compounds are needed to perform or initiate the reaction.

[0007] In one aspect of the invention, a process to produce H₂ from H₂O is described. The process can include contacting H₂O with a catalyst that can include metal sulfide at a reaction temperature of less than 600 °C (*e.g.*, 350 °C to 575 °C, or 475 °C to 525 °C, or about 500 °C) to produce a product stream that can include H₂, optional H₂S and optional SO₂, or combinations thereof. The product stream can be substantially free of elemental sulfur. Any H₂S produced during the reaction can contact the metal oxide material to produce additional H₂S. The iron oxide material can be converted to iron sulfide. In a preferred embodiment, the metal oxide can be converted to metal sulfide at a reaction temperature of 600 °C to 800 °C.

During the metal oxide conversion process, SO_2 can be formed by contact of sulfur or metal sulfide with the metal oxide material. Any water produced during the metal oxide conversion can be contacted with the iron sulfide catalyst material to produce H_2 , optionally H_2S , optionally SO_2 , or combinations thereof. The product stream can include H_2 and H_2S , and the method can further include isolating the H_2S from the product stream and providing the H_2S to the metal oxide so as to convert the metal oxide back to the metal sulfide. During this process elemental sulfur can be produced. In other instances, however, elemental sulfur may not be produced or may be produced in low amounts (e.g., 0.01 wt. % or less). The metal sulfide catalyst can include iron (Fe), tungsten (W), tin (Sn), nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), or mixtures thereof and, in some embodiments, be a bulk metal catalyst (*i.e.* unsupported catalyst). The catalyst can have a general formula of FeS_x , where x is 1 or 2, preferably 1. The FeS_x catalyst can form a metal oxide material (e.g., Fe_3O_4 , Fe_2O_3 , WO_3 , *etc.*) during the reaction. When iron sulfide is used the water can be free of sulfur dioxide (SO_2). In some embodiments, the metal sulfide is not obtained from a thermal hydrocarbon cracking process.

[0008] In another aspect of the invention, a system to produce hydrogen from water is described. The system can include an inlet for a reactant feed that include water, a reaction zone configured to be in fluid communication with the inlet, and a first outlet configured to be in fluid communication with the reaction zone. The reaction zone can have a temperature of less than 600°C and can include water and a metal sulfide catalyst. In some embodiments, the reaction zone can include the reactant feed and the product stream. The first outlet can remove a gaseous product stream that can include H_2 , optional SO_2 , and optional hydrogen sulfide (H_2S) from the reaction zone. The product stream can include H_2S , and the metal sulfide catalyst can be at least partially or fully converted to metal oxide material. The system can further include a separation zone in fluid communication (coupled) with first outlet. The separation zone can be configured to separate H_2S from H_2 in the product stream and provide the H_2S to the inlet or to the reaction zone. Contact of the H_2S with the iron oxide material can produce iron sulfide catalyst material to sustain the reaction cycle.

[0009] The following includes definitions of various terms and phrases used throughout this specification.

[0010] The terms “about” or “approximately” are defined as being close to the value, term, or phrase that follows, 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%.

[0011] The terms “wt.%”, “vol.%”, or “mol.%” refers to a weight, volume, or molar percentage of a component, respectively, based on the total weight of the material, the total volume of material, or total moles of material, that includes the component. In a non-limiting example, 10 grams of component in 100 grams of the material is 10 wt.% of component.

[0012] The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0013] 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.

[0014] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0015] 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.”

[0016] 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.

[0017] The processes 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 of the present invention are their abilities to produce H₂ from H₂O through the use of a metal sulfide catalyst.

[0018] In the context of the present invention at least twenty embodiments are now described. Embodiment 1 is a process for producing hydrogen (H₂) from water. The process includes the steps of contacting water with a metal sulfide at a reaction temperature of less than 600 °C to convert the metal sulfide to a metal oxide, and produce a product stream containing

hydrogen (H_2), optional sulfur dioxide (SO_2), and optional hydrogen sulfide (H_2S). Embodiment 2 is the process of embodiment 1, wherein the product stream has less than 0.01 wt.% of elemental sulfur or is preferably free of elemental sulfur. Embodiment 3 is the process of any one of embodiments 1 to 2, wherein the reaction temperature is 350 °C to 575 °C, or 475 °C to 525 °C, or about 500 °C. Embodiment 4 is the process of any one of embodiments 1 to 3, further including contacting H_2S with the metal oxide at a temperature of at least 600 °C to convert the metal oxide to the metal sulfide to produce additional H_2 . Embodiment 5 is the process of embodiment 4 wherein the reaction temperature for converting the metal oxide to the metal sulfide is 600 °C to 800 °C. Embodiment 6 is the process of any one of embodiments 4 to 5, wherein the product stream includes H_2 and H_2S , and the method further including isolating the H_2S from the product stream and contacting the H_2S with the metal oxide. Embodiment 7 is the process of embodiment 6, wherein elemental sulfur is produced. Embodiment 8 is the process of any one of embodiments 1 to 7, wherein less than 0.001 wt.% or no sulfuric acid (H_2SO_4) is produced during the reaction. Embodiment 9 is the process of any one of embodiments 1 to 8, wherein the metal sulfide contains iron (Fe), tungsten (W), tin (Sn), nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), or mixtures thereof. Embodiment 10 is the process of embodiment 9, wherein the metal sulfide is FeS_x , where x is 1 or 2, preferably 1, and the metal oxide contains Fe_3O_4 . Embodiment 11 is the process of embodiment 9, wherein the metal sulfide is WS_2 and the metal oxide contains WO_3 . Embodiment 12 is the process of any one of embodiments 1 to 11, wherein the process is self-sustaining. Embodiment 13 is the process of any one of embodiment 1 to 12, wherein the metal sulfide is not obtained from a thermal hydrocarbon cracking process. Embodiment 14 is the process of any one of embodiments 1 to 13, wherein the metal sulfide is a bulk metal catalyst.

[0019] Embodiment 15 is a system for producing hydrogen (H_2) from water. The system includes an inlet for a reactant feed comprising water (H_2O); a reaction zone that is configured to be in fluid communication with the inlet, wherein the reaction zone has a temperature of less than 600 °C and contains water and a metal sulfide catalyst; a first outlet configured to be in fluid communication with the reaction zone and configured to remove a first product stream comprising H_2 and optionally hydrogen sulfide (H_2S) from the reaction zone. Embodiment 16 is the system of embodiment 15, wherein the reaction zone further contains the reactant feed and the product stream. Embodiment 17 is the system of any one of embodiments 15 to 16, wherein the reaction zone contains a metal oxide and the system further includes a second inlet

in fluid communication with the reaction zone and including a second reactant feed, the second reactant feed containing H_2S ; and a heat source configured to heat the reaction zone to at least 600°C , wherein the first inlet is configured to remove a second product stream comprising H_2 and gaseous sulfur dioxide (SO_2) from the reaction zone. Embodiment 18 is the system of any one of embodiments 15 to 17, further including a separation zone coupled to the first outlet and configured to separate H_2S from the H_2 in the product stream and provide the H_2S to the first inlet or reaction zone. Embodiment 19 is the system of any one of embodiments 15 to 18, wherein the metal sulfide catalyst includes a transition metal. Embodiment 20 is the system of embodiment 19, wherein the transition metal is iron or tungsten.

10

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings.

15 [0021] FIG. 1 depicts a system to produce H_2 from H_2O using a process of the present invention.

[0022] FIG. 2 shows the gas chromatography (GC) chromatogram of the gas products of the reaction of FeS with water.

20 [0023] FIG. 3 shows the formation of FeS from Fe_3O_4 and elemental sulfur at temperatures from 200°C and 700°C .

[0024] FIG. 4 shows the percentage of Fe_3O_4 , FeS , and FeS_2 at 400°C between 5 minutes and 1 hour.

[0025] FIG. 5 shows the percentage of Fe_3O_4 , FeS , and FeS_2 at 500°C between 5 minutes and 1 hour.

25 [0026] FIG. 6 shows the X-ray diffraction (XRD) pattern of Fe_2O_3 heated with elemental sulfur at 400°C for 1 hour.

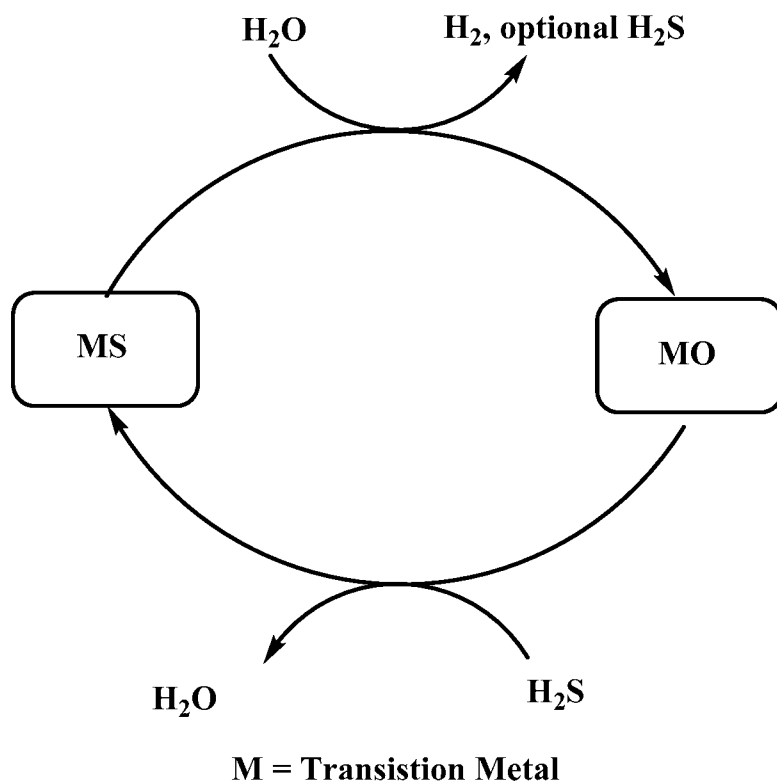
[0027] FIG. 7 shows the XRD pattern of Fe_2O_4 heated with elemental sulfur at 400°C for 1 hour.

[0028] FIG. 8 shows a graphical representation of continuous evolution of hydrogen from a water/H₂S mixture using Fe₃O₄ where the orange bars indicate the hourly rate of hydrogen evolution and the blue line the cumulative production of hydrogen H₂ produced (mmoles).

[0029] 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.

DETAILED DESCRIPTION OF THE INVENTION

[0030] A discovery has been made that provides solutions to at least some of the problems described above. The solution is premised on producing H₂ from water by contacting the water with a metal sulfide catalyst (*e.g.*, iron (Fe), tungsten W), tin (Sn), nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), or mixtures thereof). Preferably, the metal sulfide catalyst is a bulk catalyst. During contact, the metal sulfide can be converted to metal oxides (*e.g.*, Fe₂O₃ and/or Fe₃O₄, WO₃). The metal oxide material can be converted back to the metal sulfide catalyst material using hydrogen sulfide produced during the water-splitting reaction and/or addition of a sulfur source (*e.g.*, elemental sulfur or additional H₂S) to the reaction mixture. Water can be produced during the regeneration of the iron sulfide catalyst material. The produced water can contact the metal sulfide catalyst to continue the H₂ production cycle. Thus, the reaction process can be a self-sustaining cycle as shown in reaction scheme I:



(I).

[0031] 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 systems 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, controllers, piping, computers, valves, pumps, heaters, thermocouples, and/or pressure indicators may not be shown.

[0032] FIG. 1 is a schematic of a system using the process of the present invention to produce H_2 from H_2O . System 100 can include reactor 102, water inlet 104, and product stream outlet 106. Reactor 102 can include reaction zone 108 that can include a catalyst material, a reactant feed stream (water), a product stream, or combinations thereof. In the process of the present invention, water stream 110 can enter reactor *via* water inlet 104 and enter reaction zone 108. In some embodiments, the water can be provided in a continuous manner. By way of example, water can be added to the reaction zone at 0.5 to 5 mL/hour, 1 to 4 mL/hour, 1 to 3 mL/hour or any range or value there between. Water can be provided as a liquid and be vaporized in reaction zone 108. In other embodiments, water can be added as steam or in vapor form. The source of water can be from potable or non-potable sources (*e.g.*, refining operations, chemical reactions, or the like). In a preferred instance, the water contains little, substantially no, or no SO_2 .

[0033] In reaction zone 108, the water can contact the catalyst material at reaction conditions sufficient to produce product stream 112 and a metal oxide material. The catalyst material can include a metal sulfide, preferably a bulk metal sulfide (*i.e.*, less than 0.1 wt.% support material or no support material). The metal sulfide catalyst can be a transition metal.

5 Transition metals include Columns 5 to 12 of the Periodic Table. Non-limiting examples of transition metals include iron (Fe), tungsten (W), tin (Sn), nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), or mixtures thereof. Metal sulfides can be obtained from commercial sources or prepared by contact of metals with a sulfur source (*e.g.*, hydrogen sulfide, elemental sulfur, or both). In some embodiments, the catalyst includes
 10 greater than, equal to, or between two of 50 wt.%, 60 wt.%, 70 wt.%, 80 wt.%, 90 wt.% or 100 wt.% of metal sulfide. In a preferred embodiment, the catalyst is unsupported and includes 95 wt.% to 100 wt.% of metal sulfide with the balance being metal oxides (*e.g.*, 5 wt.% or less). In some instances, the metal sulfide containing catalyst can have the general formula of FeS_x where x is 1 or 2 (*e.g.*, FeS or FeS_2). In a preferred embodiment, the catalyst is unsupported
 15 and includes 95 wt.% to 100 wt.% of FeS_x with the balance being iron oxides (*e.g.*, Fe_3O_4 and/or Fe_2O_3). In some embodiments, FeS is used as the catalyst and only Fe_3O_4 is formed by contact of the FeS with water at the reaction temperatures. In other instances, however, FeS_2 is used as the catalyst and Fe_2O_3 and/or Fe_3O_4 is formed by contact of the FeS_2 with water at the reaction temperatures. In other WS_2 can form WO_3 , NiS forms NiO, SnS forms SnO_2 ,
 20 MnS forms MnO. In some instances, the metal sulfide forms higher sulfides (*e.g.*, CoS forms Co_9S_8) or elemental metals (*e.g.*, CuS form Cu).

[0034] The reaction conditions in reaction zone 108 can include a temperature less than 600 °C, or 350 °C to 575 °C, or 475 °C to 525 °C, or at least, equal to, or between any two of 350 °C, 375 °C, 400 °C, 425 °C, 450 °C, 475 °C, 500 °C, 525 °C, 575 °C, and 590 °C. In some
 25 embodiments, the reaction temperature is 475 °C to 525 °C or about 500 °C. A reaction pressure can be 0.101 MPa to 0.5 MPa or about 1 atmosphere of pressure. At these conditions no, or substantially no, elemental sulfur is formed. Product stream 112 can include gaseous hydrogen, optional gaseous hydrogen sulfide, and/or optional gaseous sulfur dioxide, depending on the metal sulfide used. For example, CdS, ZnS, and WS_2 can produce H_2 and
 30 SO_2 . NiS, SnS, PbS, FeS, MnS, and CoS can produce H_2 , H_2S , and SO_2 . CuS can produce H_2 . The amounts of H_2 , H_2S and SO_2 can vary depending on the catalyst and amounts of catalyst used. The temperature and pressure of the reaction zone 108 can be adjusted to control the amount of elemental sulfur formed during the reaction.

[0035] Generated H₂S can react with any iron oxide present and convert the iron oxide to catalytic iron sulfide, and water can also be produced. In some embodiments, the temperature in reaction zone 108 can be greater than 500 °C, but less than 600 °C during the production of H₂ from water. After the H₂ production decreases, the temperature can be raised to above 600 °C to convert the metal oxide to metal sulfide. To facilitate the conversion of the metal oxide to metal sulfide, the temperature in reaction zone 108 can be increased to 500 °C to 800 °C, 600 °C to 700 °C, or greater than, 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, and 800 °C. A reaction pressure can be 0.101 MPa to 0.5 MPa or about 1 atmosphere of pressure. By way of example, a mixture of FeS and FeS₂ can be produced at temperatures between 500 °C and 600 °C. During conversion of the metal oxide to metal sulfide SO₂ and/or H₂ can be produced. In some embodiments, elemental sulfur and/or additional H₂S can be added to reaction zone 108 to supplement the sulfur source for the sulfurization reaction. In some embodiments, a supplemental sulfur source can be added to reaction zone 108 to assist in conversion of the metal oxide material back to the catalytic metal sulfide material when the amounts of produced H₂S and/or elemental sulfur are inadequate to convert the iron oxide material to iron sulfide material. . Non-limiting examples of a supplemental sulfur source can include H₂S and elemental sulfur. The sulfur source can enter reactor 102 through reactant inlet 104. The produced water stream can contact the iron sulfide catalyst and continue the cycle. In some embodiments, the produced water can be removed from the reactor. While the invention has been described as starting with the metal sulfide catalyst, it should be understood that the self-sustaining cycle can be started with the metal oxide.

EXAMPLES

[0036] 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

(Process to Produce H₂ from Water with a Metal Sulfide Catalyst)

[0037] A metal sulfide listed in Table 1 was placed in a tubular reactor. The tubular reactor was purged with argon. The argon flow was stopped, and the tubular reactor was heated to

between 400 °C and 500 °C. Water was then injected into the tubular reactor at a rate of between 0.5 and 5 mL/h for 1 hour. The produced gasses were analyzed by GC-TCD, which showed the formation of H₂ and H₂S. FIG. 2 shows the GC chromatogram of the gas products of the iron sulfide reaction. Agilent 7820A GC (Agilent Technologies, U.S.A.) equipped with a thermal conductivity detector (TCD), using an Agilent GS-CarbonPlot column (for CO₂) or Agilent HP-Molesieve column (for all other gasses). Powder XRD was used to determine the metal oxide formed, which are listed in Table 1. Above 600 °C, elemental sulfur was detected. Mass spectrum of the gaseous product mixture confirmed the presence of H₂S with a peak at 33.98 being detected.

TABLE 1

Metal Sulfide	Products Produced			
	H ₂ (mmoles)	H ₂ S (mmoles)	SO ₂ (mmoles)	Metal Oxide (% by XRD)
CdS	0.006	---	0.105	---
NiS	0.16	0.11	0.028	NiO (< 1%)
SnS	0.22	0.039	0.1	SnO ₂ (55%)
PbS	0.06	0.1	0.06	---
CuS	0.008	0	---	Cu (100%)
ZnS	0.025	---	0.032	---
FeS	0.83	0.005	0.004	Fe ₂ O ₃ , Fe ₃ O ₄
MnS	0.1	0.12	0.005	MnO (1.2%)
WS ₂	2.09	---	1.8	WO ₃ (15%)
CoS	0.14	0	0.033	Co ₉ S ₈ (26%)

Example 2

(Reaction of Fe₃O₄ with H₂S)

[0038] Fe₃O₄ (2.32 g, 10 mmoles) was placed in a tubular reactor. Argon was flowed through the tube to purge it for 20 minutes, after which the tubular reactor was heated to between 200 °C and 700 °C. After reaching the desired temperature, H₂S was flowed at a rate of 0.5 L/hr for between 5 minutes and 1 hour. The produced gasses were analyzed by GC-TCD and showed no gas formation. Powder XRD was used to determine the iron phases (FeS, FeS₂). Both H₂O and elemental sulfur were formed as reaction products. At temperatures above 600 °C, only FeS was formed. At temperatures from 300 °C to 500 °C, a mixture of FeS and FeS₂ was formed. Below 200 °C, no products are detected. Lower reaction temperatures lead to higher proportions of FeS₂ forming. FIG. 3 shows the formation of FeS at temperatures from 200 °C and 700 °C. FIG. 4 shows the percentage of Fe₃O₄, FeS, and FeS₂ at 400 °C

between 5 minutes and 1 hour. FIG. 5 shows the percentage of Fe_3O_4 , FeS , and FeS_2 at 500 °C between 5 minutes and 1 hour.

Example 3

(Reaction of FeO_x with Elemental Sulfur)

5 [0039] Fe_2O_3 or Fe_3O_4 (2.3 mmol) was placed in a tubular reactor sealed at one end. To this, elemental sulfur (18.75 mmol) was added, and the tubular reactor was purged with argon. The argon flow was stopped, and the tubular reactor was heated to between 200 °C and 500 °C for between 5 minutes and 1 hour. The gasses were analyzed by GC-TCD, which showed the formation of SO_2 . XRD was used to identify the iron species present. From the
10 XRD pattern, it was determined that FeS_2 was formed from Fe_2O_3 and Fe_3O_4 , with traces of Fe(m) in the case of Fe_2O_3 only. FIG. 6 shows the XRD pattern of Fe_2O_3 heated with elemental sulfur at 400 °C for 1 hour. The XRD showed peaks for FeS_2 (peaks designated by stars) and Fe metal (peaks designated by circles). FIG. 7 shows the XRD pattern of Fe_2O_4 heated with elemental sulfur at 400 °C for 1 hour. The XRD showed peaks for FeS_2 (peaks designated by
15 stars) and Fe_3O_4 (peaks designated by circles).

Example 4

(Reaction of FeO_x with H_2S followed by H_2O at 700 °C)

[0040] Fe_3O_4 (14 g, 60 mmol) was placed in a tube. Argon was flowed through the tube to purge it for 20 minutes after which the mixture was heated to 700 °C. A mixture of H_2S and
20 H_2O at flow rate of 0.5 L /hr was passed through the tube. A linear evolution of hydrogen was observed as a function of time during a several hours run (See, FIG. 8). After 7 hours, over 27 mmol of hydrogen had been produced from 3 mmol of Fe_3O_4 . Sulfur was also produced (14 mmol).

Example 5

(Reaction of FeO_x with H_2S followed by H_2O at 600 °C)

25 [0041] Fe_3O_4 (7g, 30 mmol) was heated to 600 °C and reacted with H_2S at a flow rate 0.5 L /hr for 15 minutes using the protocol described in Example 2. The tube was then purged with inert gas to prevent the presence of H_2S , which may result in sulfur formation. Water was injected at the same temperature for 30 minutes. In the first cycle of $\text{H}_2\text{S}/\text{H}_2\text{O}$, no sulfur was
30 produced. However, in the second cycle of $\text{H}_2\text{S}/\text{H}_2\text{O}$, in the water step sulfur was formed.

Example 6

(Reaction of FeO_x with H_2S followed by H_2O at 500 °C)

[0042] The temperature of the H₂S addition to the Fe₃O₄ was kept at 600 °C due to the clean formation of only FeS (no FeS₂), while the addition to water to the FeS₂ part was performed at 500 °C, as at this temperature no sulfur was previously observed in this step (higher temperatures showed sulfur formation). However, in the second cycle of H₂S/H₂O

5 sulfur was also produced.

CLAIMS

1. A process for producing hydrogen (H_2) from water, the process comprising contacting water with a metal sulfide at a reaction temperature of less than $600\text{ }^{\circ}\text{C}$ to convert the metal sulfide to a metal oxide, and produce a product stream comprising hydrogen (H_2), optional sulfur dioxide (SO_2), and optional hydrogen sulfide (H_2S).
2. The process of claim 1, wherein the product stream has less than 0.01 wt.% of elemental sulfur or is preferably free of elemental sulfur.
3. The process of any one of claims 1 to 2, wherein the reaction temperature is $350\text{ }^{\circ}\text{C}$ to $575\text{ }^{\circ}\text{C}$, or $475\text{ }^{\circ}\text{C}$ to $525\text{ }^{\circ}\text{C}$, or about $500\text{ }^{\circ}\text{C}$.
4. The process of any one of claims 1 to 3, further comprising contacting H_2S with the metal oxide at a temperature of at least $600\text{ }^{\circ}\text{C}$ to convert the metal oxide to the metal sulfide to produce additional H_2 .
5. The process of claim 4 wherein the reaction temperature for converting the metal oxide to the metal sulfide is $600\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$.
6. The process of any one of claims 4 to 5, wherein the product stream comprises H_2 and H_2S , and the method further comprising isolating the H_2S from the product stream and contacting the H_2S with the metal oxide.
7. The process of claim 6, wherein elemental sulfur is produced.
8. The process of any one of claims 1 to 7, wherein less than 0.001 wt.% or no sulfuric acid (H_2SO_4) is produced during the reaction.
9. The process of any one of claims 1 to 8, wherein the metal sulfide comprises iron (Fe), tungsten (W), tin (Sn), nickel (Ni), manganese (Mn), cobalt (Co), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), or mixtures thereof.
10. The process of claim 9, wherein the metal sulfide is FeS_x , where x is 1 or 2, preferably 1, and the metal oxide comprises Fe_3O_4 .
11. The process of claim 9, wherein the metal sulfide is WS_2 and the metal oxide comprises WO_3 .
12. The process of any one of claims 1 to 11, wherein the process is self-sustaining.
13. The process of any one of claim 1 to 12, wherein the metal sulfide is not obtained from a thermal hydrocarbon cracking process.

14. The process of any one of claims 1 to 13, wherein the metal sulfide is a bulk metal catalyst.
15. A system for producing hydrogen (H_2) from water, the system comprising:
 - an inlet for a reactant feed comprising water (H_2O);
 - a reaction zone that is configured to be in fluid communication with the inlet, wherein the reaction zone has a temperature of less than $600\text{ }^{\circ}C$ and comprises water and a metal sulfide catalyst;
 - a first outlet configured to be in fluid communication with the reaction zone and configured to remove a first product stream comprising H_2 and optionally hydrogen sulfide (H_2S) from the reaction zone.
16. The system of claim 15, wherein the reaction zone further comprises the reactant feed and the product stream.
17. The system of any one of claims 15 to 16, wherein the reaction zone comprises a metal oxide and the system further comprises:
 - a second inlet in fluid communication with the reaction zone and comprising a second reactant feed, the second reactant feed comprising H_2S ; and
 - a heat source configured to heat the reaction zone to at least $600\text{ }^{\circ}C$,wherein the first inlet is configured to remove a second product stream comprising H_2 and gaseous sulfur dioxide (SO_2) from the reaction zone.
18. The system of any one of claims 15 to 17, further comprising a separation zone coupled to the first outlet and configured to separate H_2S from the H_2 in the product stream and provide the H_2S to the first inlet or reaction zone.
19. The system of any one of claims 15 to 18, wherein the metal sulfide catalyst comprises a transition metal.
20. The system of claim 19, wherein the transition metal is iron or tungsten.

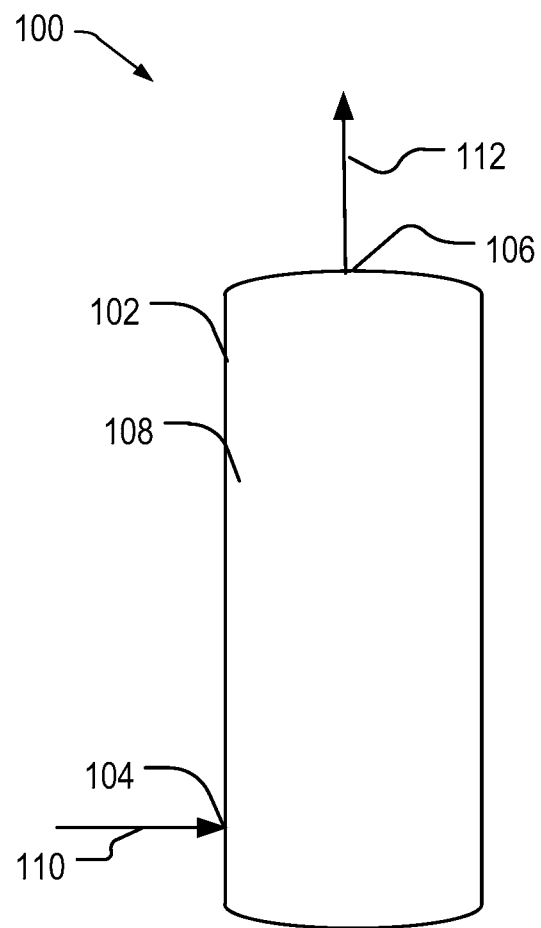


FIG. 1

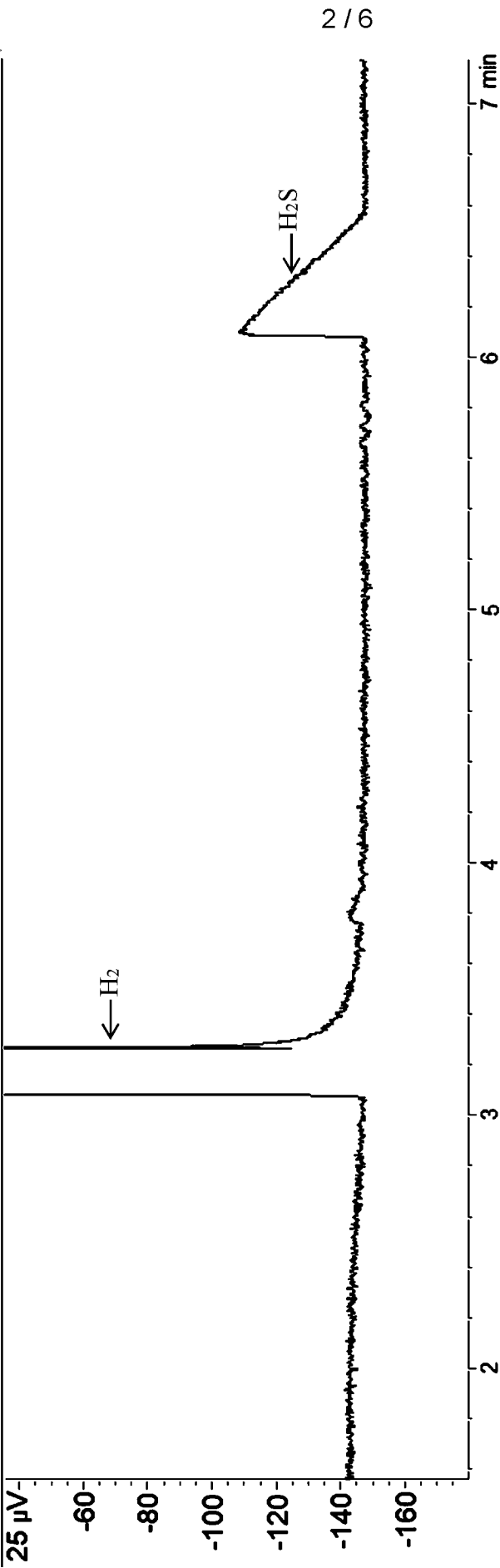


FIG. 2

3 / 6

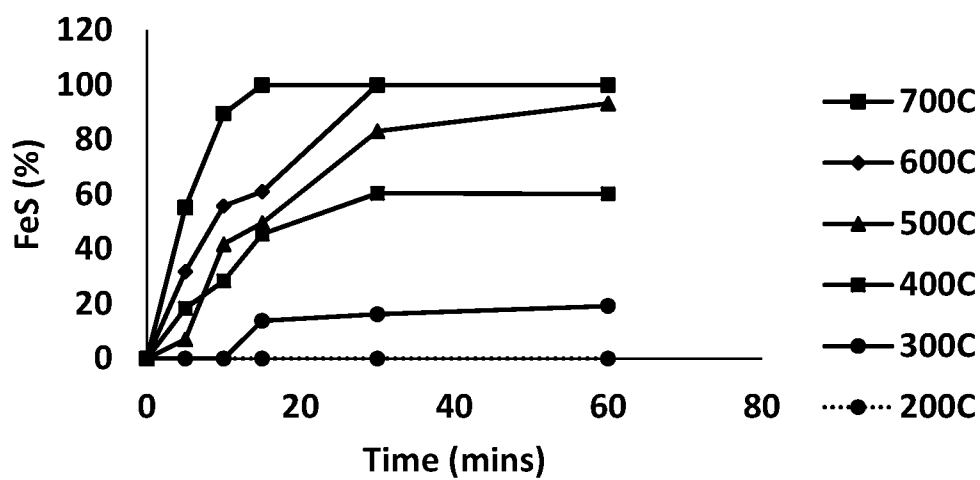


FIG. 3

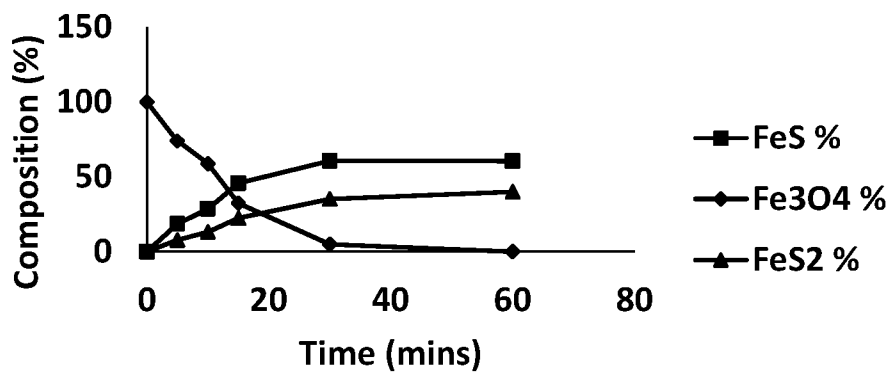


FIG. 4

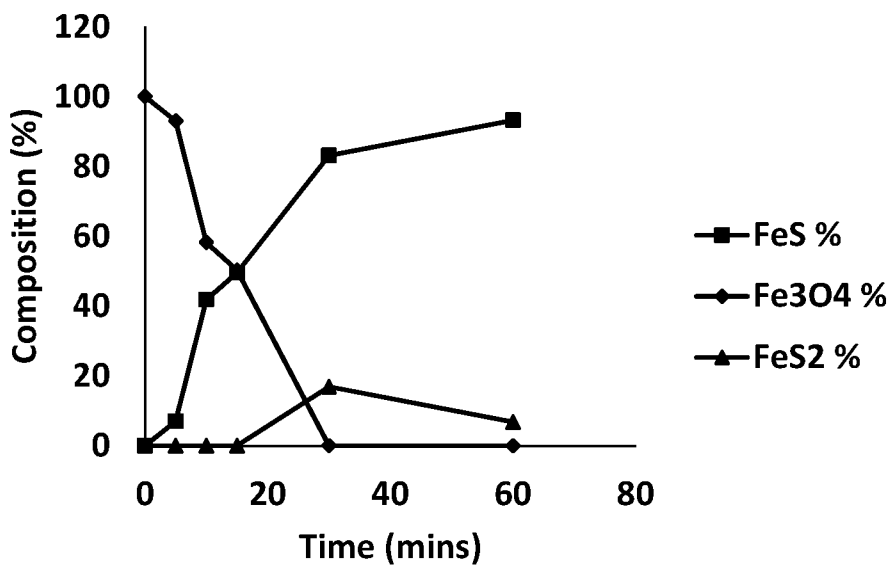


FIG. 5

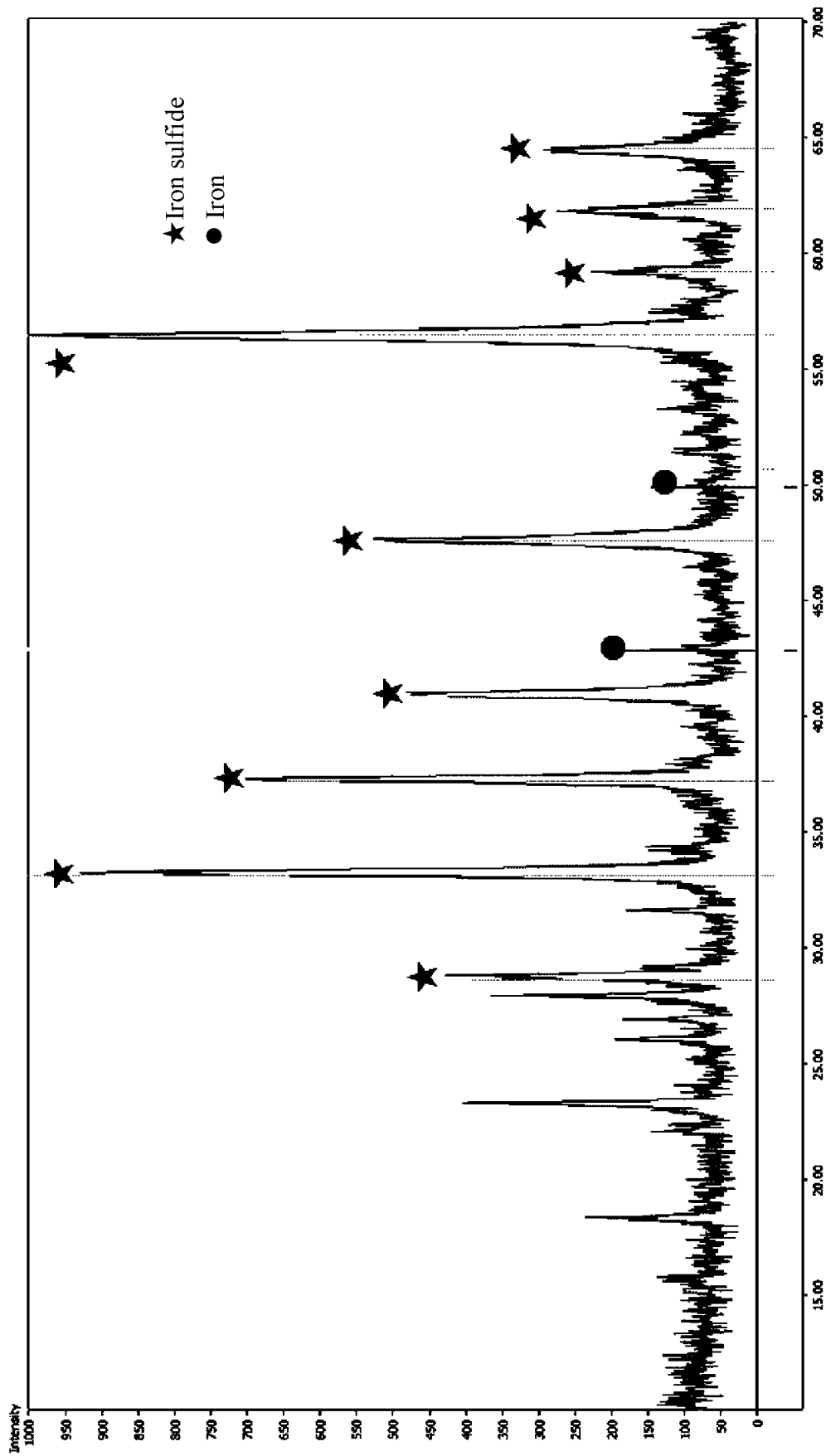


FIG. 6

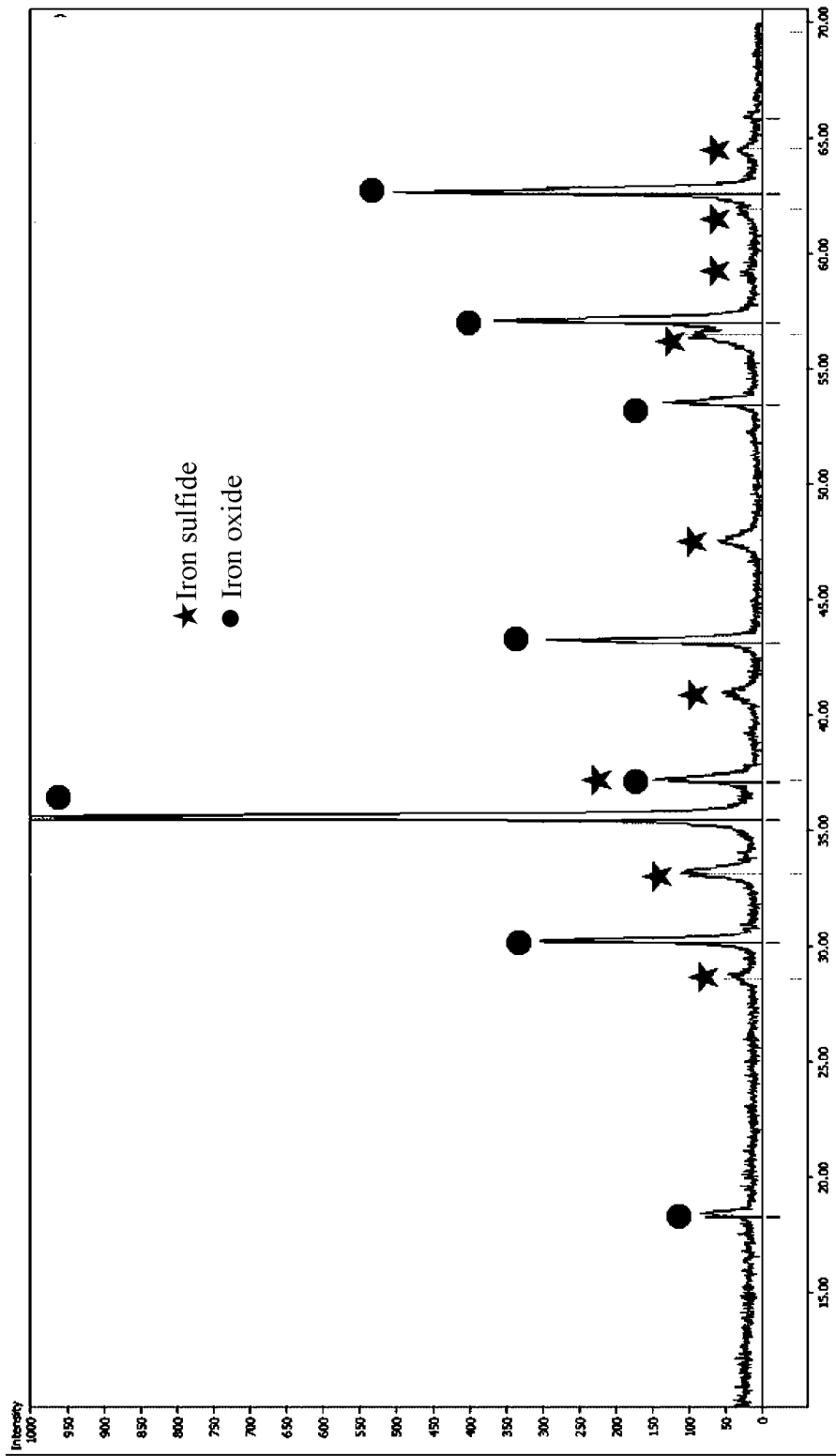
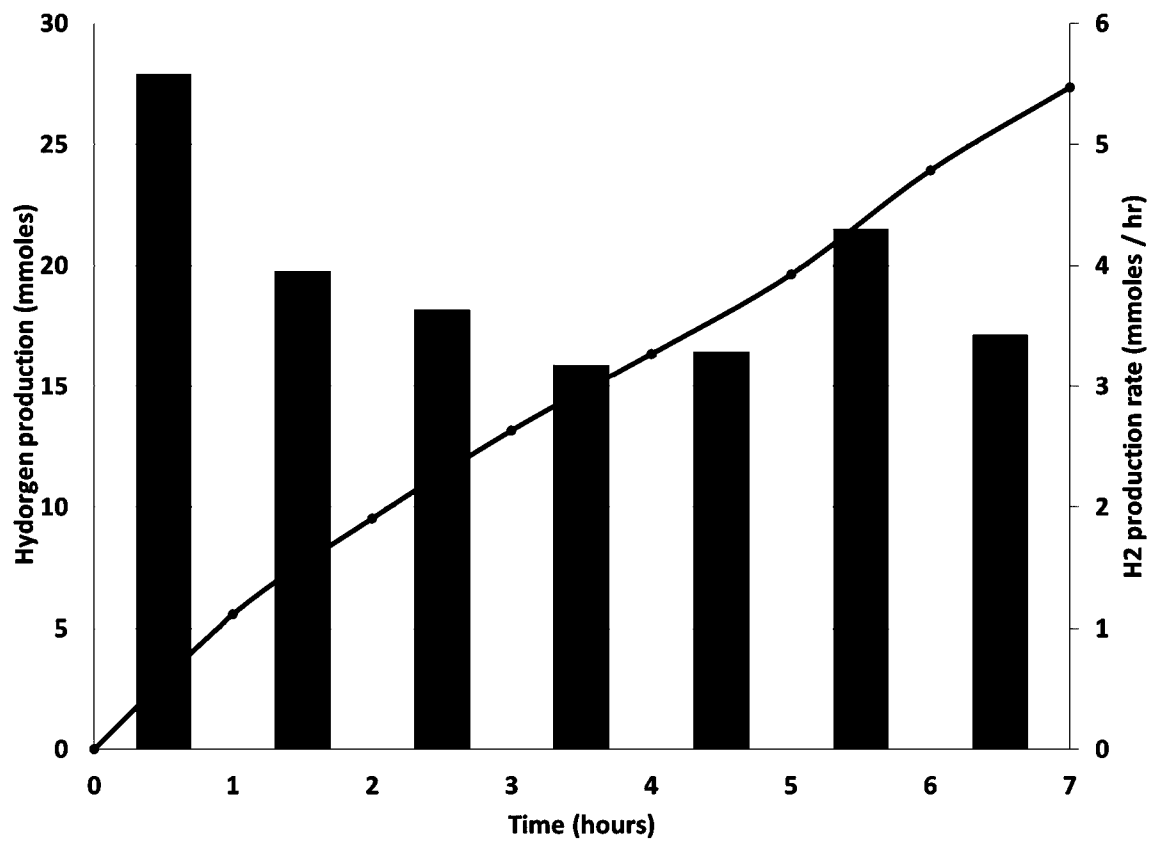


FIG. 7

*FIG. 8*

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/054441

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B3/06 C01B17/16 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		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 635 947 A (REED HOMER C ET AL) 21 April 1953 (1953-04-21)	1,3, 8-10, 12-17, 19,20 4-7,18
Y	column 7, line 15 - column 8, line 70; figure 1; table 1 ----- -/--	
☒ 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 22 August 2019		Date of mailing of the international search report 30/08/2019
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 Cristescu, Ioana

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/054441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SOLIMAN M A ET AL: "Hydrogen production via thermochemical cycles based on sulfur chemistry", INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, ELSEVIER SCIENCE PUBLISHERS B.V., BARKING, GB, vol. 1, no. 3, 1 January 1976 (1976-01-01) , pages 265-270, XP025413880, ISSN: 0360-3199, DOI: 10.1016/0360-3199(76)90022-7 [retrieved on 1976-01-01]	1-3, 8-17,19, 20
Y	tables 1,2	4-7,18

X	KAI ZHANG ET AL: "Metal sulphide semiconductors for photocatalytic hydrogen production", CATALYSIS SCIENCE & TECHNOLOGY, vol. 3, no. 7, 1 January 2013 (2013-01-01) , page 1672, XP055614422, United Kingdom ISSN: 2044-4753, DOI: 10.1039/c3cy00018d figures 13,17; table 1	1-3, 8-10, 12-14

X	WU JINXIA ET AL: "Ternary Transitional Metal Chalcogenide Nanosheet with Significantly Enhanced Electrocatalytic Hydrogen-Evolution Activity", CATALYSIS LETTERS, SPRINGER NEW YORK LLC, UNITED STATES, vol. 147, no. 1, 12 November 2016 (2016-11-12), pages 215-220, XP036147549, ISSN: 1011-372X, DOI: 10.1007/S10562-016-1907-2 [retrieved on 2016-11-12] paragraph [0002]	1-3,8-14

Y	DE 25 41 824 A1 (RHEINISCHE BRAUNKOHLENW AG) 31 March 1977 (1977-03-31) cited in the application page 6, line 15 - page 7, line 26	4-7,18

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Information on patent family members

International application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2635947	A	21-04-1953	NONE	

DE 2541824	A1	31-03-1977	NONE	
