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(54) **Title:** HYDROGEN PRODUCTION FROM AQUEOUS FORMALDEHYDE UNDER MILD BASIC CONDITIONS

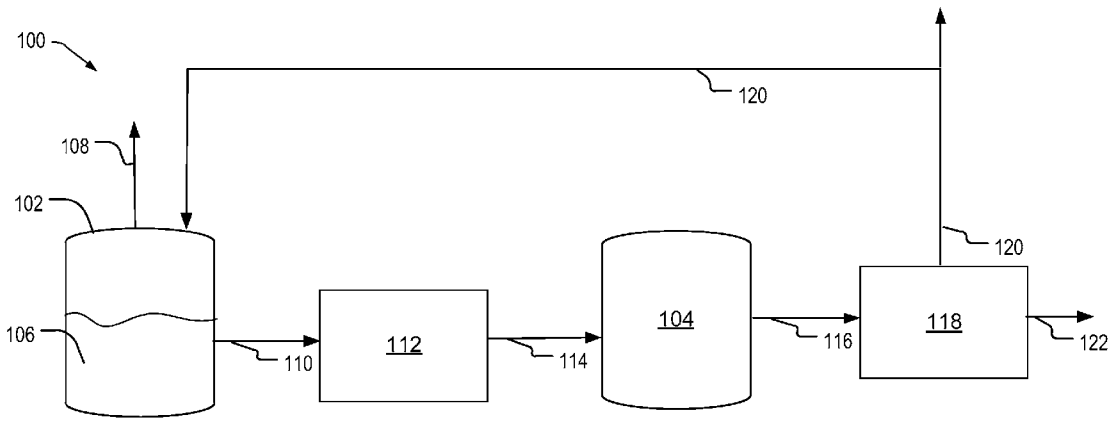


FIG. 1

(57) **Abstract:** Methods of producing H2 from formaldehyde are described. A method can include contacting an aqueous reaction mixture that includes water, formaldehyde (H2CO), and base with a dehydrogenation catalyst and a metal hydroxide co-catalyst under conditions sufficient to produce a product stream comprising hydrogen (H2) gas and a formate product. The reaction mixture can have a pH of 7.0 to 8.0.

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HYDROGEN PRODUCTION FROM AQUEOUS FORMALDEHYDE UNDER MILD BASIC CONDITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/670,978 filed May 14, 2018, which is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns a method for producing hydrogen (H_2) gas from formaldehyde. In particular, the method involves contacting a neutral to slightly basic aqueous reaction mixture comprising water, formaldehyde, and a base with a dehydrogenation catalyst and a metal hydroxide co-catalyst under conditions sufficient to produce a product stream comprising H_2 and a formate product.

B. Description of Related Art

[0003] There is increasing global demand for hydrogen gas, and there are various strategies for obtaining hydrogen gas by dehydrogenating organic molecules. The primary technical issues in the field of hydrogen production are rapid release, recyclability, and efficiency. Finding an efficient and renewable hydrogen-producing process would be aided by being able to shuttle a suitable molecule between its reduced and oxidized forms. However, this is challenging because each step of such a process—reduction and oxidation—may require its own catalyst.

[0004] Simple organic reagents like formaldehyde can be used to produce hydrogen in processes that use metal catalysts to oxidize formaldehyde, releasing hydrogen gas, and selectively generating formate anion as the only co-product. An example of a process using formaldehyde in this way can be found in U.S. Patent App. Pub. No. 2016/0340186 to Al-Bahily *et al.*, which describes a homogeneous system that includes exposing an aqueous basic solution at a pH of 8 to 12 having an iron containing photocatalyst and formaldehyde (*e.g.*, methanediol or paraformaldehyde) to light, resulting in production of hydrogen gas from the formaldehyde, with formate as the sole by-product. The produced formate can be decomposed to H_2 and CO_2 in the presence of catalytic metals and heat with a small amount of formaldehyde formed. U.S. Patent Application Publication No. 2017/042661 to Al-Bahily *et al.* describes producing H_2 from formaldehyde at a pH of 8 to 12 using a transition metal complex catalyst.

Heim *et al.* (*Nature Communications*, 2014, Vol. 5, 3621) describes converting aqueous formaldehyde under acidic or buffered conditions at 95 °C to produce formic acid, which is then contacted with an [(Ru(p-cymene))2μ-H(μ-HCO_2)μ-Cl]+BF_4− catalyst to produce H_2 and CO_2. Suenobu *et al.* (*Chem. Commun.* 2015, Vol. 51, 1670-1672) describes contacting an [IrIII(Cp*)(4-(1H-pyrazol-1-yl-κN_2)benzoic acid-κC_3)(H_2O)]$_2SO_4$) catalyst with aqueous formaldehyde under basic conditions (pH of 11) to produce H_2 and CO_2 at 25 °C. U.S. Patent No. 4,414,182 to Okamoto *et al.* describes contacting a basic aqueous solution of formaldehyde with a Column 6 carbide catalyst or copper, silver, or gold catalyst at 18 °C to 50 °C. Okamoto describes that the acidic or neutral solutions produce no or negligible amounts of H_2.

[0005] While there have been various attempts to produce hydrogen from formaldehyde, there remains a need for methods of improving the efficiency of this process in an economical and sustainable manner.

SUMMARY

[0006] A discovery has been made that provides a solution to the aforementioned necessity for an economical and sustainable method of producing hydrogen gas (H_2) and formate products from formaldehyde. The formaldehyde in this process is suitable as part of a cycle by which formaldehyde is shuttled between a reduced state (formaldehyde) and an oxidized state (formic acid) in the production of H_2. The discovery is premised on contacting a homogeneous mixture that includes formaldehyde, water, and a base with the dehydrogenation catalyst and a metal hydroxide co-catalyst (*e.g.*, $Zn(OH)_2$) under neutral to mildly basic conditions (*e.g.*, pH of 7.0 to 8.0), thereby converting the formaldehyde to H_2 and a formate product. Notably, the reaction can be run in the absence of visible or ultra-violet light. The formate product can be complexed with the counter ion of the base or metal hydroxide co-catalyst to produce a metal formate product (*e.g.*, zinc formate, sodium formate, potassium formate, calcium formate, aluminum formate, or mixtures thereof, preferably zinc formate). The formate product or metal formate product can be converted to H_2 and carbon oxides (*e.g.*, CO_2 and/or CO) under thermal or hydrothermal conditions.

[0007] In an aspect of the present invention, methods of producing hydrogen gas from formaldehyde are described. A method can include subjecting an aqueous mixture that includes formaldehyde, water, a base, a dehydrogenation catalyst and a metal hydroxide co-catalyst under conditions suitable to produce a H_2 gas product and a formate (HCO_2^-) product

at a pH of 7.0 to 8.0. In certain aspects, the pH of the reaction mixture is about 7.4 to 7.8, or more preferably about 7.6. The dehydrogenation catalyst can be $Ru(OH)_3$, $IrCl_3$, $Na_4Fe(CN)_6$, $RuCl_3$, a Ir-H complex, a Ru-cymene complex, or combinations thereof. In some embodiments, the co-catalyst can be $Zn(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$, $Cu(OH)_2$, or $Mg(OH)_2$. In a preferred aspect, the co-catalyst can be $Zn(OH)_2$. In certain aspects, the temperature of the mixture can be 10 °C to 80 °C, preferably about 60 °C. The molar ratio of formaldehyde to dehydrogenation catalyst can be 500:1 to 1:500, 50:1 to 1:50, 10:1, to 1:10, or about 3:1 to 1:3. In a preferred aspect, the molar ratio of formaldehyde to dehydration catalyst is about 1:1. In certain aspects, the molar ratio of formaldehyde to base (*e.g.*, NaOH, KOH, $Ca(OH)_3$, or $Al(OH)_3$) is 2:1 to 1:2 or the molar ratio of formaldehyde to base to co-catalyst (*e.g.*, $Zn(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$, or $Mg(OH)_2$) is 2:1:0.1 to 1:2:0 with the proviso that the co-catalyst and base are different. In particular aspects, the molar ratio of formaldehyde to base is about 1:1 or the molar ratio of formaldehyde to base to co-catalyst (*e.g.*, $Zn(OH)_2$) is 1:1:0.3). The formaldehyde can be para-formaldehyde, hydrated formaldehyde, or a combination thereof. In particular aspects, the formaldehyde is para-formaldehyde.

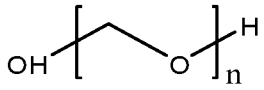
[0008] The methods can further include converting the formate product to formaldehyde. In certain aspects, the formate product can be a metal formate salt (zinc formate, sodium formate, potassium formate, calcium formate, aluminum formate, or mixtures thereof, preferably zinc formate). In a preferred instance, the metal formate salt can be zinc formate. The conversion reaction can be performed under an inert atmosphere. The formate product (*e.g.*, metal formate salt) can be thermally converted at a temperature of 200 °C to 500 °C. In certain aspects, an aqueous metal formate product/steam composition can be heated at temperature of 250 °C to 400 °C to produce formaldehyde and H_2. The obtained formaldehyde can be further used to produce H_2 as described above.

[0009] In another aspect of the invention, systems to produce H_2 and a formate product from formaldehyde are described. The system can include (a) a hydrogen generation zone and (b) a formate conversion zone operatively connected to the hydrogen generation zone. The hydrogen generation zone can include a formaldehyde dehydrogenation catalyst and a co-catalyst configured for production of H_2 and a formate ($HCOO^-$) product. The formate conversion zone can be configured (i) to receive the formate product for conversion to formaldehyde (H_2CO) and (ii) to cycle the converted formaldehyde to the hydrogen generation zone. In certain aspects, the formaldehyde dehydrogenation catalyst is $IrCl_3$, $Na_4Fe(CN)_6$, $RuCl_3$, $Ru(OH)_3$, a Ir-H complex, a Ru-cymene complex, or combinations thereof.

[0010] It can be appreciated from the above that the methods of the present invention can be designed as a cycle of self-sustaining reactions: formaldehyde can be used to produce hydrogen gas and a formate product, and the cycle can start again with reduction of the formate product to formaldehyde. The two primary steps in the cycle—production of hydrogen and formate product from formaldehyde and the production of formaldehyde from formate product—can be performed using different catalysts and different reaction conditions. The production of hydrogen and formate product from formaldehyde can use a metal catalyst in a homogeneous, mildly basic, aqueous solution at relatively low temperatures (*i.e.*, not more than 80 °C) and neutral to mildly basic conditions (*i.e.*, pH of 7 to 8). In contrast, the production of formaldehyde from formate can use a solid metal catalyst at relatively high temperatures (*i.e.*, not less than 200 °C) with gaseous reactants.

[0011] The following includes definitions of various terms and phrases used throughout this specification.

[0012] The term "homogeneous" as used herein is defined as a reaction equilibrium in which the catalysts, reactants, and products are all or substantially all in the same phase (*e.g.*, the catalysts, reactants and products are dissolved or substantially dissolved in a basic aqueous medium).

[0013] "Formaldehyde" as used herein includes gaseous, liquid, and solid forms of formaldehyde. "Formaldehyde" includes its aldehyde form (CH_2O), its hydrated form (methanediol), and its *para*-formaldehyde form of , where n can be up to 100.

[0014] The term "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%.

[0015] The term "substantially" and its variations are defined to include to ranges within 10%, within 5%, within 1%, or 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 of 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.

[0017] 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.

[0018] The term "effective," as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0019] 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."

[0020] 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.

[0021] The methods of the present invention to produce H_2 and formate products from formaldehyde 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 methods of the present invention are their abilities to selectively oxidize formaldehyde to a formate product and produce H_2 in an aqueous solution at a pH of 7 to 8.

[0022] In the context of the present invention, at least twenty embodiments are now described. Embodiment 1 is a method of producing hydrogen from formaldehyde. The method includes the steps of subjecting an aqueous reaction mixture containing water, formaldehyde, a base, a dehydrogenation catalyst and a metal hydroxide co-catalyst to sufficient to produce a product stream containing hydrogen (H_2) gas and a formate product, wherein the reaction mixture has a pH of 7.0 to 8.0. Embodiment 2 is the method of embodiment 1, wherein the pH of the reaction mixture is about 7.6. Embodiment 3 is the method of any one of embodiments 1 to 2, wherein the metal hydroxide co-catalyst is zinc hydroxide ($Zn(OH)_2$), calcium hydroxide ($Ca(OH)_2$), aluminium hydroxide ($Al(OH)_3$), copper hydroxide ($Cu(OH)_2$), or magnesium hydroxide ($Mg(OH)_2$). Embodiment 4 is the method of any one of embodiments 1 to 3, wherein the dehydrogenation catalyst is $IrCl_3$, $Na_4Fe(CN)_6$, $RuCl_3$, $Ru(OH)_3$, or an Ir-H complex, or Ru-cymene. Embodiment 5 is the method of any one of embodiments 1 to 4, wherein the

temperature of the reaction mixture is 10 °C to 80 °C, preferably about 60 °C. Embodiment 6 is the method of any one of embodiments 1 to 5, wherein the base is sodium hydroxide (NaOH), potassium hydroxide (KOH), $Ca(OH)_2$, $Al(OH)_3$, or combinations thereof, preferably NaOH, with the proviso that the base and co-catalyst are different. Embodiment 7 is the method of any one of embodiments 1 to 6, wherein the molar ratio of formaldehyde to dehydration catalyst is 50:1 to 1:50 or 3:1 to 1:3. Embodiment 8 is the method of embodiment 7, wherein the molar ratio of formaldehyde to dehydration catalyst is about 1:1. Embodiment 9 is the method of any one of embodiments 1 to 8, wherein the molar ratio of formaldehyde to the base is 2:1 to 1:2 or the molar ratio of formaldehyde to base to co-catalyst is 2:1:0.1 to 1:2:0.6. Embodiment 10 is the method of any one of embodiments 1 to 9, wherein the molar ratio of formaldehyde to the base is about 1:1 or the molar ratio of formaldehyde to the base to the co-catalyst is 1:1:0.3. Embodiment 11 is the method of any one of embodiments 1 to 10, wherein the formaldehyde is para-formaldehyde, hydrated formaldehyde, or a combination thereof. Embodiment 12 is the method of embodiment 11, wherein the formaldehyde is para-formaldehyde. Embodiment 13 is the method of any one of embodiments 1 to 12, further including the step of converting the formate product to formaldehyde. Embodiment 14 is the method of embodiment 13, wherein the formate product contains a metal formate salt, and the method further includes the step of heating the metal formate salt to form formaldehyde. Embodiment 15 is the method of any one of embodiments 13 to 14, wherein the metal formate salt is zinc formate, sodium formate, potassium formate, calcium formate, aluminum formate, or mixtures thereof, preferably zinc formate. Embodiment 16 is the method of any one of embodiments 13 to 15, wherein the metal salt is heated at a temperature of 200 to 500 °C, preferably 250 to 400 °C. Embodiment 17 is the method of any one of embodiments 13 to 16, wherein the metal salt is heated in an inert atmosphere or in the presence of steam. Embodiment 18 is the method of any one of embodiments 13 to 17, wherein the conversion is done in the presence of a catalyst. Embodiment 19 is the method of embodiment 18, wherein the catalyst is a Columns 6-8 transition metal catalyst. Embodiment 20 is the method of any one of embodiments 1 to 17, wherein production of H_2 is self-sustaining.

[0023] Other objects, features, and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit

and scope of the invention will become apparent to those skilled in the art from this detailed description. In further embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments. In further embodiments, additional features may be added to the specific embodiments described herein.

DESCRIPTION OF THE DRAWINGS

[0024] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of the specification embodiments presented herein.

[0025] **FIG. 1** is a schematic of systems and method of the present invention to produce H_2 from formaldehyde and thermal decomposition of formate to produce additional H_2 and formaldehyde.

[0026] **FIG. 2** is a schematic of systems and method of the present invention to produce H_2 from formaldehyde and hydrothermal decomposition of formate to produce additional H_2 and formaldehyde.

[0027] **FIG. 3** shows the relationship between H_2 production over time in the presence and absence of zinc hydroxide.

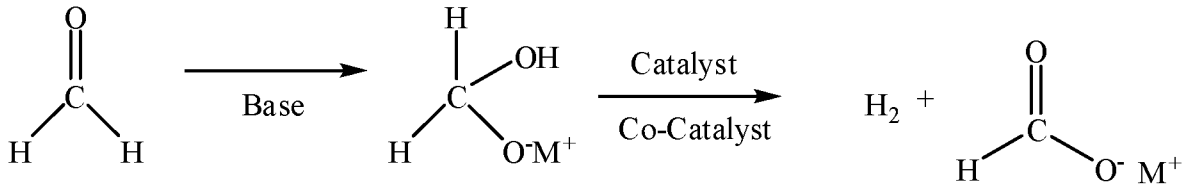
DESCRIPTION OF THE INVENTION

[0028] The present invention provides for an efficient process for producing H_2 from formaldehyde (*e.g.*, methanediol or *para*-formaldehyde or a combination thereof). The process can be performed under neutral to mildly basic conditions in the presence of a dehydrogenation catalyst and co-catalyst such that formaldehyde is oxidized to a formate product and H_2 is produced. This method can be part of a cycle in which formaldehyde is used produce hydrogen gas and a formate product, and the cycle can start again with reduction of the formate product to formaldehyde.

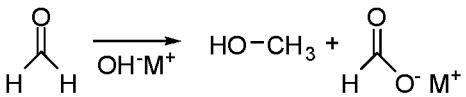
[0029] These and other non-limiting aspects of the present invention are discussed in further detail in the following sections with reference to FIGS. 1 and 2. The systems and methods described in FIGS. 1 and 2 can also include various equipment that is not shown and is known to one of skill in the art of chemical processing. For example, controllers, piping, computers, valves, pumps, heaters, thermocouples, and/or pressure indicators may not be shown.

A. Generation of Hydrogen

[0030] As illustrated in the Examples section, hydrogen can be produced by combining an aqueous composition having a pH of 7 to 8 and formaldehyde with a dehydrogenation catalyst and a co-catalyst as shown in the reaction scheme below.



[0031] In preferred instances, the catalyst, the co-catalyst, and the formaldehyde are partially or fully solubilized within the aqueous composition. FIGS. 1 and 2 are schematic of embodiments of a reaction system 100 for producing formate and hydrogen from formaldehyde and then converting the formate back to formaldehyde. System 100 includes hydrogen generating zone 102 and formate product conversion zone 104. In some embodiments, hydrogen generating zone 102 and formate product conversion zone 104 are separate reactors coupled by piping or two zones in one reaction unit. Hydrogen generating zone 102 can include reaction mixture 106. Reaction mixture 106 can include aqueous formaldehyde (*e.g.*, methanediol), a dehydrogenation catalyst, a co-catalyst (*e.g.*, $Zn(OH)_2$), and a base. Non-limiting examples of these materials are provided below in Section B. The dehydrogenation catalyst and co-catalyst can be used to catalyze the production of formate product and hydrogen from formaldehyde. When equimolar solutions of formaldehyde and base are combined, a slow Cannizzaro's disproportionation to MeOH and (HCOO)M, where M is a metal counter ion can occur as shown in equation below. The addition of a catalytic amount of the dehydrogenation catalyst of the present invention does not appear to inhibit this disproportionation.



where M^+ is a counter ion.

[0032] Without wishing to be bound by the theory, the production of hydrogen is in the homogeneous phase of the aqueous mixture. The reaction mixture can be agitated under conditions sufficient to produce H_2-containing stream 108 and formate product stream 110. Conditions sufficient to produce H_2 include a temperature of 10 °C to 80 °C, or greater than,

equal to, or between any two of 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, and 80 °C. In a preferred embodiment, the reaction temperature is about 50 °C to 70 °C, or more preferably about 60 °C. The reaction can be run at atmospheric pressure or ambient pressure. H_2-containing stream 108 can exit reaction zone 102 and be collected. The generated H_2 can be used as an energy source, sold, or used in other chemical reactions.

[0033] The dehydrogenation catalyst can precipitate or be precipitated from the solution by addition of acid to decrease the pH of the solution. The resulting precipitate can be removed, or substantially removed, through known solid/liquid filtration methods (*e.g.*, centrifugation, filtration, gravity settling, *etc.*). In some embodiments, the catalyst is not removed or is partially removed from the solution. The formate product (*e.g.*, metal formate salts), which is also dissolved in the solution, can then be used as a carbon source for production of other compounds (*e.g.*, oxalate and/or monoethylene glycol) and/or be thermally or hydrothermally converted to formaldehyde to continue the cycle. In some embodiments, the metals salts are isolated from the aqueous solution using known solvent removal techniques (*e.g.*, evaporation, distillation, or the like). Referring to FIG. 1, crude formate product stream 110, can exit reaction zone 102 and enter collection zone 112. In collection zone 112, the formate product can be isolated from crude formate product stream (*e.g.*, removal of catalyst and water). In some embodiments, collection zone 112 is not necessary. In some embodiments, the catalyst can be removed in reaction zone 102, and formate product 110 is isolated in collection zone 112. The formate product can be a metal formate salt or a mixture of such metal formate salts (*e.g.*, zinc formate, sodium formate, potassium formate, calcium formate, aluminum formate, or mixtures thereof). In a preferred embodiment, the metal formate salt is zinc formate. In some embodiments, the metal formate salts are not isolated and crude formate product stream is used in formate conversion reaction zone 104. Isolated formate product stream 114 can exit collection zone 112 and enter reaction zone 104. Alternatively, product stream 110 can enter reaction zone 104 without entering collection zone 112 (not shown).

[0034] In formate conversion reaction zone 104, formate product stream 114 can be subjected to conditions suitable to convert the formate product to formaldehyde and H_2. The formate can be converted to formaldehyde by thermally decomposing or hydrothermally decomposing the formate salt. Reaction conditions for thermally decomposing the formate salt can include heating the formate product to a temperature of 250 °C to 500 °C, or greater than, equal to, or between any two of 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, and 500 °C in an inert atmosphere to produce gaseous product stream 116 that includes formaldehyde, H_2,

CO_2, and CO. Thermal decomposition of the formate product can be performed under inert conditions (*e.g.*, under an argon or nitrogen atmosphere). Gaseous product stream 116 can exit reaction zone 104 and enter collection zone 118. In collection zone 118, the gases can be separated using known gas separation techniques (*e.g.*, membranes, cryogenic distillation, adsorption methods and the like) to produce formaldehyde product stream 120 and H_2 product stream 122. H_2 product stream 122 can include at least 90 mol.% H_2 or about 100 mol.% H_2. H_2 product stream 122 can be collected, sold, or provided to other units for further processing or energy uses. Formaldehyde product stream 120 can exit reaction zone 104 and be collected and/or provided to reaction zone 102 to continue the cycle.

[0035] In some embodiments, the formate product can be hydrothermally decomposed by contacting the formate product with aqueous formic acid and/or steam. FIG. 2 is a schematic of system 100 that includes the use of aqueous formic acid and/or hot water for conversion of the formate product to H_2 and formaldehyde. The production of formate product is the same as described above. Referring to FIG. 2, aqueous formic acid or hot water (*e.g.*, steam) stream 202 can enter formate conversion reaction zone 104. Contact of the formate product stream 114 with aqueous formic acid and/or steam can produce formaldehyde and a gaseous product stream that includes H_2, CO_2, and CO. Contact temperatures can range from 250 °C to 500 °C, or be greater than, equal to, or between any two of 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, and 500 °C in an inert atmosphere. In some embodiments, a catalyst can be provided to reaction zone 104 to promote the conversion of formate product to formaldehyde and H_2. Gaseous product stream 204 can exit reaction zone 104 and be collected (*e.g.*, collection zone 116) and/or further purified to produce a product stream containing at least 90 mol.% H_2 as previously described. In some embodiment, product stream 204 contains predominately H_2 (*e.g.*, at least 90 mol.%) and is not purified. Formaldehyde product stream 206 can exit reaction zone 104 and be collected or provide to reaction zone 102 to continue the cycle.

B. Reactants and Medium for Production of Formate and Hydrogen

1. Reactants

[0036] The reactants in the step of producing formate and H_2 can include formaldehyde, paraformaldehyde, or other organic molecules that release formaldehyde in aqueous solution. Formaldehyde can be formaldehyde, aqueous formaldehyde solutions (for example, 37% in water), para-formaldehyde, or combinations thereof. *para*-Formaldehyde is the polymerization of formaldehyde with a typical degree of polymerization of 1 to up to 100 units. Aqueous

formaldehyde (methanediol) and para-formaldehyde are available from many commercial manufacturers, for example, Sigma Aldrich® (USA). The basic reagent can include a metal hydroxide (MOH or $M(OH)_2$), where M is a alkali metal, alkaline earth metal or aluminum. Non-limiting examples of alkali or alkaline earth metals include lithium, sodium, potassium, and calcium. In a preferred embodiment, the base is sodium hydroxide (NaOH). The molar ratio of small organic molecule (*e.g.*, formaldehyde) to base is equal to or less than 2:1, 1.9:1, 1.8:1, 1.7:1, 1.6:1, 1.5:1, 1.2:1, 1.1:1, 1:1, 0.5:1 or any range there between.

2. Medium

[0037] The production of formate and hydrogen from formaldehyde can be performed in any type of medium that can solubilize the catalyst and reagents. In a preferred embodiment, the medium is an aqueous medium. Non-limiting examples of water that can be used in the aqueous medium include de-ionized water, salt water, river water, canal water, city canal water or the like.

[0038] The aqueous medium used in the hydrothermal conversion of formate to formaldehyde can be water, high pressure steam, medium pressure steam, low pressure steam, formic acid, and/or aqueous formic acid. The amount of formic acid in the aqueous medium can be greater than, equal to, or between any two of 5, 10 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 99.0 wt.%.

3. Dehydrogenation Catalyst and Co-Catalyst

[0039] The dehydrogenation catalyst can be any catalyst capable of dehydrogenating formaldehyde and soluble in the reaction medium. The dehydrogenation catalyst can be obtained from various chemical suppliers such as Sigma-Aldrich® (U.S.A.) and/or Alfa Aesar (U.S.A.). Non-limiting examples of the dehydrogenation catalyst include iridium chloride ($IrCl_3$), sodium ferrocyanide ($Na_4Fe(CN)_6$), ruthenium chloride ($RuCl_3$), ruthenium hydroxide ($Ru(OH)_3$, Ir-H complex, or Ru-cymene, or combinations thereof. A non-limiting example of an iridium-H complex is chlorodihydrido[bis(2-di-i-propylphosphino-ethyl)amine]iridium. The molar ratio of formaldehyde to dehydrogenation catalyst can be 50:1, 40:1, 30:1, 20:1, 10:1, 5:1, 3:1 to 1:3, 1:5, 1:10, 1:20, 1:30, 1:40, or 1:50. In a preferred embodiment, the molar ratio is 3:1 to 1:3.

[0040] The co-catalyst can be a metal hydroxide capable of undergoing a redox reaction and can be obtained from various commercial sources. Non-limiting examples of the co-catalyst include $Zn(OH)_2$, $Al(OH)_3$, $Ca(OH)_2$, $Mg(OH)_2$ or $Cu(OH)_2$. The molar ratio of base

to co-catalyst can be 1:0.1 to 2:0.6 or 1.3:0.4 or 1.5:0.5 or any range there between, with the proviso that the co-catalyst and base are different. The molar ratio of small organic molecule to base to co-catalyst can be 2:1:0.1 to 1:2:0.6, or 1:1:0.3.

4. Hydrothermal Catalyst

[0041] The hydrothermal catalyst can be any catalyst capable of catalyzing the reduction of formate to formaldehyde and H_2. The hydrothermal catalyst can be obtained from various chemical suppliers such as Sigma-Aldrich® (U.S.A.) and/or Alfa Aesar (U.S.A.). Non-limiting examples of the hydrothermal catalyst include transition metal catalysts. Non-limiting examples of transition metal catalysts include $BiOHCrO_4$, 2 wt.% Cr/ZSM-5, 2 wt.% Mn/ZSM-5 and RuO_2/TiO_2. In a preferred embodiment, $BiOHCrO_4$ is used. The molar ratio of formate ion (HCO_2^-) to hydrothermal catalyst can be 100:1, 60:1, 50:1, 20:1, 10:1, 5:1, 3:1 to 1:3, 1:5, 1:10, 1:20, 1:30, 1:40, 1:50, 1:60, 1:100. In a preferred embodiment, the molar ratio is 1:10.

EXAMPLES

[0042] 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.

Materials and Testing Procedures

[0043] **Materials**. Paraformaldehyde, 37% formaldehyde solution, and zinc hydroxide ($Zn(OH)_2$), NaOH and $Na_4Fe(CN)_6$ were purchased from Sigma-Aldrich® (USA). Formic acid was purchased from Acros Organics (BELGIUM). Ruthenium chloride ($RuCl_3$) and iridium chloride ($IrCl_3$) were purchased from Sigma-Aldrich® (USA). Chlorodihydrido[bis(2-di-i-propylphosphino-ethyl)amine]iridium was purchased from Strem Chemicals (USA). Chemicals were used without further purification. If not specifically mentioned, all reactions were carried out in distilled water without degassing or other modifications.

[0044] **Analytical Equipment**. pH measurements were taken with a Hanna HI 2210 benchtop pH meter with a general purpose combination pH electrode, both purchased from Sigma-Aldrich®.

[0045] **Product Analysis**. H_2, CO_2, CO, and O_2 gas identification and detection was carried out with an Agilent 7820A GC equipped with a thermal conductivity detector (TCD), using an

Agilent GS-CarbonPlot column (for CO_2) or Agilent HP-Molesieve column (for all other gasses).

Example 1

(Production of H_2 and Formate Product from Formaldehyde with $Zn(OH)_2$ and Catalyst)

[0046] Water (50 mL), *p*-formaldehyde (33.3 mmoles), and $Zn(OH)_2$ (10.06 mmoles) were placed in a reactor and catalyst (0.34 mmoles) added. The homogeneous solution was stirred for 300 minutes in the dark unless otherwise indicated, with hydrogen evolution being measured by an up-turned measuring cylinder in water. Table 1 lists the dehydrogenation catalyst used, temperature of the reaction, conditions, and mmoles of H_2 and CO_2 produced.

Table 1

Sample No.	Catalyst	pH	Temp (°C)	H_2 (mmol)	CO_2 (mmol)
1	No Catalyst- Control	7.6	60	0	0
2	$IrCl_3$	7.6	RT	0	0
3	$Na_4Fe(CN)_6$	7.6	RT / hv	0.001	0
4	$IrCl_3$	7.6	60	0.0007	0.013
5	$RuCl_3$	7.6	60	0.031	0.014
6	Ir-H complex	7.6	60	0.030	0.235
7	Ru-cymene (1 hour)	7.6	60	1.06	0.05

Comparative Example

(Production of H_2 and Formate Product from Formaldehyde with $IrCl_3$)

[0047] Water (50 mL), p-FA (33.3 mmoles) and NaOH (50.24 mmoles) were placed in a round-bottomed flask and $IrCl_3$ (0.34 mmoles) was added. The homogeneous mixture was stirred for 300 minutes in the dark, with hydrogen evolution measured by an up-turned measuring cylinder in water. FIG. 3 shows the comparison of $IrCl_3$ in the presence and absence of zinc hydroxide. From the data, it was concluded that the addition of zinc as a co-catalyst increased the production of H_2 as compared to the reaction run in the absence of zinc.

Example 2

(Thermal Decomposition of Zinc Formate to Produce H_2)

[0048] **General Procedure**. Processes for the study of reducing formate produced with zinc hydroxide as described in Example 1 were performed. Zinc formate was added to a 1 cm ID glass tube and placed in a tube furnace. Glass wool was used to secure zinc formate inside of the glass tube. Argon was passed through the glass tube as a carrier gas with a flow of 5-100 mL/min. The outlet gas/vapor mixture was cooled in an ice bath and collected. The gas samples were collected and measured by an upturned measuring cylinder in water and analyzed by GC. The liquid samples were measured by a photometric test for formaldehyde and by GC for methanol and other liquid products after 3 hours reaction. Table 2 lists the results of the reduction of zinc formate in the absence of water. From the data, it was determined that zinc formate can be thermally decomposed to H_2 at temperatures above 200 °C, preferably 250 °C.

Table 2

Sample No.		Mmoles used	Temp °C	umol H_2CO	% H_2CO	CO_2 mmol	H_2 mmol	CO mmol
8	$Zn(HCOO)_2$ + C*	13.06	150	0.002	----	Traces	----	0
9		13.06	200	0.389	0.02	Traces	63	0
10		13.06	250	601.5	4.6	6885.5	2164.3	3104
11	$Zn(HCOO)_2$	15.89	150	0.035	----	Traces	21	0
12		15.89	200	18.67	0.76	11200	2027	0
13		15.89	250	753.9	4.74	5726.5	2486.3	5492.2

*+C refers to addition of a sacrificial agent.

Example 3

(Hydrothermal Decomposition of Zinc Formate to Produce H_2)

[0049] **General Procedure**. Processes for the study of reducing formate produced with zinc hydroxide as described in Example 1 were performed. Zinc formate was added to a 1 cm ID glass tube and placed in a tube furnace. Glass wool was used to secure zinc formate and catalyst in Examples 18-22 inside of the glass tube. Argon was passed through the glass tube as a carrier gas with a flow of 5-100 mL/min. The samples were heated to temperatures ranging from 150 °C to 400 °C. Upon reaching the desired temperature, steam (H_2O) was injected into the tube at a flow of 10 mL/hr. The outlet gas/vapor mixture was cooled in an ice bath and collected. The gas samples were collected and measured by an upturned measuring cylinder in water and analyzed by GC. The liquid samples were measured by a photometric test for formaldehyde and by GC for methanol and other liquid products after 3 hours reaction. Table 3 lists the results of the reduction of zinc formate with a steam flow for 90 minutes. From the

data, it was determined that zinc formate can be thermally decomposed to H_2 at temperatures above 200 °C, preferably 250 °C.

Table 3

Sample No.	Catalyst	H_2O mL	Zn formate g	Zn formate mmol	Temp °C	H_2CO umol	H_2CO %	CO_2 mmol	H_2 mmol	CO mmol
14	_	1.25	15	96.53	250	27.97	0.03	1.19	11.14	7.14
15	_	1.38	8	51.48	215	8.22	0.02	0.26	1.05	0.66
16	_	1.41	8	51.48	215	14.62	0.03	0.00	0.91	1.31
17	_	1.5	1	6.44	250	22.64	0.35	0.00	2.11	1.63
18	$BiOHCrO_4$	1.5	1	6.44	200	187.41	2.91	0.56	3.16	5.35
19	$BiOHCrO_4$	1.47	0	0.00	200	0.17	0.00	0.00	0.06	0.47
20	2%Cr/ZSM-5	2.28	1	6.44	200	0.42	0.01	21.29	0.30	0.78
21	2%Mn/ZSM-5	1.95	1	6.44	200	0.21	0.00	14.32	0.13	0.28
22	RuO_2/TiO_2	1.58	1	6.44	200	3.16	0.05	3.18	5.08	3.59

Example 4

(Hydrothermal Decomposition of Zinc Formate In the Presence of Formic Acid to Produce H_2)

[0050] General Procedure. Processes for the study of reducing formate produced with zinc hydroxide as described in Example 1 were performed. Zinc formate was added to a 1 cm ID glass tube and placed in a tube furnace. Glass wool was used to secure zinc formate and catalyst in Examples 18-22 inside of the glass tube. Argon was passed through the glass tube as a carrier gas with a flow of 5-100 mL/min. The samples were heated to 200 °C to 400 °C. Upon reaching the desired temperature, formic acid (5 to 100% in water) was injected into the tube at a flow of 10 mL/hr. The outlet gas/vapor mixture was cooled in an ice bath and collected. The gas samples were collected and measured by an upturned measuring cylinder in water and analyzed by GC. The liquid samples were measured by a photometric test for formaldehyde and by GC for methanol and other liquid products after 3 hours reaction. Table 3 lists the results of the reduction of zinc formate with a steam flow for 90 minutes. From the data, it was determined that zinc formate can be thermally decomposed to H_2 at temperatures above 200 °C, preferably 250 °C. Table 4 lists the amount of formic acid, formaldehyde and hydrogen formed from the reduction of zinc formate after 1 hour.

Table 4

Zinc Formate (mmoles)	Formic acid (mmoles)	Formaldehyde (mmoles)	H_2 (mmoles)
6.4	7.8	0.005	0.065

CLAIMS

1. A method of producing hydrogen from formaldehyde, the method comprising subjecting an aqueous reaction mixture comprising water, formaldehyde, a base, a dehydrogenation catalyst and a metal hydroxide co-catalyst to sufficient to produce a product stream comprising hydrogen (H_2) gas and a formate product, wherein the reaction mixture has a pH of 7.0 to 8.0.

2. The method of claim 1, wherein the pH of the reaction mixture is about 7.6.

3. The method of any one of claims 1 to 2, wherein the metal hydroxide co-catalyst is zinc hydroxide ($Zn(OH)_2$), calcium hydroxide ($Ca(OH)_2$), aluminium hydroxide ($Al(OH)_3$), copper hydroxide ($Cu(OH)_2$), or magnesium hydroxide ($Mg(OH)_2$).

4. The method of any one of claims 1 to 3, wherein the dehydrogenation catalyst is $IrCl_3$, $Na_4Fe(CN)_6$, $RuCl_3$, $Ru(OH)_3$, or an Ir-H complex, or Ru-cymene.

5. The method of any one of claims 1 to 4, wherein the temperature of the reaction mixture is 10 °C to 80 °C, preferably about 60 °C.

6. The method of any one of claims 1 to 5, wherein the base is sodium hydroxide (NaOH), potassium hydroxide (KOH), $Ca(OH)_2$, $Al(OH)_3$, or combinations thereof, preferably NaOH, with the proviso that the base and co-catalyst are different.

7. The method of any one of claims 1 to 6, wherein the molar ratio of formaldehyde to dehydration catalyst is 50:1 to 1:50 or 3:1 to 1:3.

8. The method of claim 7, wherein the molar ratio of formaldehyde to dehydration catalyst is about 1:1.

9. The method of any one of claims 1 to 8, wherein the molar ratio of formaldehyde to the base is 2:1 to 1:2 or the molar ratio of formaldehyde to base to co-catalyst is 2:1:0.1 to 1:2:0.6.

10. The method of any one of claims 1 to 9, wherein the molar ratio of formaldehyde to the base is about 1:1 or the molar ratio of formaldehyde to the base to the co-catalyst is 1:1:0.3.

11. The method of any one of claims 1 to 10, wherein the formaldehyde is para-formaldehyde, hydrated formaldehyde, or a combination thereof.

12. The method of claim 11, wherein the formaldehyde is para-formaldehyde.

13. The method of any one of claims 1 to 12, further comprising converting the formate product to formaldehyde.

14. The method of claim 13, wherein the formate product comprises a metal formate salt, and the method further comprises heating the metal formate salt to form formaldehyde.

15. The method of any one of claims 13 to 14, wherein the metal formate salt is zinc formate, sodium formate, potassium formate, calcium formate, aluminum formate, or mixtures thereof, preferably zinc formate.

16. The method of any one of claims 13 to 15, wherein the metal salt is heated at a temperature of 200 to 500 °C, preferably 250 to 400 °C.

17. The method of any one of claims 13 to 16, wherein the metal salt is heated in an inert atmosphere or in the presence of steam.

18. The method of any one of claims 13 to 17, wherein the conversion is done in the presence of a catalyst.

19. The method of claim 18, wherein the catalyst is a Columns 6-8 transition metal catalyst.

20. The method of any one of claims 1 to 17, wherein production of H_2 is self-sustaining.

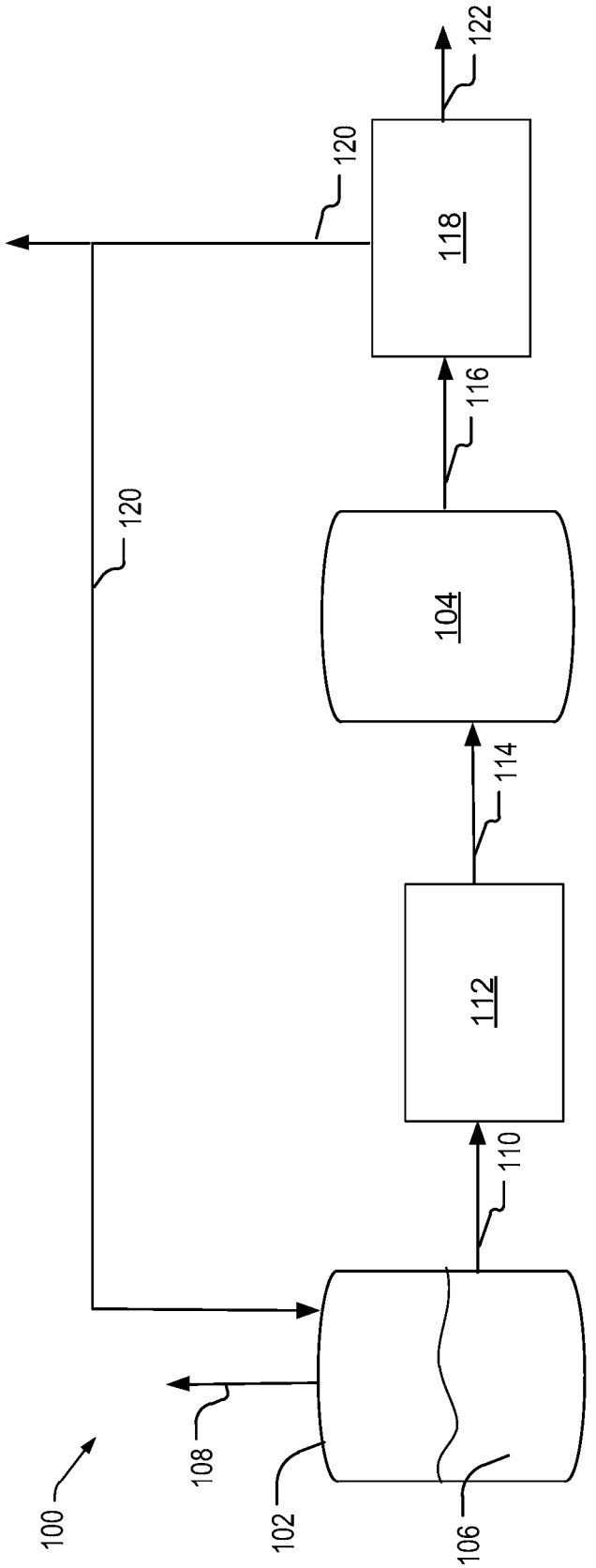


FIG. 1

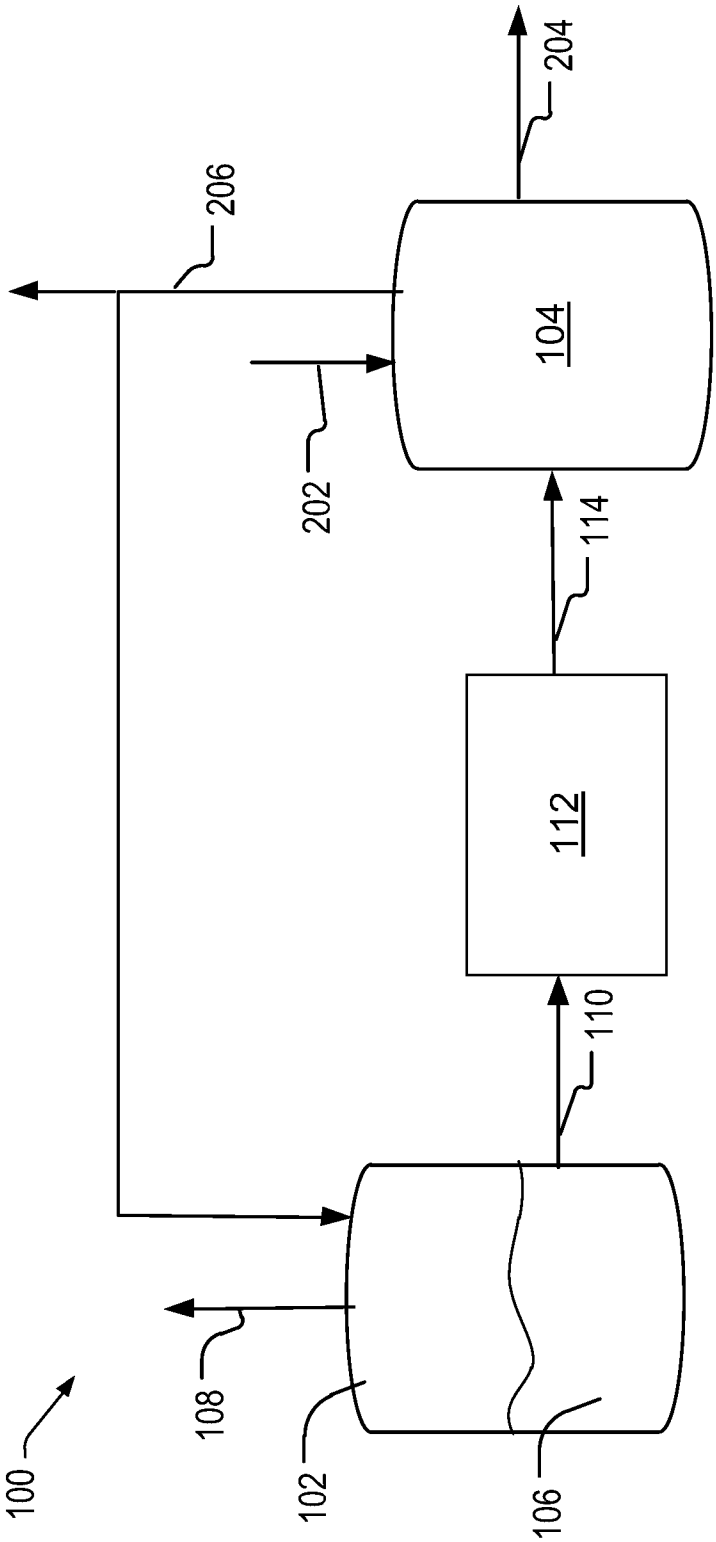


FIG. 2

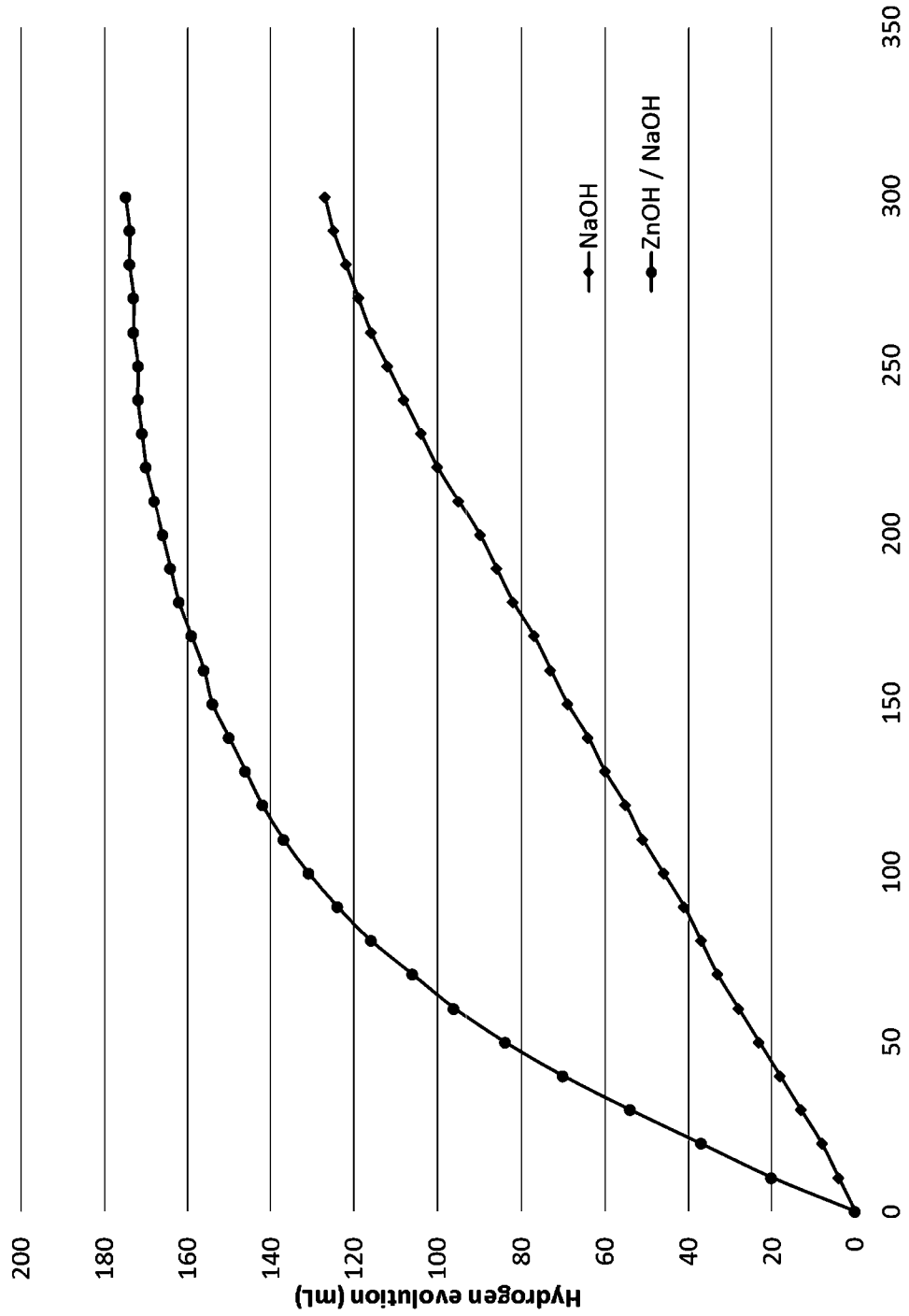

Hydrogen evolution (mL)
0
20
40
60
80
100
120
140
160
180
200
Time (mins)
0
50
100
150
200
250
300
350
NaOH
ZnOH / NaOH

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/053951

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/22 C07C45/00
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 C07C

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	PANKAJ CHOWDHURY ET AL: "Sacrificial Hydrogen Generation from Formaldehyde with Pt/TiO 2 Photocatalyst in Solar Radiation", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 52, no. 14, 10 April 2013 (2013-04-10), pages 5023-5029, XP055324411, ISSN: 0888-5885, DOI: 10.1021/ie3029976	1,2, 5-12,20
Y	paragraphs [02.4], [03.3] - paragraph [03.5]; figures 4,5,7,8	13-19

X	WO 2017/042661 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 16 March 2017 (2017-03-16)	1-12,20
Y	paragraphs [0030], [0034]; claims 1-3,8-9,14; examples 1-3	13-19

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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	Date of mailing of the international search report
26 August 2019	09/09/2019

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/053951

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2017/145027 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 31 August 2017 (2017-08-31) paragraph [0045] - paragraph [0054]; claim 1; examples 1-5 -----	1,5-15, 18-20 16,17
Y	FRANZ FISCHER: "Liquid Fuels from Water Gas", INDUSTRIAL & ENGINEERING CHEMISTRY, vol. 17, no. 6, 1 June 1925 (1925-06-01), pages 574-576, XP055207151, ISSN: 0019-7866, DOI: 10.1021/ie50186a009 page 574 -----	13-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2019/053951

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		DE 112017000998 T5	22-11-2018
		WO 2017145027 A1	31-08-2017