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(71) Applicant: SABIC GLOBAL TECHNOLOGIES B.V.

[NL/NL]; Plasticslaan 1, 4612 PX Bergen Op Zoom (NL).

(72) Inventors: VIDJAYACOMAR, Balamurugan; SABIC

Corporate Research and Innovation Center at KAUST, P.O.

Box 4545-4700, Thuwal, 23955-6900 (SA). AL-BAHILY,

Khalid; SABIC Corporate Research and Innovation Cen-

ter at KAUST, P.O. Box 4545-4700, Thuwal, 23955-6900 (SA). GAMBARTTA, Sandro; University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5 (CA). PENEAU, Virginie; University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5 (CA). ALDERMAN, Nicholas P.; University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5 (CA).

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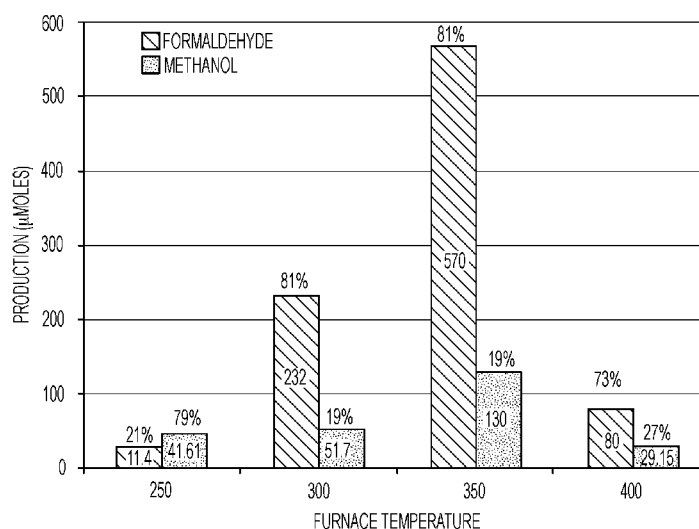


FIG. 1

(57) Abstract: Disclosed is a method of producing formaldehyde from formic acid. The method includes obtaining a gaseous mixture comprising formic acid and water vapor and contacting the gaseous mixture with a metal catalyst in a reaction chamber under conditions sufficient to reduce the formic acid to formaldehyde and oxidize the metal to a metal oxide.



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FORMALDEHYDE FROM FORMIC ACID WITH PRODUCTION OF METAL OXIDE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/468,483 filed March 8, 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 method for producing formaldehyde from formic acid and a metal catalyst. In particular, the method involves contacting a metal catalyst with a gaseous mixture containing formic acid and water vapor, which leads to the reduction of formic acid to formaldehyde and the oxidization of the metal to a metal oxide.

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 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 H₂ and CO₂ in the presence of catalytic metals and heat with a small amount of formaldehyde formed. U.S. Patent No. 1,648,692 to Arsem describes a process that increases the amount of formaldehyde

produced from formic acid by reacting formic acid with metal oxide catalysts in the presence of carbon dioxide so that water would be excluded from the catalyst surface.

[0005] While there have been various attempts to produce formaldehyde from formic acid, there remains a need for methods of reducing formic acid to formaldehyde in an economical and sustainable manner.

SUMMARY OF THE INVENTION

[0006] A discovery has been made that provides a solution to the aforementioned necessity for an economical and sustainable method of reducing formic acid to formaldehyde. The formaldehyde produced in this process can be part of a cycle by which formaldehyde is shuttled between an oxidized state (formic acid) and a reduced state (formaldehyde) in the production of hydrogen gas (H_2). The discovery is premised on the use of a zero valent or metal catalyst, for example zinc, to reduce formic acid to formaldehyde. This can be accomplished by contacting a mixture that includes formic acid and water with the metal catalyst in a reaction chamber at a temperature of between about 200 and 500 °C, thereby reducing the formic acid to formaldehyde and oxidizing the metal to a metal oxide. The metal oxides produced in the process can be useful in other chemical processes, such as desulfurization in the production of syngas.

[0007] In one aspect of the invention, a method of reducing formic acid to formaldehyde is described. The method can include obtaining a mixture that includes formic acid and water and contacting the mixture with a metal in a reaction chamber under reaction conditions sufficient to reduce the formic acid to formaldehyde and oxidize the metal to a metal oxide. In certain aspects, the mixture can be a gaseous mixture comprising formic acid and water vapor. The gaseous mixture can be made by vaporizing a liquid solution that includes formic acid at a concentration of from 1 to 99% (V/V), from 7 to 50% (V/V), from 10 to 20% (V/V), or about 15% (V/V), with the balance of the solution being water. The metal can be a transition metal, such as zinc (Zn), copper (Cu), manganese (Mn), bismuth (Bi), iron (Fe), nickel (Ni), aluminum (Al), or cadmium (Cd). In some instances, the transition metal is a zero valent metal and/or is not present in the form of a salt.

[0008] The conditions of the reaction chamber can be chosen to ensure the most efficient reduction of the formic acid and/or oxidation of the metal in the reaction chamber. The temperature of the reaction chamber can be 200 °C to 500 °C, 250 °C to 400 °C, 275 °C to 400 °C, 325 °C to 375 °C, or about 350 °C or any range or value there between.

[0009] The formaldehyde produced in the method of reducing formic acid to formaldehyde can be in one or more different forms, including its aldehyde form (CH_2O), its

hydrated form (methanediol), and its *para*-formaldehyde form of $\text{OH}-\left[\text{CH}_2-\text{O}\right]_n-\text{H}$, where n can be up to 100. The formaldehyde produced can also be a combination of these forms.

[0010] It was unexpectedly found that the size of the metal catalyst particles affected the production of formaldehyde from formate. The metal used in the method of reducing formic acid to formaldehyde can have an average particle size of about 1 μm to 2000 μm , preferably 30 μm to 700 μm , or more preferably 44 μm to 600 μm . In some embodiments, the metal can be obtained by passing the metal through a mesh, which prevents particles above a certain size from passing through. In some embodiments of the method of the invention, the maximum particle size of the metal in the reaction mixture and/or chamber can be between about 44 μm and 600 μm . In some embodiments, the maximum particle size can be about 10, 20, 30, 40, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1500, or 2000 μm or is between any two of these values. The amount of metal in the reaction chamber can also be varied to optimize the production of formaldehyde. An excess of metal can be used in the reaction chamber, with the “excess” being determined relative to the amount of metal needed to reduce the amount of formic acid provided in the reaction chamber.

[0011] In addition to the formic acid and water, the mixture provided in the reaction chamber can include an inert carrier gas. The inert carrier gas can be, for example, a noble gas such as argon. Other suitable inert carrier gases will be readily apparent to a person having ordinary skill in the art. The flow rate of the inert carrier gas can be less than 50 mL/min, preferably less than 25 mL/min, more preferably less than 10 mL/min, even more preferably 1 mL/min to 10 mL/min, or most preferably about 3 mL/min to about 7 mL/min, or about 5 mL/min.

[0012] The method described above can be part of a process that produces hydrogen gas from the formaldehyde that is produced by the method described above. Such a process can include separating formaldehyde from other reaction products, which may include the metal oxide formed during the production of the formaldehyde; combining the separated formaldehyde in an aqueous solution that can include an aqueous base and an appropriate catalyst to form a homogeneous aqueous solution having a basic pH, and producing hydrogen (H_2) gas and formic acid or a salt thereof from the formaldehyde present in the homogeneous aqueous solution. The formic acid produced in this process can optionally be recycled by being

reduced to formaldehyde using the method of reducing formic acid described above. The homogeneous aqueous solution in the method of producing hydrogen from formaldehyde can have a molar ratio of formaldehyde to aqueous base equal to or less than 2:1, preferably equal to or less than 1.5:1, more preferably equal to or less than 1.2:1, even more preferably from 0.5:1 to 1.5:1, or most preferably from 1:1 to 1.3:1. The production of hydrogen gas can be accomplished at a temperature of ranging from greater than 0 °C to less than 50 °C, preferably from 10 °C to 40 °C, more preferably from 15 °C to 30 °C, and most preferably from 20 °C to 25 °C. The catalyst used in this process can be a transition metal complex having a coordination bond between a transition metal and a leaving group, where the leaving group dissociates from the transition metal complex in response to light and/or the basic pH of the solution. Preferably, the catalyst is an iron containing photocatalyst and/or a transition metal complex having a transition metal—halide bond.

[0013] In some instances, the formic acid that is reduced to produce formaldehyde according to the method of the invention is a product of a process of producing hydrogen gas from formaldehyde. Such a process can include combining an aqueous base, formaldehyde, and an appropriate catalyst to form a homogeneous aqueous solution having a basic pH and producing hydrogen gas (H₂) and the formic acid or a salt thereof from the formaldehyde present in the homogeneous aqueous solution. The formaldehyde can be para-formaldehyde, hydrated formaldehyde, or a combination thereof. The homogeneous aqueous solution can have a molar ratio of formaldehyde to aqueous base equal to or less than 2:1, preferably equal to or less than 1.5:1, more preferably equal to or less than 1.2:1, even more preferably from 0.5:1 to 1.5:1, or most preferably from 1:1 to 1.3:1. The temperature at which H₂ gas is produced can be at a temperature of ranging from greater than 0 °C to less than 50 °C, preferably from 10 °C to 40 °C, more preferably from 15 °C to 30 °C, and most preferably from 20 °C to 25 °C. The catalyst used in the process of producing hydrogen gas from formaldehyde can be any suitable catalyst known in the art, including, for example, a transition metal complex having a coordination bond between a transition metal and a leaving group, where the leaving group dissociates from the transition metal complex in response to light and/or the basic pH of the solution. In some embodiments, the catalyst can be further defined as an iron containing photocatalyst and/or a transition metal complex having a transition metal—halide bond.

[0014] The transition metal in the catalysts used to produce hydrogen gas from formaldehyde can be iron (Fe), ruthenium (Ru), iridium (Ir), copper (Cu), or silver (Ag), or combinations thereof, or alloys thereof. The leaving group can be any group that is capable of

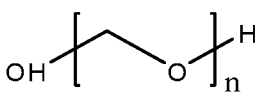
dissociating under basic conditions (*e.g.*, pH 8 to 14, 10 to 14, or 12 to 14). Non-limiting examples of such a leaving group are water (H_2O), ammonia (NH_3), cyanide (CN^-), thiocyanate (SCN^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), a halide (*e.g.*, fluoride (F^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), or astatide (At^-)) or combinations thereof. In a preferred aspect, the leaving group is chloride ion. In some instances, the transition metal complex can be a Fe(II) complex, a Ru(III) complex, a Ir(III) complex, a Cu(I) complex, a Ag(I) complex, or any combination thereof. In a preferred embodiment, the catalyst can be FeCl_2 , RuCl_3 , IrCl_3 , CuCl , AgCl , or any combination thereof. The pH of the aqueous solution can be adjusted to a pH from 8 to 14, preferably 10 to 14, and most preferably 12 to 14 using an inorganic base (*e.g.*, NaOH or KOH).

[0015] It can be appreciated from the above that the method of reducing formic acid to produce formaldehyde can be part of a cycle of reactions: formic acid can be reduced to formaldehyde, which can be used to produce hydrogen gas and formic acid, and the cycle can start again with reduction of formic acid to formaldehyde. The cycle can also start with formaldehyde, which can be used to produce hydrogen gas and formic acid, which formic acid can be reduced to formaldehyde, and the cycle can start again with production of hydrogen gas and formic acid from formaldehyde. The two primary steps in the cycle—production of hydrogen and formic acid from formaldehyde and the production of formaldehyde from formic acid—can be performed using different catalysts and different reaction conditions. The production of hydrogen and formic acid from formaldehyde can use a metal catalyst in a homogeneous, basic, aqueous solution at relatively low temperatures (*i.e.*, not more than 50 °C). In contrast, the production of formaldehyde from formic acid can use a solid metal catalyst at relatively high temperatures (*i.e.*, not less than 200 °C) with gaseous reactants.

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

[0017] 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).

[0018] “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.

[0019] 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%.

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

[0021] 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.

[0022] 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.

[0023] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0024] 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.”

[0025] 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.

[0026] The methods of the present invention to produce formaldehyde can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, etc. disclosed throughout the specification. With respect to the transitional phrase “consisting essentially of,” in one non-limiting aspect, a basic and novel characteristic of the methods of

the present invention are their abilities to selectively reduce formic acid in the presence of a metal to produce formaldehyde and a corresponding metal oxide.

[0027] 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] 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.

[0029] **FIG. 1** shows the amounts of formaldehyde and methanol produced at the indicated furnace temperatures. The left bar in each pair of bars represents formaldehyde produced, and the right bar represents methanol produced.

[0030] **FIG. 2** shows the amounts of formaldehyde and methanol produced using Zn metal catalysts passed through the indicated mesh sizes. The left-most bar in each set of bars represents formaldehyde produced, the middle bar represents methanol produced, and the right-most bar represents the sum of the amounts of formaldehyde and methanol produced.

[0031] **FIG. 3** shows the amounts of formaldehyde and methanol produced in reactions using the indicated amounts of zinc metal in the reaction chamber. The left bar in each pair of bars represents the amount of formaldehyde produced, and the right bar represents the amount of methanol produced.

[0032] **FIG. 4** shows the amounts of formaldehyde and methanol produced in reactions using the indicated flow rates of argon carrier gas. The left bar in each pair of bars represents the amount of formaldehyde produced, and the right bar represents the amount of methanol produced.

[0033] FIG. 5 shows the amounts of formaldehyde, methanol, and methyl formate produced in reactions using the indicated concentrations of formic acid. The left-most bar in each set of bars represents formaldehyde produced, the middle bar represents methanol produced, and the right-most bar represents methyl formate produced.

[0034] FIG. 6 shows an X-ray diffraction pattern for Zn metal catalyst after being used in a reaction to reduce formic acid to formaldehyde. The peaks marked by triangles represent unreacted Zn metal, and the peaks marked by ovals represent ZnO.

[0035] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale.

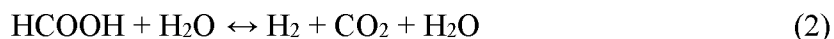
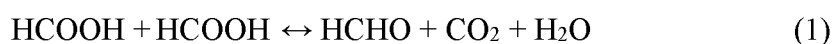
DETAILED DESCRIPTION OF THE INVENTION

[0036] The present invention provides for an efficient process for producing formaldehyde from formic acid, while at the same time producing a metal oxide from a metal. The process can include contacting a metal catalyst with a gaseous mixture of formic acid and water vapor under conditions sufficient to reduce the formic acid to formaldehyde and oxidize the metal to a metal oxide. This method can be part of a cycle in which formic acid is reduced to formaldehyde, which is then used to produce hydrogen gas and formic acid, and the cycle can start again with reduction of formic acid to formaldehyde.

A. Reduction of Formic Acid to Formaldehyde

1. Reaction Schemes

[0037] The method of the invention involves reduction of formic acid to formaldehyde. It is known that formic acid can be decomposed by heat and that formaldehyde can be a product of the decomposition. The following two reactions are known to take place during thermal decomposition of formic acid:



In addition, methanol can form according to the following reaction:



Without wishing to be bound by theory, it is thought that reaction (1) can be favored under certain conditions, including by the presence of a metal catalyst, such as zinc. Indeed, as

illustrated in the Examples, the inventors have discovered that contacting formic acid with zinc metal at a temperature of 350 °C results in relatively high levels of formaldehyde production and a greater ratio of formaldehyde to methanol. In addition, it was found that the particle sizes of the metal catalyst, the flow rate of an inert carrier gas, and the amount of metal catalyst used affected the formaldehyde yield.

2. Metal Catalyst for Reduction of Formic Acid to Formaldehyde

[0038] A variety of metal catalysts can be used in the reaction in which formic acid is reduced to formaldehyde. The metal catalysts can include, for example, a transition metal. Exemplary transition metals for use as catalysts can include zinc (Zn), copper (Cu), manganese (Mn), bismuth (Bi), iron (Fe), nickel (Ni), aluminum (Al), or cadmium (Cd), or combinations/mixtures thereof, or alloys thereof. The metals can have different valences, including zero valence. In preferred embodiments, the metal catalyst is a zero valent metal before the reduction of formic acid begins. In some embodiments, the metal is not a metal oxide or a basic metal salt (*e.g.* metal chlorides).

[0039] The metal catalysts can be particulate solids. The particle sizes of the metal catalyst can be varied by passing particulate metals through meshes of various sizes, which screen out particles above a certain size. In some embodiments, the metal particles used in the method of reducing formic acid have a maximum size or an average size of about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1100, 1200, 1300, 1400, 1500 μm or between any two of these values.

[0040] The metal catalysts can be present in a reaction chamber in excess relative to the amount needed to reduce the formic acid in a particular run of a reaction. The metal catalyst can be placed on trays in the reaction chamber, fluidized with the inert gas, coated on the side of the reaction chamber, or mechanically agitated. It was unexpectedly found that an excess of metal catalyst increased the efficiency and selectivity of formaldehyde production from formic acid. The amount of metal catalyst needed in order to be in excess can be determined by performing X-ray diffraction of the metal catalyst after a reaction at a certain amount of metal is completed, which can reveal the presence of unreacted metal catalyst, as well as the presence of metal oxide formed during the reaction. The molar ratio of metal catalyst to total formic acid in the reaction can be about 100:1, 50:1, 25:1, 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3.5:1, 3:1, 2.5:1, 2:1, or 1.5:1 or between any two of these values.

[0041] The metal catalysts can be oxidized to form metal oxides as they react with formic acid to produce formaldehyde. For example, zinc can be converted into ZnO. This is a particular advantage of the method of the invention because metal oxides such as ZnO have their own uses in industrial processes, including in desulfurization during the production of syngas. Other metal oxides that can be produced according to the method of the invention include CuO, MnO, Bi₂O₃, Fe₂O₃, NiO, Ni₂O₃, Al₂O₃, and CdO, among others.

3. Reaction Conditions for Reduction of Formic Acid

[0042] Reaction conditions for the reduction of formic acid to formaldehyde can be varied according to the desired yield of formaldehyde and other reaction products, such as methanol. It was unexpectedly found that the following parameters affected the yield and selectivity of formaldehyde production: the reaction temperature, the concentration of formic acid in the reactant composition, the flow rate of inert carrier gas, and the amount and particle size of metal catalyst.

[0043] The temperature of the reaction can be varied by preheating the reaction chamber in which metal catalyst has been placed and maintaining the temperature throughout the reaction. The reaction chamber temperature can be about 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, or 450 °C or between any two of those values. In preferred embodiments, the reaction chamber is heated to temperature is about 350 °C. The reaction chamber can be heated using known commercial heat sources, such as heaters, heat exchangers, or the like.

[0044] The formic acid can be introduced into the reaction chamber in the form of an aqueous mixture. The molar ratio of formic acid to water in the aqueous mixture can be about 100:1, 50:1, 25:1, 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3.5:1, 3:1, 2.5:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10, 1:25, 1:50, or 1:100 or between any two of these values. In some embodiments, the concentration of formic acid in the liquid can be about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99% (V/V) or between any two of these values, with the balance being water. The aqueous mixture can be vaporized upon introduction of the mixture into the reaction chamber. By way of example, the aqueous mixture can be converted into gaseous formic acid and water vapor (steam). In other aspects, however, gaseous formic acid and water vapor can be introduced into the reaction chamber as a combined feed or as separate feeds. In this aspect, the formic acid and water can be heated and vaporized prior to being introduced into the reaction chamber by methods known in the art (*e.g.*, heater, heat exchanger, *etc.*).

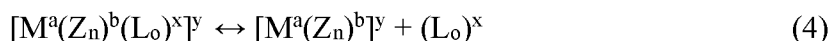
[0045] An inert carrier gas can be made to flow through the reaction chamber during the reaction. As a non-limiting example, the inert carrier gas can be a noble gas such as, for example, argon. Other suitable carrier gases include gases that do not react with formaldehyde or the metal catalyst such as nitrogen, helium, xenon, carbon dioxide, or mixtures thereof. The flow rate of the inert carrier gas can be varied and can affect the efficiency of the reaction. Without wishing to be bound by theory, it is thought that an inert carrier gas can help reaction products to desorb from the surface of catalysts, increasing the efficiency of the reaction. The flow rate of the inert carrier gas can be about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, 50, 55, or 60 mL/min or between any two of these values.

B. Production of Hydrogen and Formic Acid from Formaldehyde

[0046] The formaldehyde that is produced by reducing formic acid according to the method of the invention can subsequently be used in a method of producing hydrogen (with formic acid as a byproduct). Methods of doing so are described in more detail in this section.

1. Catalyst for Production of Hydrogen and Formate from Formaldehyde

[0047] In some instances, a transition metal complex having a coordination bond between the transition metal and a leaving group acts as a catalyst for the production of formate and H₂ from formaldehyde. The transition metal complex can undergo a reversible dissociation reaction of at least one leaving group. Without wishing to be bound by theory, it is believed that the dissociation of at least one leaving group can produce a transient electrophilic species. A non-limiting example of a transition metal complex catalyst undergoing a dissociation reaction is shown in equation (4) below:



where M is a transition metal having a charge a , Z is one or more ligands bonded to the metal with a total charge of b , L is one or more leaving group with total charge of x , and a is a positive integer from 0 to 6, preferably 0 to 3, b is a negative integer from 0 to -5, x is a negative integer from -1 to -2, y is the total charge of the transition metal complex, and n and o are the atomic ratio relative to M, where n ranges from 0 to 6 and o ranges from 1 to 3. In some instances y is 0, -1, -2, -3, -4, -5, or -6.

[0048] The transition metal complex can react with nucleophiles in the reaction mixture, for example, hydroxide ion as shown in equation (5) below.



where M is a transition metal having a charge a , Z is one or more ligands bonded to the metal with a total charge of b , L is one or more leaving group with total charge of x , and a is a positive integer from 0 to 6, preferably 0 to 3, b is a negative integer from 0 to -5, x is a negative integer from -1 to -2, y is the total charge of the transition metal complex, and n , o , and p are the atomic ratio relative to M, where n ranges from 0 to 6, o ranges from 1 to 3, and p ranges from 0 to 1. In some instances y is 0, -1, -2, -3, -4, -5, or -6.

[0049] Without wishing to be bound by theory, it is believed that the $[(M)^a(Z_n)^b(OH^-)_p]^y$ species can react with small organic molecules (*e.g.*, formaldehyde in either intact or hydrated form), followed by reductive elimination of hydrogen and consequent formation of the formate anion. Alternatively, the partly deprotonated form of methanediol ($CH_2(OH)_2$), as obtained from the attack of hydroxide ion to *p*-formaldehyde, may also directly coordinate to the $[(M)^a(Z_n)^b(OH^-)_p]^y$ intermediate to form the same species.

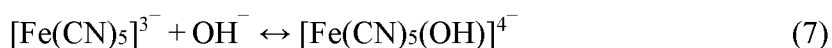
[0050] In some instances, the transition metal in the transition metal complex catalyst can be, for example, iron (Fe), ruthenium (Ru), iridium (Ir), or silver (Ag). Preferably, the transition metal is Fe(II), Ru(III), Ir(III), Cu(I), or Ag(I). In some instances, the leaving group (L) can be from two general categories: (1) leaving groups that dissociate from the transition metal complex in response to light and (2), leaving groups that dissociate from the transition metal complex in response to the basic pH of the solution. The former category of leaving groups can include, for example, CN^- . The latter category can include, for example halides, including fluoride (F^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), or astatide (At^-). Ligand Z can be the same or different than leaving group L. In some embodiments, Z can be an inorganic ligand, an organic ligand or both. Non-limiting examples of organic groups include aromatic groups, a cyano group, a substituted cyano group, an acetate group, a thiocyanate group, an aminidate group, a nitrate group, or combinations thereof. Non-limiting examples of inorganic groups include a halide, phosphate, or both. In some complexes Z is not necessary (*e.g.*, when M has a charge of +1).

[0051] In some instances, the transition metal complex contains iron and has a cyano (CN^-) leaving group. The iron containing catalyst can be a saturated 18-electron complex with Fe(II) in an octahedral, strong ligand-field. The iron containing catalyst can undergo a reversible dissociation reaction of at least one leaving group upon irradiation with visible light. Without wishing to be bound by theory it is believed that the dissociation of at least one leaving group can produce a transient penta-coordinated 16-electron species isolobal with an organic carbocation. Such an electrophilic species can react with nucleophiles. A non-limiting

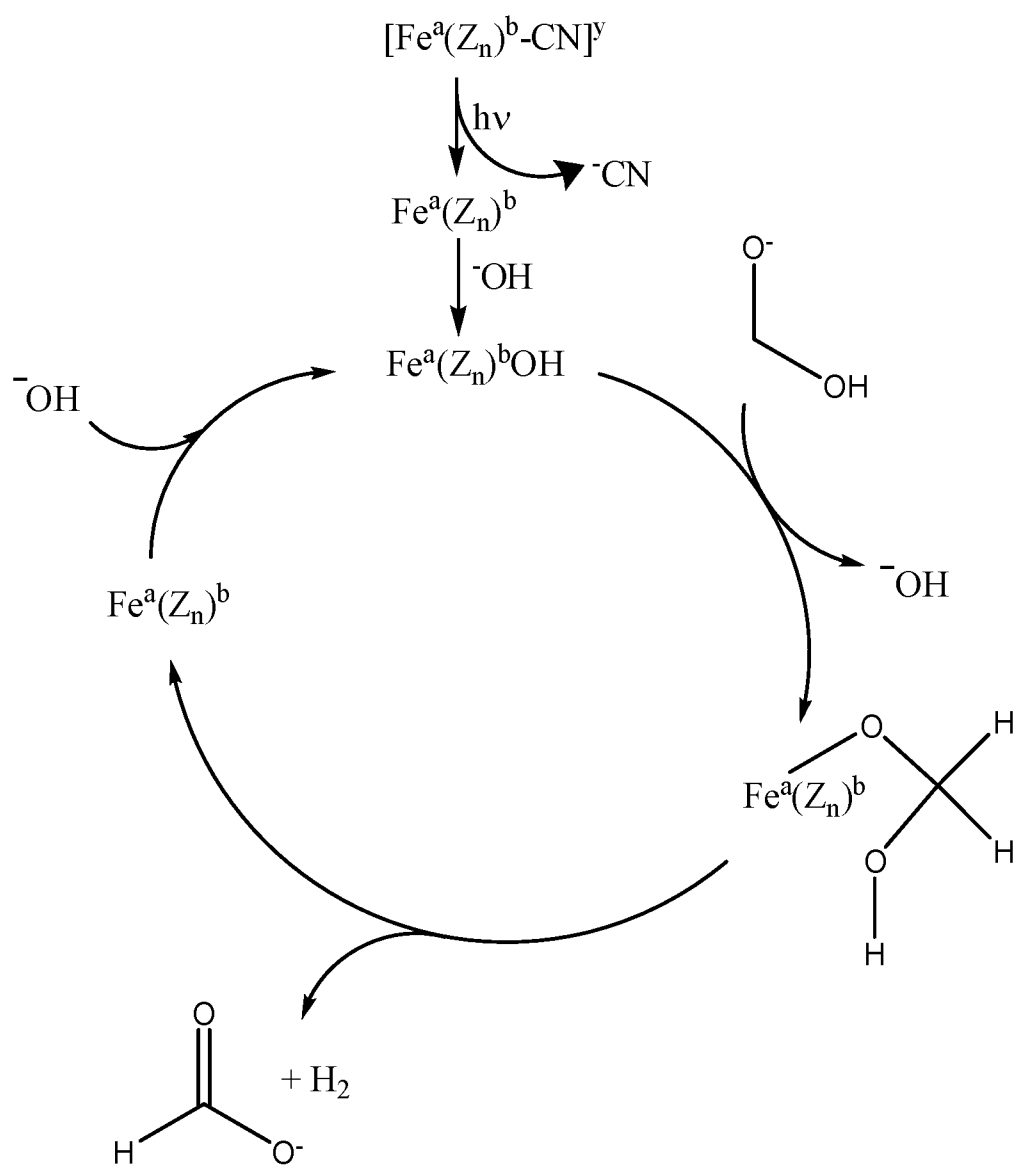
example of such an iron(II) complex is ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$). In this instance, leaving group CN and ligand Z are the same group. Ferrocyanide is available from many commercial manufacturers, for example, Sigma-Aldrich® (USA), as sodium ferrocyanide decahydrate ($[(\text{CN})_6\text{Fe}] \text{Na}_4(\text{H}_2\text{O})_{10}$). A non-limiting example of an iron containing catalyst, ferrocyanide, undergoing a reversible dissociation reaction is shown in equation (6) below.



The iron containing catalyst can react with nucleophiles in the reaction mixture, for example, hydroxide ion as shown in equation (7) below.

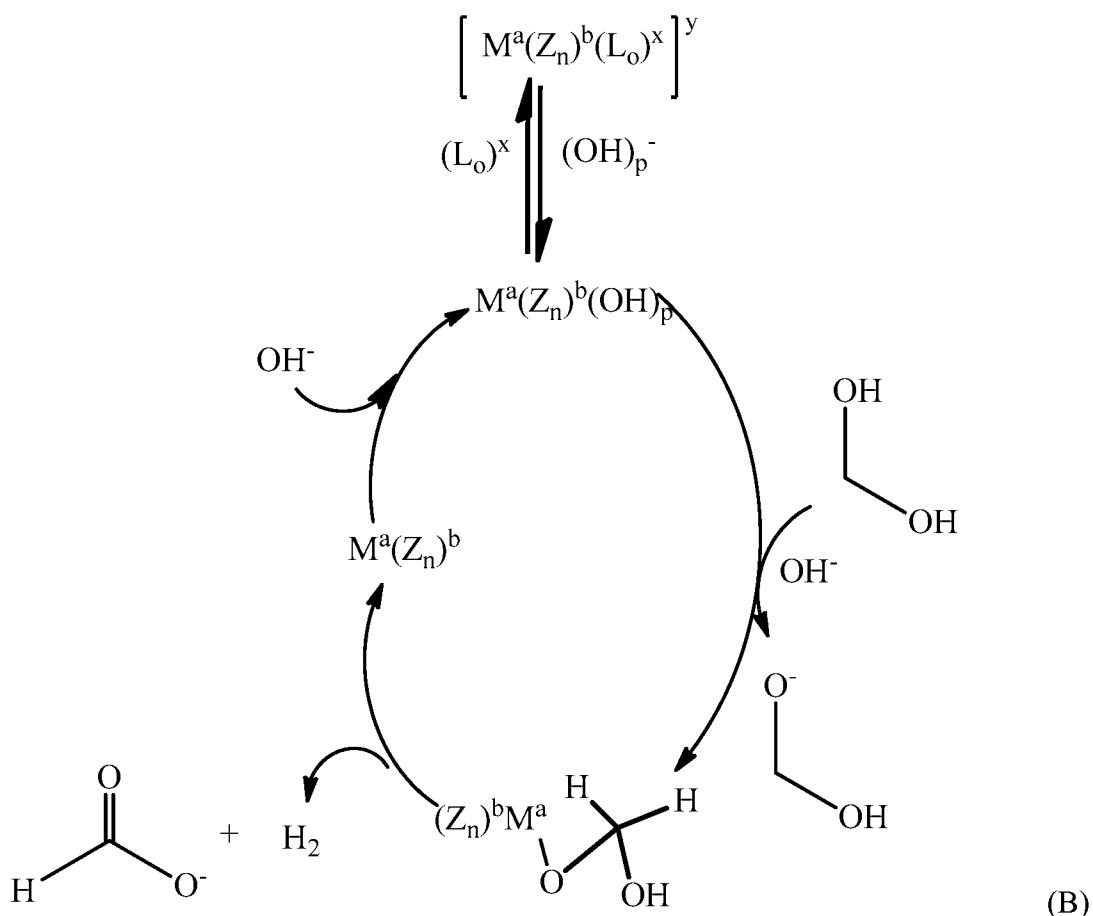


[0052] Without wishing to be bound by theory, it is believed that the $[\text{Fe}(\text{CN})_5(\text{OH})]^{4-}$ species is responsible for the reaction with small organic molecules (*e.g.*, formaldehyde in either intact or hydrated form), followed by reductive elimination of hydrogen and consequent formation of the formate anion as shown in the reaction pathway (B) below. Alternatively, the partly deprotonated form of methanediol ($\text{CH}_2(\text{OH})_2$), as obtained from the attack of hydroxide ion to *p*-formaldehyde, may also directly coordinate to the 16-electron $[\text{Fe}(\text{CN})_5]^{3-}$ intermediate to form the same species as shown in reaction pathway (A) below, where Z is CN, a is +2, n is 5, and b is -5.



(A)

[0053] A non-limiting example of a transition metal complex undergoing a reversible dissociation reaction under basic pH is shown in reaction pathway (B) below. In a preferred embodiment, Z and L are halides.



where M is a transition metal having a charge a, Z is a ligand bonded to the metal with a charge of b, L is a leaving group with a charge of x, and a is a positive integer from 0 to 6, preferably 0 to 3, b is an negative integer from 0 to -5, x is a negative integer from -1 to -2, y is the total charge of the transition metal complex, and n, o, and p are the atomic ratio relative to M, where n is 0 to 6, o is 1 to 3, p is 0 to 1, and y is 0, -1, -2, -3, -4, -5, or -6.

2. Reactants and Medium for Production of Formate and Hydrogen

[0054] The reactants in the step of producing formate and H₂ 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 or alkaline earth metal. Non-limiting examples of alkali or alkaline earth metals include lithium, sodium, potassium, magnesium, calcium, and barium. In a preferred embodiment, the base is sodium hydroxide (NaOH). The

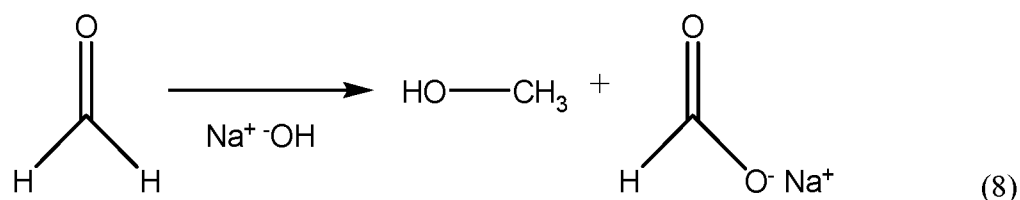
molar ratio of small organic molecule (*e.g.*, formaldehyde) to base is equal to or less than 2:1, 1.9:1, 1.8:1, 1.7:1, 1.6:1, 1.5:1, 1.2:1, 1.1:1, 1:1, 0.5:1 or any range there between.

[0055] 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 water. Non-limiting examples of water include de-ionized water, salt water, river water, canal water, city canal water or the like.

3. Generation of Formate and Hydrogen

[0056] In some instances, formate and hydrogen can be produced by irradiating, with light, an aqueous composition having a basic pH, formaldehyde, and a transition metal complex catalyst. In preferred instances, the catalyst and the formaldehyde are partially or fully solubilized within the aqueous composition.

[0057] When equimolar solutions of *p*-formaldehyde and sodium hydroxide are combined, a slow Cannizzaro's disproportionation to MeOH and (HCOO)Na can occur as shown in equation (8) below. The addition of a catalytic amount of the transition metal catalyst containing does not appear to inhibit this disproportionation.



[0058] The production of formate (*e.g.*, sodium formate) can be as illustrated in the reaction pathways (A) and (B) above and equation (9) below.



Without wishing to be bound by the theory, the production of hydrogen is in the homogeneous phase of the aqueous mixture. The spent transition metal complex (*e.g.*, (M)^a(Zn)^b) can be a precipitate or be precipitated from the solution by addition of acid to increase 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 transition metal complex is not removed or is partially removed from the solution. The formate (or formic acid), which is also dissolved in the solution, can then be reduced to formaldehyde using the methods described herein.

EXAMPLES

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

Example 1 Production of Formaldehyde from Formic Acid

[0060] **Procedures.** Experiments were run in a tube furnace with a 1 cm ID glass tube. Zinc metal particles (2-10 g) were secured inside the glass tube using glass wool. The zinc particles were passed through a mesh of either size 30 (600 μm) or 325 (44 μm) prior to use. Argon was flowed through the glass tube as a carrier gas with a flow of between 5-100 mL/min. After heating the glass tube in a furnace at temperatures ranging between 250 and 400 $^{\circ}\text{C}$, aqueous formic acid (5-100% (V/V), with the balance being water vapor) was then injected into the tube with 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 gas chromatography (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. Gas identification and detection was carried out with an Agilent 7820A (Agilent Technologies, U.S.A.). The GC was equipped with a thermal conductivity detector (TCD), using an Agilent GS-CarbonPlot column (for CO_2) and Agilent HP-Molesieve column (for all other gasses). (45 $^{\circ}\text{C}$ for 2.5 min, 20 $^{\circ}\text{C}/\text{min}$ till 100 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$ for 13 min)

[0061] Formaldehyde concentrations were determined through a colorimetric reaction with acetyl acetone. To a solution of ammonium acetate (15.4 g) in water (50 mL), acetyl acetone (0.2 mL) and glacial acetic acid (0.3 mL) were added whilst stirring. This was further diluted with water (49.5 mL) and stored in the fridge for up to 3 days. To determine the formaldehyde concentration, the sample (2 mL) was mixed with an equal volume of the acetyl acetone solution (2 mL) and heated to 60 $^{\circ}\text{C}$ for 10 minutes. After cooling for 10 minutes, the absorbance of the solution was measured at 412 nm and compared to a calibration curve.

[0062] **Optimization of reaction temperature.** Reactions were run at 250, 300, 350, and 400 $^{\circ}\text{C}$ using Zn catalyst (31 mmol) and formic acid (79 mmol), with 25 mL/min of Argon flow for 3 hours. The amounts of formaldehyde and methanol produced were measured as

described above. FIG. 1 shows the measured amounts. The reaction run at 350 °C produced the most formaldehyde (570 μmol ; 0.72% conversion; 81% selectivity vs. methanol).

[0063] Effect of metal particle size. Zn particles passed through size 30 (600 μm) or size 325 (44 μm) mesh were used in reactions that included 31 mmol of Zn catalyst and 79 mmol of formic acid, with 25 mL/min of Argon flow at 350 °C for 3 hours. The amounts of formaldehyde and methanol produced are shown in FIG. 2. The catalyst with the larger maximum particle size (600 μm) produced higher amounts of formaldehyde and resulted in greater selectivity (81% formaldehyde vs. 19% methanol) than the catalyst with the smaller maximum particle size (44 μm). The catalyst with the larger particle size also led to a higher combined amount of formaldehyde and methanol produced. Without being bound by theory, it is believed that the finer particles caused a longer residence time and, hence, more thermal decomposition of formaldehyde into H_2 and CO_2 .

[0064] Effect of amount of metal used. Varying amounts of Zn particles (2 g, 5 g, or 10 g) that had been passed through size 30 mesh were used in reactions that included 79 mmol of formic acid and 25 mL/min of argon at 350 °C for 3 hours. FIG. 3 shows that as the amount of Zn particles was increased, the total yield of formaldehyde plus methanol increased, as did the selectivity towards formaldehyde.

[0065] Effect of inert carrier gas flow rate. Varying rates of carrier gas flow (5, 25, 50, or 100 mL/min) were used in reactions that included 155 mmol Zn particles (passed through size 30 mesh) and 79 mmol formic acid at 350 °C for 3 hours. FIG. 4 shows that as the carrier gas flow rate is increased, both the total product yield (formaldehyde plus methanol) and formaldehyde selectivity decreased.

[0066] Effect of formic acid concentration. Varying concentrations of formic acid liquid solution (5, 10, 20, 50, or 100% (V/V), with the balance being water) were vaporized and used in reactions using 31 mmol Zn particles (passed through size 30 mesh) and an argon flow of 5 mL/min. at 350 °C for 3 hours. FIG. 5 shows that the reaction with a formic acid concentration of 20% had the best combination of formaldehyde production and selectivity. At formic acid concentrations above 20%, methyl formate started to be produced, reducing the selectivity toward formaldehyde.

[0067] Formation of metal oxide. Zn metal particles were examined by X-ray diffraction (XRD) after being used in a reaction to reduce formic acid to formaldehyde. FIG. 6 shows the XRD pattern. The peaks labeled with triangles represent unreacted zinc metal (showing that

the zinc metal was present in excess), and the peaks labeled with ovals represent zinc oxide produced during the reaction.

[0068] Summary of experimental results. Table 1 below summarizes experimental results for production of formaldehyde from formic acid using a Zn catalyst.

TABLE 1

No.	Argon Flow (mL/min)	Zn (mmol)	Formic Acid Used (mmol)	Formaldehyde Produced (mmol)	Methanol Produced (mmol)	Yield (%)
1	5	31	66	0.57	0.13	1.1
2	5	76	43	0.47	0.13	1.4
3	5	153	44	3.30	0.14	7.8
4	10	153	43	1.44	0.22	3.4
5	25	153	65	3.71	0.40	6.3

While the highest yield ((formaldehyde produced + methanol produced) divided by formic acid used) in the experiments summarized in Table 1 was 7.8%. It is believed that the yield can readily be increased by decreasing the residence time in the tube furnace and/or better trapping of formaldehyde by using a water bubbler.

CLAIMS

1. A method of reducing formic acid to formaldehyde, the method comprising:
obtaining a mixture comprising formic acid and water; and
contacting the mixture with a metal under reaction conditions sufficient to reduce the formic acid to formaldehyde and oxidize the metal to a metal oxide.
2. The method of claim 1, wherein the metal is a transition metal, preferably zinc (Zn), copper (Cu), manganese (Mn), bismuth (Bi), iron (Fe), nickel (Ni), aluminum (Al), or cadmium (Cd), or combinations thereof.
3. The method of any one of claims 1 to 2, wherein the metal is a zero valent metal.
4. The method of any one of claims 1 to 3, wherein the mixture is a gaseous mixture comprising formic acid and water vapor.
5. The method of any one of claims 1 to 4, wherein the reaction conditions comprise a temperature of 200 °C to 500 °C, 250 °C to 400 °C, 275 °C to 400 °C, 325 °C to 375 °C, or about 350 °C.
6. The method of any one of claims 1 to 5, wherein the formaldehyde is para-formaldehyde, hydrated formaldehyde, or a combination thereof.
7. The method of any one of claims 1 to 6, wherein the metal has maximum particle size of 1 micron to 2000 microns, preferably 30 microns to 700 microns, or more preferably 44 microns to 600 microns.
8. The method of any one of claims 1 to 7, wherein an excess of metal, relative to an amount of metal needed to reduce the formic acid, is contained in the reaction chamber.
9. The method of any one of claims 1 to 8, further comprising providing an inert carrier gas to the reaction mixture.
10. The method of claim 9, wherein the inert carrier gas is provided at a flow rate of less than 50 mL/min, preferably less than 25 mL/min, more preferably less than 10 mL/min, even more preferably 1 mL/min to 10 mL/min, or most preferably about 3 mL/min to about 7 mL/min, or about 5 mL/min.
11. The method of any one of claims 1 to 10, wherein the gaseous mixture is made by vaporizing a liquid solution comprising formic acid at a concentration of from 1 to 99% (V/V), from 7 to 50% (V/V), from 10 to 20% (V/V), or about 15% (V/V).

12. The method of any one of claims 1 to 11, wherein the formic acid is obtained by a method comprising:
combining an aqueous base, formaldehyde, and an appropriate catalyst to form a homogeneous aqueous solution having a basic pH; and
producing hydrogen (H₂) gas and the formic acid or a salt thereof from the formaldehyde present in the homogeneous aqueous solution.
13. The method of claim 12, wherein the homogenous aqueous solution has a molar ratio of formaldehyde to base equal to or less than 2:1, preferably equal to or less than 1.5:1, more preferably equal to or less than 1.2:1, even more preferably from 0.5:1 to 1.5:1, or most preferably from 1:1 to 1.3:1.
14. The method of any one of claims 12 to 13, wherein the production of H₂ gas is at a temperature ranging from greater than 0 °C to less than 50 °C, preferably from 10 °C to 40 °C, more preferably from 15 °C to 30 °C, and most preferably from 20 °C to 25 °C.
15. The method of any of claims 12 to 14, wherein the catalyst is a transition metal complex having a coordination bond between a transition metal and a leaving group, wherein the leaving group dissociates from the transition metal complex in response to light and/or the basic pH of the solution.
16. The method of any of claims 12 to 15, wherein the catalyst is further defined as an iron containing photocatalyst and/or a transition metal complex having a transition metal—halide bond.
17. The method of any one of claims 1 to 16, further comprising:
separating the metal oxide and the formaldehyde;
combining the separated formaldehyde in an aqueous solution comprising an aqueous base and an appropriate catalyst to form a homogeneous aqueous solution having a basic pH; and
producing hydrogen (H₂) gas and formic acid or a salt thereof from the formaldehyde present in the homogeneous aqueous solution and optionally recycling the formic acid by reducing it to formaldehyde.
18. The method of claim 17, wherein the homogenous aqueous solution has a molar ratio of formaldehyde to base equal to or less than 2:1, preferably equal to or less than 1.5:1,

more preferably equal to or less than 1.2:1, even more preferably from 0.5:1 to 1.5:1, or most preferably from 1:1 to 1.3:1.

19. The method of either of claims 17 or 18, wherein the production of H₂ gas is at a temperature of ranging from greater than 0 °C to less than 50 °C, preferably from 10 °C to 40 °C, more preferably from 15 °C to 30 °C, and most preferably from 20 °C to 25 °C.
20. The method of any of claims 17 to 19, wherein the catalyst is a transition metal complex having a coordination bond between a transition metal and a leaving group, wherein the leaving group dissociates from the transition metal complex in response to light and/or the basic pH of the solution, preferably an iron containing photocatalyst and/or a transition metal complex having a transition metal—halide bond.

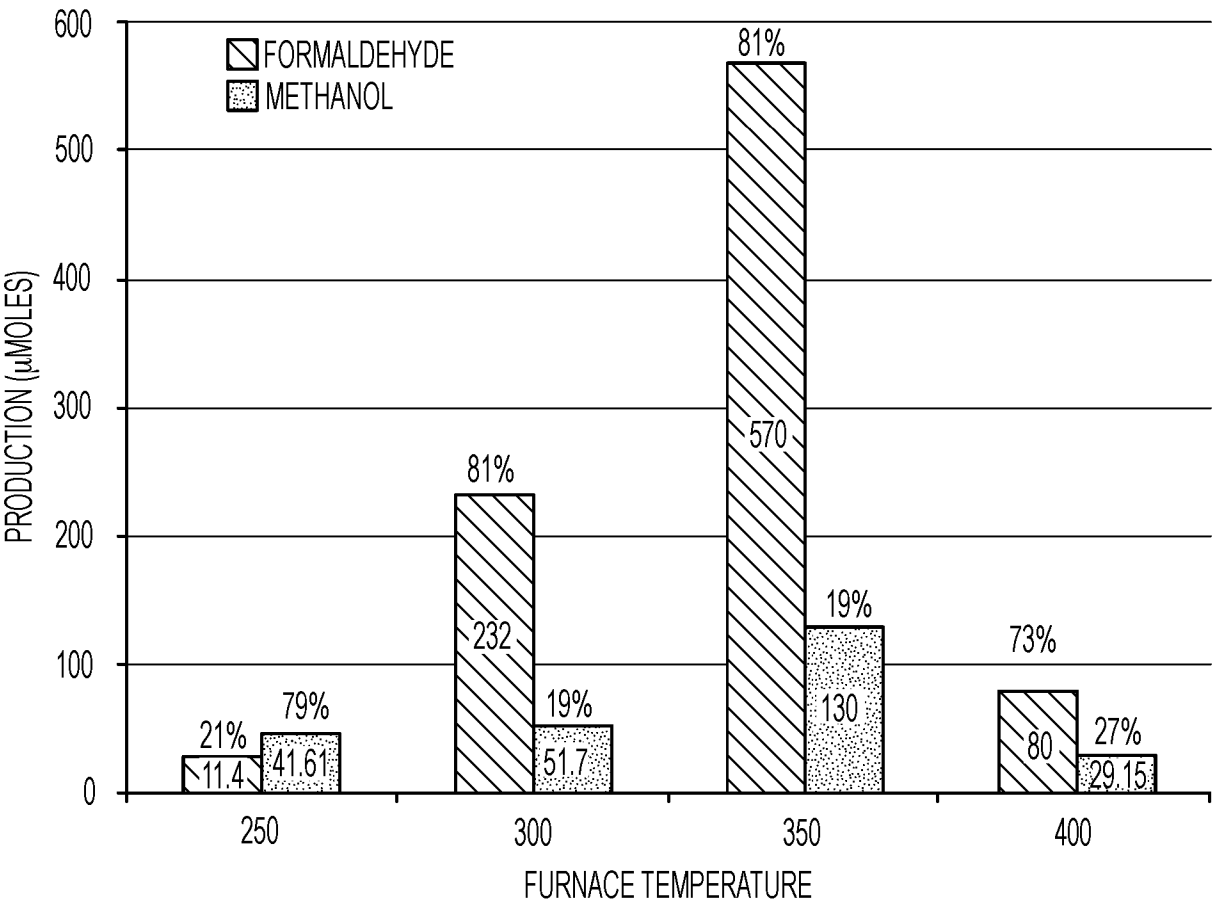


FIG. 1

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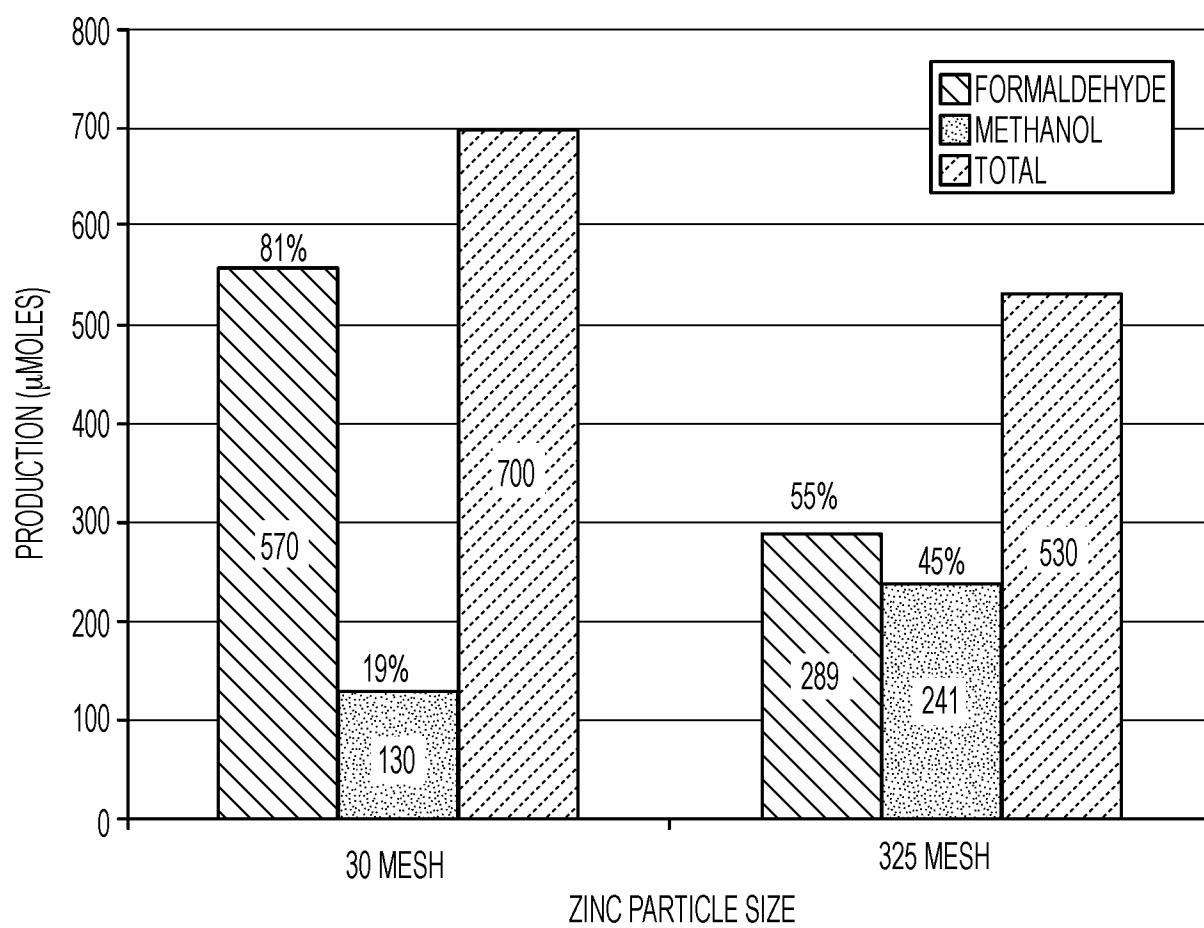


FIG. 2

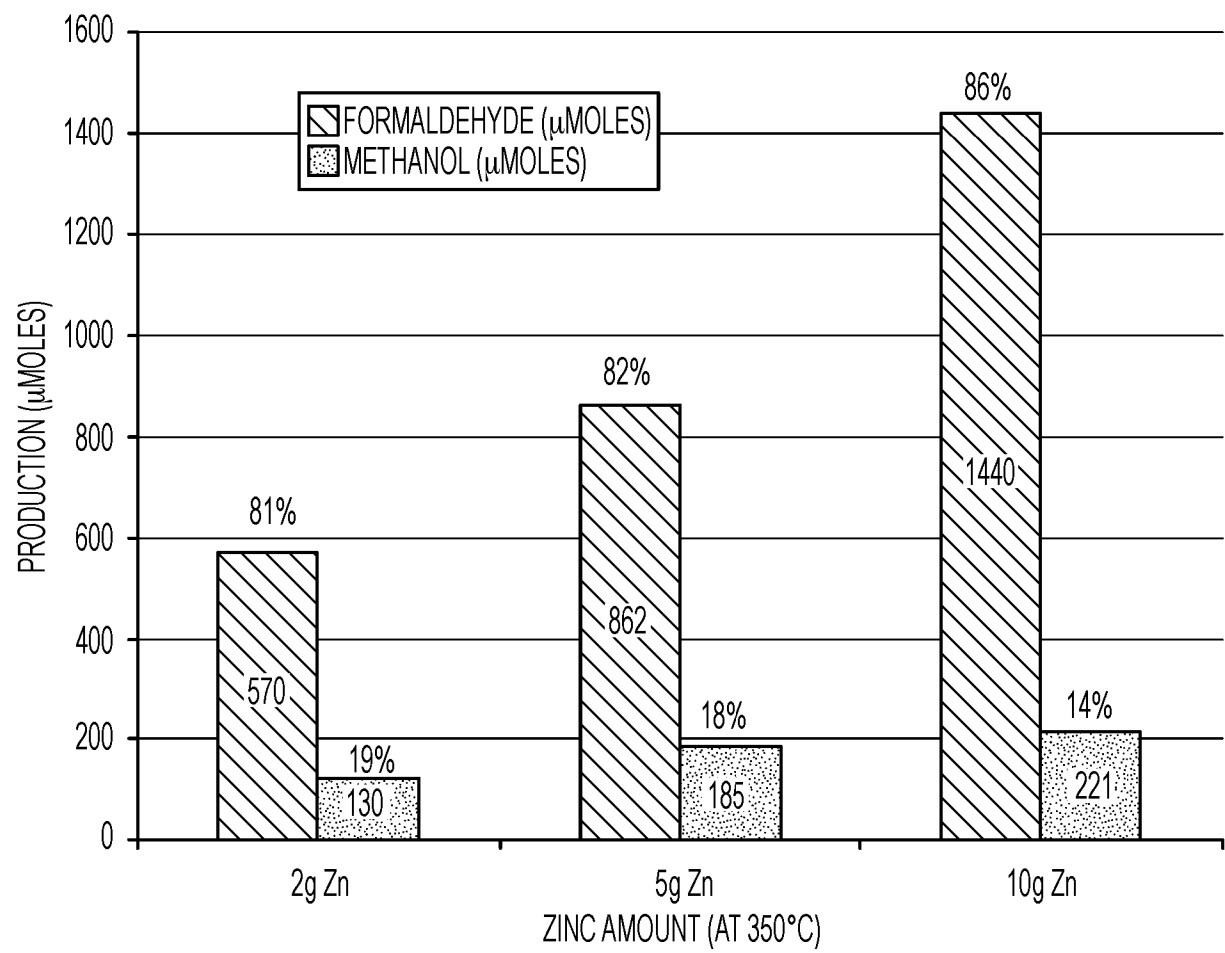


FIG. 3

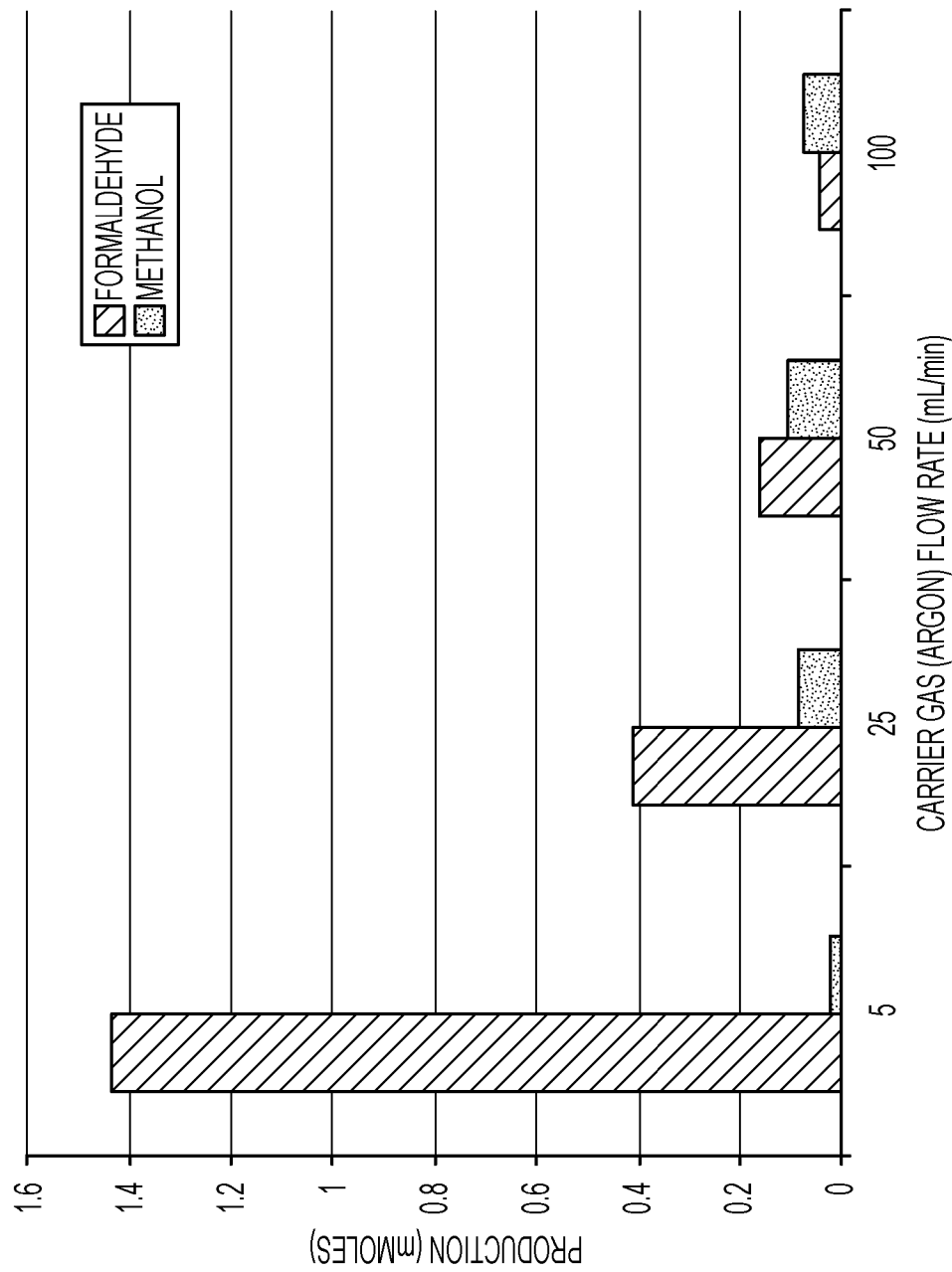


FIG. 4

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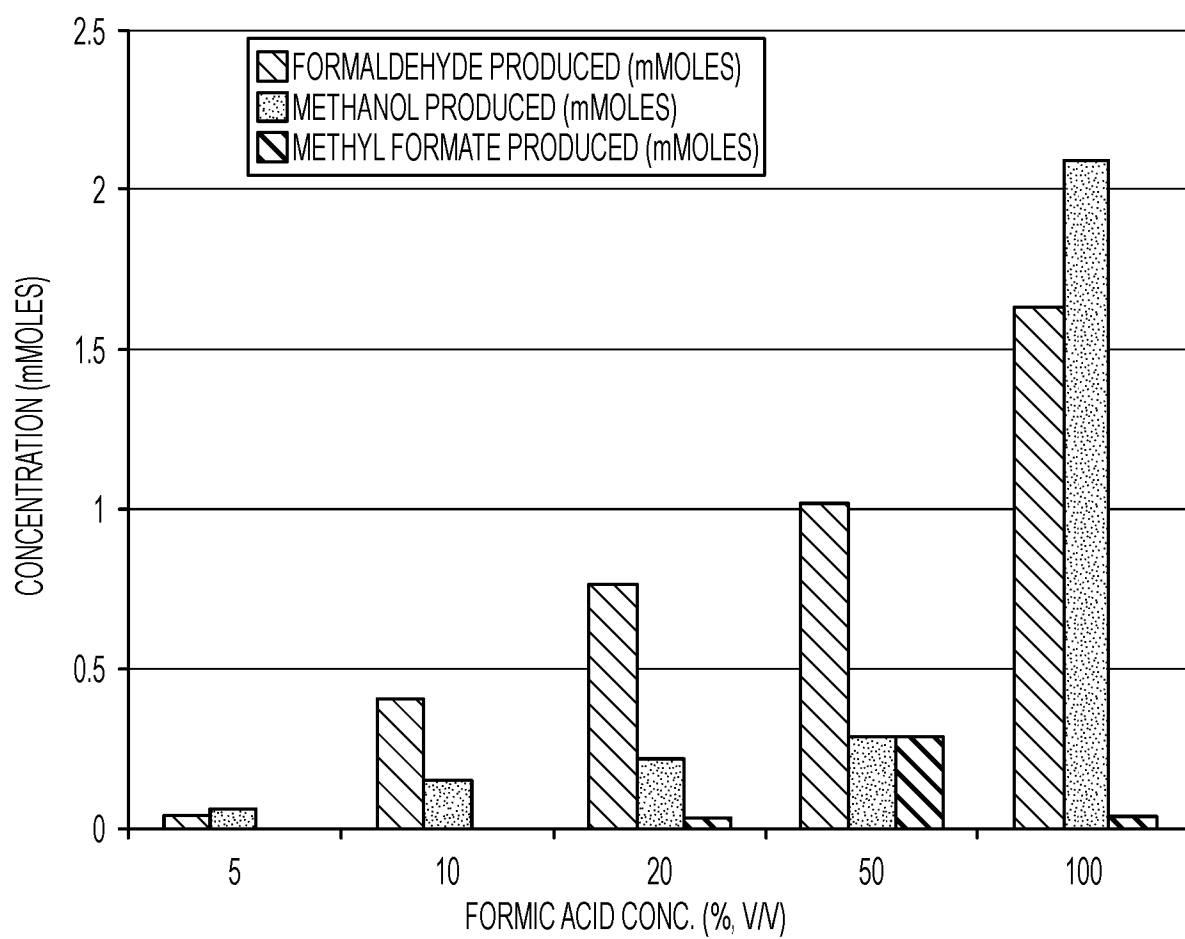


FIG. 5

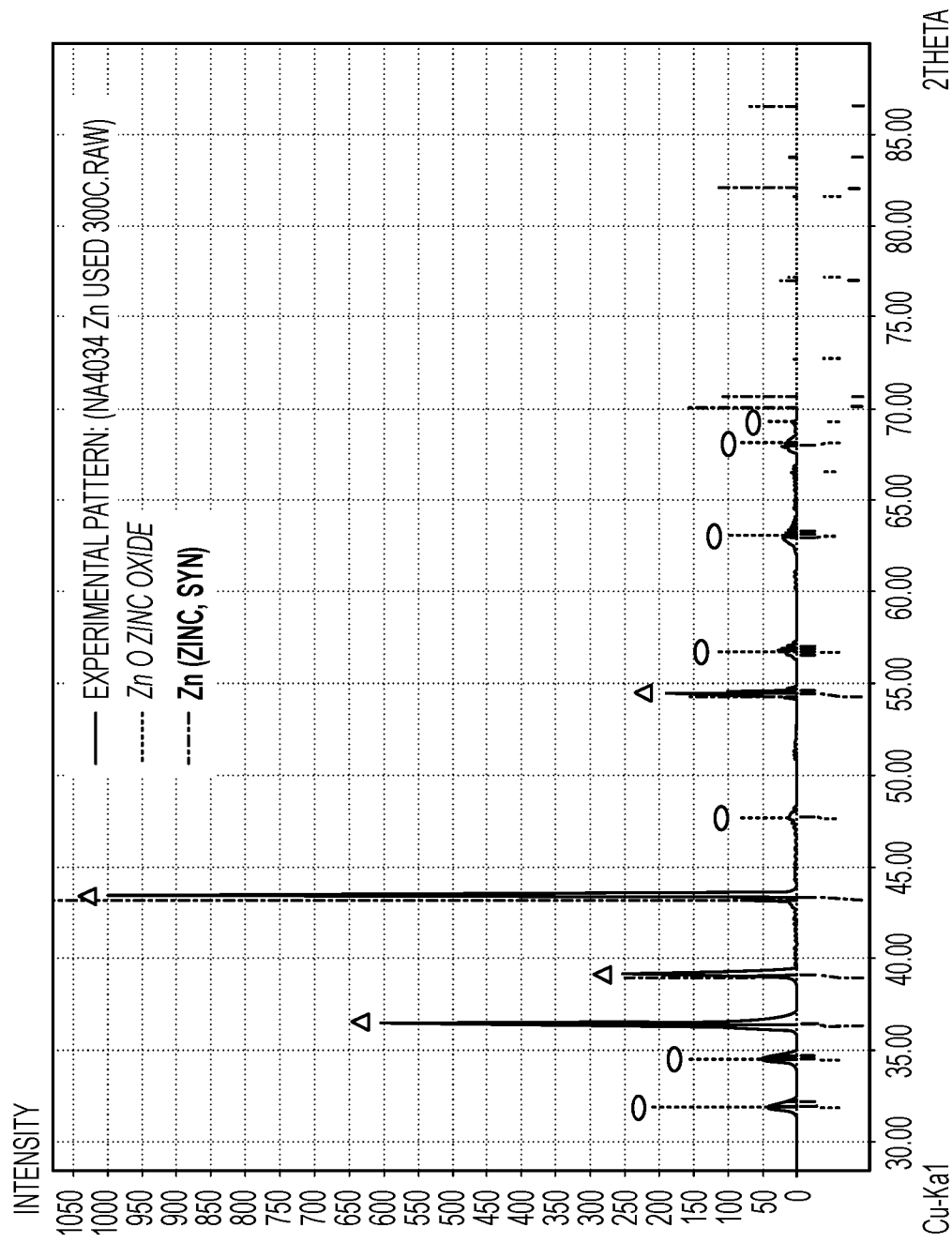


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/051156

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C07C45/41 C01B3/22	C07C47/04 C01G9/02
	C07C29/147	C07C31/20
		C08G2/08
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) C07C C08G C01B C01G		
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, CHEM ABS Data, 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	HENRY JOHN HORSTMAN FENTON: "The reduction of carbon dioxide to formaldehyde in aqueous solution", JOURNAL OF THE CHEMICAL SOCIETY, TRANSACTIONS, vol. 91, 1907, pages 687-693, XP9504944, ISSN: 0368-1645, DOI: 10.1039/CT9079100687 Experimental; pages 690-691	1-3,5-10
A	----- WO 2014/130962 A1 (DIOXIDE MATERIALS INC [US]) 28 August 2014 (2014-08-28) claims; example 2	1-20
A	----- DE 185 932 C (BASF AG [DE]) 7 June 1907 (1907-06-07) claims; examples	1-20
	----- -/-	
☒ 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 25 April 2018		Date of mailing of the international search report 04/05/2018
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 Kardinal, Siegmars

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/051156

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	N. P. ALDERMAN ET AL: "Photochemical water splitting mediated by a C1 shuttle", DALTON TRANSACTIONS: THE INTERNATIONAL JOURNAL FOR INORGANIC, ORGANOMETALLIC AND BIOINORGANIC CHEMISTRY, 31 October 2016 (2016-10-31), XP055324420, GB ISSN: 1477-9226, DOI: 10.1039/C6DT03658A the whole document figure 1 -----	1
A	N P Alderman ET AL: "Supplementary Materials", Dalton Transactions, 31 October 2016 (2016-10-31), XP055468894, Retrieved from the Internet: URL: http://www.rsc.org/suppdata/c6/dt/c6dt03658a/c6dt03658a1.pdf [retrieved on 2018-04-19] page 2 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/051156

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		AU 2014218628 A1	15-10-2015
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