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

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

(72) Inventors: DIWAKAR, Makarand M.; SABIC R&T Pvt.

Ltd., Plot # 81-85, Chikkadunnasandra, Off Sarjapur-Attibele Road, Bangalore 562125 (IN). SANKAR, Uma K.; SABIC R&T Pvt. Ltd., Plot # 81-85, Chikkadunnasandra, Off Sarjapur-Attibele Road, Bangalore 562125 (IN). DESHPANDE, Raj; SABIC R&T Pvt. Ltd., Plot # 81-85, Chikkadunnasandra, Off Sarjapur-Attibele Road, Bangalore 562125 (IN). NAIR, Sreejit; SABIC R&T Pvt. Ltd., Plot # 81-85, Chikkadunnasandra, Off Sarjapur-Attibele Road, Bangalore 562125 (IN). DHOKE, Chaitanya; SABIC R&T Pvt. Ltd., Plot # 81-85, Chikkadunnasandra, Off Sarjapur-Attibele Road, Bangalore 562125 (IN).

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(54) Title: CATALYST SYSTEMS AND METHODS FOR THEIR USE IN SELECTIVE HYDROFORMYLATION OF FORMALDEHYDE TO GLYCOLALDEHYDE

(57) Abstract: A method of producing glycolaldehyde through hydroformylation of formaldehyde in the presence of a rhodium-amine or rhodium-phosphine ligand complex catalyst. The reaction can be performed in aqueous and/or ionic liquid solvent-based reaction systems.

**CATALYST SYSTEMS AND METHODS FOR THEIR USE IN SELECTIVE
HYDROFORMYLATION OF FORMALDEHYDE TO GLYCOLALDEHYDE**

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Patent
5 Application No. 62/756,695, filed November 7, 2018, the entire contents of which are hereby
incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns a method for converting formaldehyde to
10 glycolaldehyde. The method can include producing glycolaldehyde through
hydroformylation of formaldehyde in the presence of a rhodium-amine or rhodium-phosphine
ligand complex catalyst. The reaction can be performed in aqueous solvent-based reaction
systems.

B. Description of Related Art

15 [0003] Glycolaldehyde is an important intermediate to the chemical industry. By way of
example, it can undergo reactions like oxidation or hydrogenation to industrially important
chemicals that includes glycolic acid, ethylene glycol, and their derivatives. Glycolic acid is
used in the textile industry as a dyeing and tanning agent, in food processing as a flavoring
agent, and as a preservative, and in the pharmaceutical industry as a skin care agent. It is also
20 used in adhesives and plastics. Glycolic acid can also be included into emulsion polymers,
solvents, and additives for ink and paint in order to improve flow properties and impart gloss.
It is used in surface treatment products that increase the coefficient of friction on tile flooring.
Glycolic acid is also a useful intermediate for organic synthesis, in a range of reactions
including oxidation-reduction, esterification and long chain polymerization. It is used as a
25 monomer in the preparation of polyglycolic acid and other biocompatible copolymers (*e.g.*,
PLGA).

[0004] There are several known processes for producing glycolaldehyde. One such
process is hydroformylation of formaldehyde. Most of the catalyst systems reported for

hydroformylation of formaldehyde use paraformaldehyde as the source of formaldehyde and are non-aqueous in nature. However, the same catalyst systems when applied for aqueous systems (like aqueous formaldehyde / or systems containing water) facilitate methanol formation due to hydrogenation of formaldehyde. Therefore, the use of water in currently available systems is typically avoided or may be used in low amounts and/or be used in complex bi-phasic reaction systems where the formation of glycolaldehyde takes place in the non-aqueous phase.

[0005] By way of example, US Patent 4,405,814 Carroll *et al.* describes a process for hydroformylation of paraformaldehyde using a catalyst having both a tertiary organo phosphorous ligand and a basic organo amine ligand in acetamide as a solvent. Notably, however, the catalyst fails to provide sufficient selectivity to glycolaldehyde when the system contains water.

[0006] As another example, U.S. Patent 7,511,178 to Lenero *et al.* discloses conversion of formaldehyde and synthesis gas to glycolaldehyde using a rhodium catalyst and 2-phospha-tricyclo[3.3.1.1{3,7}]-decyl-based (*e.g.*, adamantane-based) ligands at low reaction pressures (preferably from 0.10 to 0.50 MPa, col. 5, li. 13-15) in water-immiscible amide solvents. This results in a biphasic reaction system, where the aqueous phase and organic phase are segregated. The reaction occurs in the organic phase containing catalyst. This can increase the costs and complexities of the process, and limits its commercial scalability.

[0007] The currently available processes for hydroformylation of formaldehyde to glycolaldehyde fail to either have acceptable selectivity to glycolaldehyde and/or attempt to avoid or limit the use of water, which can result in more complicated bi-phasic reaction systems that may not be commercially scalable.

SUMMARY OF THE INVENTION

[0008] A discovery has been made that provides a solution to at least some of the problems associated with hydroformylation of formaldehyde to glycolaldehyde. The discovery is premised on the use of a rhodium-amine or rhodium-phosphine ligand complex catalyst in a homogenous reaction system that can include relatively high amounts of water (*e.g.*, at least 10 wt. % or more), a water-miscible organic solvent, and formaldehyde. This system can be contacted with syngas having a carbon monoxide to hydrogen (CO:H₂) molar

ratio of 1:10 to 10:1, preferably about 1:1, under reaction conditions (*e.g.*, temperature of 90 °C to 140 °C and/or pressure of 0.1 MPa to 15 MPa) sufficient to produce glycolaldehyde with good selectivity (at least 60% selectivity, preferably at least 70% selectivity, or even more preferably 90% to 100% selectivity for glycolaldehyde). Notably, it was surprisingly found that the presence of water can help increase the selectivity towards glycolaldehyde. Without wishing to be bound by theory, it is believed that the increased presence of water can help reduce polymerization of glycolaldehyde.

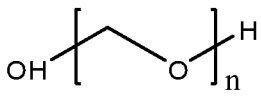
[0009] In one aspect of the present invention methods of producing glycolaldehyde are described. A method can include contacting a homogeneous aqueous solution that includes a water-miscible organic solvent, formaldehyde, water, and a catalytic rhodium metal complex with a gaseous mixture of hydrogen (H₂) and carbon monoxide (CO), and catalytically reacting the gas and the formaldehyde to form glycolaldehyde. The catalytic rhodium metal complex can include at least one water soluble phosphine-containing ligand or at least one amine-containing ligand. In some instances, the catalytic rhodium metal complex can be formed *in situ* from a rhodium catalyst precursor (*e.g.*, (acetylacetonato)dicarbonylrhodium(I) or chloro(1,5-cyclooctadiene)rhodium(I) dimer) and at least one water soluble phosphine-containing compound or at least amine-containing compound. The water-miscible organic solvent can include tetrahydrofuran (THF), N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), a higher alcohol, or a diol, preferably THF. The selectivity of glycolaldehyde can be at least 60%, 70%, 90%, or 100%. The homogeneous solution can include 0 wt. % to 30 wt. % water. The catalytic rhodium metal complex can include the at least one phosphine-containing ligand and does not include the at least one amine-containing ligand or *vice versa*. Water soluble phosphine-containing ligand can be a substituted aryl phosphine ligand, preferable a substituted triphenyl phosphine ligand, or an alkyl phosphine ligand, preferably, a trialkylphosphine ligand. In one preferred instance, at least one water soluble phosphine-containing ligand is a substituted triphenyl phosphine ligand, preferably, a triphenylphosphine trisulfonate ligand. The amine-containing ligand can be an aryl amine ligand, preferably a tribenzylamine ligand, or an alkyl amine ligand, preferably, a tribenzylamine ligand. In one preferred embodiment, at least one amine-containing ligand is a tribenzylamine ligand. Catalytically reacting can include a reaction temperature of 90 °C to 150 °C and/or a reaction pressure of 0.1 MPa to 15 MPa. The CO and H₂ can be in CO:H₂ molar ratio of 10:1 to 1:10, preferably 5:1 to 1:5, or more preferably 1:1. The amount CO and H₂O is controlled through pressure regulation. In some embodiments, the catalyst to

formaldehyde molar ratio is 1:25 to 1:10,000. Formaldehyde can be an aqueous solution of formaldehyde, paraformaldehyde, or gaseous formaldehyde. In one instance, the formaldehyde is the aqueous solution of formaldehyde.

[0010] The following includes definitions of various terms and phrases used throughout this specification.

[0011] The term “homogeneous” means the catalyst is in the same phase as the reactants (*e.g.*, catalyst and reactants are solubilized in a reaction solution or reaction stream). The term “heterogeneous” refers to the form of catalysis where the phase of the catalyst differs from that of the reactants.

[0012] “Formaldehyde” includes gaseous, liquid, and solid forms of formaldehyde. “Formaldehyde” includes its aldehyde form (CH₂O), its hydrated form (methanediol), and its

para-formaldehyde form of  , where n can be up to 100. Combinations of the various forms of formaldehyde can be used. In one instance, aqueous formaldehyde can be used, which can include its aldehyde form, its hydrated form, or its *para*-formaldehyde form, or any combination thereof.

[0013] An “alkyl group” is a linear or branched, substituted or unsubstituted, saturated hydrocarbon. In the context of this invention, an alkyl group has 1 to 50, 2 to 30, 3 to 25, or 4 to 20 carbon atoms. When an alkyl group is disclosed in this application the term includes all isomers and all substitution types unless otherwise stated. For example: butyl includes n-butyl, isobutyl, and tert-butyl; pentyl includes n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and neopentyl. Non-limiting examples of alkyl group substituents include halogen, hydroxyl, alkyloxy, haloalkyl, haloalkoxy, carboxylic acid, ester, amine, amide, nitrile, acyl, thiol and thioether.

[0014] An “aryl group” or an “aromatic group” is a substituted or unsubstituted, mono- or polycyclic hydrocarbon with alternating single and double bonds within each ring structure. Non-limiting examples of aryl group substituents include alkyl, halogen, hydroxyl, alkyloxy, haloalkyl, haloalkoxy, carboxylic acid, ester, amine, amide, nitrile, acyl, thiol and thioether.

[0015] A “heteroatom” refers to unsubstituted or substituted atom that is not carbon unless otherwise specified. Non-limiting examples of heteroatoms are oxygen (O), nitrogen

(N), phosphorous (P), or sulfur (S). Non-limiting examples of heteroatoms substituents include hydrogen, aliphatic, alkyl, alkynyl, and alkenyl.

[0016] A “heteroaryl group” or “hetero-aromatic group” is a mono-or polycyclic hydrocarbon with alternating single and double bonds within each ring structure, and at least one atom (heteroatom) within at least one ring is not carbon. Non-limiting examples of heteroaryl group substituents include alkyl, sulfonates, halogen, hydroxyl, alkyloxy, haloalkyl, haloalkoxy, carboxylic acid, ester, amine, amide, nitrile, acyl, thiol, and thioether.

[0017] The terms “about” or “approximately” are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment, the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

[0018] The terms “wt.%,” “vol.%,” or “mol.%” refers to a weight percentage of a component, a volume percentage of a component, or molar percentage of a component, respectively, based on the total weight, the total volume of material, or total moles, that includes the component. In a non-limiting example, 10 grams of component in 100 grams of the material is 10 wt.% of component.

[0019] The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0020] 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.

[0021] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0022] 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.”

[0023] 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.

[0024] The methods and catalysts of the present invention can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, *etc.* disclosed throughout the specification. With respect to the transitional phase “consisting essentially of,” in one non-limiting aspect, a basic and novel characteristic of the methods and catalysts of the present invention are their abilities to produce glycolaldehyde from formaldehyde.

[0025] Any methods of the present invention are contemplated as being useful with any compositions, catalysts, or catalyst reaction systems of the present invention, and *vice versa*. By way of example, any aspects or embodiments of the present invention are contemplated as being used with other aspects or embodiments of the present invention.

[0026] In the context of the present invention, at least twenty embodiments are now described. Embodiment 1 is a method of producing glycolaldehyde. The method includes the steps of contacting a homogeneous aqueous solution containing a water-miscible organic solvent, formaldehyde, water, and a catalytic rhodium metal complex with a gas comprising hydrogen (H₂) and carbon monoxide (CO), the catalytic rhodium metal complex containing at least one water soluble phosphine-containing ligand or at least one amine-containing ligand, and catalytically reacting the H₂, CO, and the formaldehyde to form glycolaldehyde. Embodiment 2 is the method of embodiment 1, wherein the selectivity of glycolaldehyde is at least 60%, preferably at least 70%, or more preferably 90% to 100%. Embodiment 3 is the method of any one of embodiments 1 to 2, wherein the homogenous solution contains 0 wt. % to 30 wt. % water. Embodiment 4 is the method of any one of embodiments 1 to 3, wherein the catalytic rhodium metal complex includes the at least one phosphine-containing ligand and does not include the at least one amine-containing ligand. Embodiment 5 is the method of embodiment 4, wherein the at least one water soluble phosphine-containing ligand is a substituted aryl phosphine ligand, preferable a substituted triphenyl phosphine ligand, or an alkyl phosphine ligand, preferably, a trialkylphosphine ligand. Embodiment 6 is the method of embodiment 5, wherein the at least one water soluble phosphine-containing ligand is a substituted triphenyl phosphine ligand, preferably, a triphenylphosphine trisulfonate ligand. Embodiment 7 is the method of any one of embodiments 1 to 3, wherein the catalytic

rhodium metal complex includes the at least one amine-containing ligand and does not include the at least one phosphine-containing ligand. Embodiment 8 is the method of embodiment 7, wherein the at least one amine-containing ligand is an aryl amine ligand, preferably a tribenzylamine ligand, or an alkyl amine ligand, preferably, a trialkyl amine ligand. Embodiment 9 is the method of embodiment 8, wherein the at least one amine-containing ligand is a tribenzylamine ligand. Embodiment 10 is the method of any one of embodiments 1 to 9, wherein the catalytic rhodium metal complex is formed *in situ* from a rhodium metal precursor and at least one water soluble phosphine-containing compound or at least amine-containing compound. Embodiment 11 is the method of embodiment 10, wherein the rhodium metal precursor is (acetylacetonato)dicarbonylrhodium(I) or chloro(1,5-cyclooctadiene)rhodium(I) dimer. Embodiment 12 is the method of any one of embodiments 10 to 11, wherein the at least one water soluble phosphine-containing compound is a substituted triphenyl phosphine compound, preferably, triphenylphosphine trisulfonate. Embodiment 13 is the method of any one of embodiments 10 to 11, wherein the at least one amine-containing compound is substituted tribenzylamine. Embodiment 14 is the method of any one of embodiments 1 to 13, wherein the reaction temperature is 90 °C to 150 °C and/or the reaction pressure is 0.1 MPa to 15 MPa. Embodiment 15 is the method of any one of embodiments 1 to 14, wherein the molar ratio of CO:H₂ is 10:1 to 1:10, preferably 5:1 to 1:5, or more preferably 1:1. Embodiment 16 is the method of any one of embodiments 1 to 15, wherein the catalyst to formaldehyde molar ratio is 1:25 to 1:10,000. Embodiment 17 is the method of any one of embodiments 1 to 16, wherein the formaldehyde is an aqueous solution of formaldehyde, paraformaldehyde, or gaseous formaldehyde. Embodiment 18 is the method of embodiment 17, wherein the formaldehyde is the aqueous solution of formaldehyde. Embodiment 19 is the method of any one of embodiments 1 to 18, wherein the water-miscible organic solvent is tetrahydrofuran (THF), N,N-dimethyl acetamide, N,N-dimethyl formamide, a higher alcohol, or a diol, preferably THF.

[0027] Embodiment 20 is a method of producing glycolaldehyde. This method includes the steps of contacting a composition comprising an ionic liquid solvent, formaldehyde, and a catalytic rhodium metal complex with a gas containing hydrogen (H₂) and carbon monoxide (CO), the rhodium metal complex comprising at least one phosphine-containing ligand or at least one amine-containing ligand, and catalytically reacting the gas and the formaldehyde to form glycolaldehyde.

[0028] 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.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The present invention provides for an efficient and scalable process for hydroformylation of formaldehyde to glycolaldehyde. As illustrated in non-limiting aspects in the Examples, high selectivity towards glycolaldehyde production can be obtained when a homogenous reaction system that includes catalytic rhodium metal complexed with least one phosphine-containing ligand or at least one amine-containing ligand, a water-miscible organic solvent, formaldehyde, and water is contacted with a gaseous mixture of hydrogen (H₂) and carbon monoxide (CO). It was surprisingly found that increased amounts of water (*e.g.*, at least 5 wt. %, at least 10 wt. %, or more, based on the total weight of the homogenous reaction system) can improve glycolaldehyde selectivity.

[0030] These and other non-limiting aspects of the present invention are discussed in further detail in the following sections.

A. Rhodium Catalysts

[0031] The rhodium metal used to prepare the catalyst of the present invention can be provided in various oxidation states (*e.g.*, 0, +1, +2, +3, *etc.*). The rhodium metal precursor used to make the catalytic rhodium metal complex of the present invention can be provided as water soluble rhodium metal complexes including a stabilizing ligand or ligands (L) that are displaced by other compounds (*e.g.*, coordinating ligands, CO and/or H₂). In some aspects, the rhodium metal complex can include one or more coordinating ligands selected from amines or water-soluble phosphorous ligands. Water soluble ligands can include

hydrophilic groups, which aids in solubilizing the ligand in water. Non-limiting examples of hydrophilic groups include a phosphate group, a sulfonate group, an acetate group, a polyether group and the like. In some embodiments, the ligand can be a water soluble substituted phosphine group. A non-limiting example of a substituted phosphine includes a substituted triphenyl phosphine ligands or an alkyl phosphine ligand. In one preferred embodiment, at least one ligand complexed with the rhodium metal is triphenylphosphine trisulfonate. In some embodiments, the catalytic rhodium metal complex includes an amine ligand. Non-limiting examples of coordination amine ligands include triaryl amines, trialkyl amines, tri(aryl)(alkyl) amines, arylalkyl amines, cyclic amines and the like. In some embodiments, the amine ligand can include hydrophilic groups as described above to improve water solubility. Non-limiting examples of amine ligands include tribenzylamine. In one instance, the catalytic rhodium metal complex includes only a water soluble ligand phosphine ligand and no amine ligands. In another instance, the catalytic rhodium metal complex includes an amine ligand and not a water soluble ligand phosphine ligand.

[0032] The catalytic rhodium metal complex can be made *in situ* from a rhodium metal precursor material having stabilizing ligands that can be exchanged with the water-soluble coordinating phosphine ligand or the coordinating amine ligand of the present invention. Non-limiting examples of stabilizing ligands include (acetylacetonato)dicarbonyl (acac), cycloocta-1,3-diene (COD), bis(cyclooctatetraene), bis(cycloocta-1,3,7-triene), bis(o-tolylphosphito) metal (ethylene), tetrakis (triphenylphosphite) bis(ethylene), 4-butyl-naphthalene-1,2-bisolate, 1-methyl-naphthalene-1,2-bisolate, 4-ethyl catecholate, 3,5-di(butyl)-4-(bromo)catecholate, 4-(propyl)catecholate, halides (*e.g.*, bromides and chlorides) or combinations thereof. The rhodium metal precursor can be prepared by known methods or purchased from a commercial supplier. Rh precursor materials can be (acetylacetonato)dicarbonylrhodium(I) ($\text{Rh}(\text{CO})_2\text{acac}$), chloro(1,5-cyclooctadiene)rhodium(I) dimer ($\{\text{Rh}(\text{COD})\text{Cl}\}_2$) $\text{Rh}(\text{Cl})(\text{CO})(\text{L})$, where L is a ligand described above. A non-limiting example of a commercial source of the above mentioned rhodium, ligands, and rhodium metal catalyst precursors is MilliporeSigma (U.S.A). The materials can be purified prior to use.

[0033] The water soluble rhodium metal catalyst precursor and the coordinating ligand can be dissolved in a mixture that includes water and a water-miscible solvent.

B. Reactants and Medium for Production of Glycolaldehyde

1. Reactants

[0034] The CO and H₂ can be obtained from commercial sources. In a non-limiting example, the CO and H₂ can be obtained from a synthesis gas (“syngas”) process. Syngas can include CO₂ and other gases (*e.g.*, nitrogen, helium, and argon). Syngas can be produced through reformation of hydrocarbons. The CO and H₂ can be in a mole ratio of about 1:1 as available in synthesis gas, but can also be employed in widely varying ranges, such as CO:H₂ mole ratios varying from about 10:1 to 1:10 or at least, equal to, or between any two of 10:1, 8:1, 5:1, 3:1, 1:1, 1:3, 1:5, and 1:10.

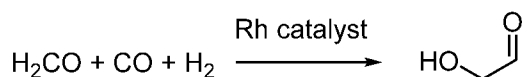
[0035] Formaldehyde can be formaldehyde, aqueous formaldehyde solutions (for example 37% in water), para-formaldehyde, or combinations thereof. *para*-Formaldehyde is the polymerization of formaldehyde with a typical degree of polymerization of 1 to up to 100 units. Aqueous formaldehyde (methanediol) and *para*-formaldehyde are available from many commercial manufacturers, for example, S D Fine-Chem Limited (India).

2. Medium

[0036] The medium can be a homogeneous solution of water and at least one water miscible solvent. Non-limiting examples of water miscible solvents include THF, DMAc, DMF, acetonitrile, a higher alcohol, or a diol. Non-limiting examples of alcohols and diols include glycerol, ethylene glycol, propylene glycol, triethylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, dimethoxyethane, methanol, ethanol, 1-propanol, 2-propanol, acetone, dimethyl sulfoxide (DMSO), 2-butoxyethanol, furfuryl alcohol, and/or 1,4-dioxane. In some embodiments, THF is used. Solvent used in the present invention can be obtained from commercial sources.

C. Method of Making Glycolaldehyde

[0037] Glycolaldehyde can be made in a catalytic manner using the catalytic rhodium metal complex of the present invention. The reaction scheme to make glycolaldehyde is shown below.



In step 1 of the method, the rhodium catalyst precursor material and coordinating ligand can be solubilized in a water-miscible solvent. Formaldehyde and water can be added to the water miscible solvent to form a homogeneous aqueous composition. The amount of water in the homogeneous aqueous composition can range from 0, 5, 10, 15, 20, 25, 30 wt.% and all values there between based on the total weight of the solution. In some embodiments, all ingredients are added at one time to the solvent. In another embodiment, the solvent solution is added to the formaldehyde solution. In some embodiments, water is added to the mixture in the absence of formaldehyde. The catalytic rhodium metal complex forms *in situ* in the homogenous solution prior to addition of the gaseous reactant feed, or during the addition of the gaseous reactant feed, or during heating of the reaction mixture. In a preferred embodiment, the rhodium metal complexed is solubilized in the solvent prior to addition of the other reactive ingredients. Without wishing to be bound by theory, it is believed that a stabilizing ligand of the rhodium catalyst precursor is replaced by the water-soluble phosphine ligand or the amine ligand. In step 2, a gaseous reactant feed of CO, H₂, and optional gaseous formaldehyde can be contacted to the homogeneous aqueous composition to form a reaction mixture that includes the catalytic rhodium metal complex, formaldehyde, CO and H₂. The CO, H₂, gaseous formaldehyde can be added as a mixture or as separate streams. The gaseous feed stream(s) can include gases chemically inert to the reaction (*e.g.*, nitrogen, helium, argon, methane, *etc.*).

[0038] The amount of catalyst employed in the processes is sufficient to catalyze the reaction of formaldehyde with carbon monoxide and hydrogen to form glycolaldehyde, and should be sufficient to achieve a reasonably practical reaction rate. In some embodiments, the rhodium catalysts are used in amounts sufficient to provide at least about 0.001 gram of rhodium, and up to about 1 gram of rhodium, per liter of the reaction medium. In some embodiments, the catalyst to formaldehyde molar ratio can be 1:25 to 1:10,000 or any value or range there between.

[0039] The reaction can be carried out under conditions suitable to catalytically generate glycolaldehyde by contact of the CO, H₂, and formaldehyde with the catalytic rhodium metal complexed with a coordinating ligand of the present invention (*e.g.*, water soluble phosphine ligand or amine ligand) to produce a product stream. Reaction pressure can range from 0.1 MPa to 15 MPa, or at least, equal to, or between any two of 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 13.5, 14, 14.5, and 15.

The pressures referred to above are usually attained by the quantities of carbon monoxide and hydrogen charged to the reaction zone or system. Reaction zones or system can include commercially available pressure resistant reaction units. Reaction temperatures can range from 90 °C. up to 150 °C, or at least, equal to, or between any two of 90 °C, 95 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, and 150 °C.

[0040] The product stream can include glycolaldehyde, water, catalyst and unreacted formaldehyde, CO and H₂. Glycolaldehyde can be separated from the gaseous products by releasing the pressure of the reaction vessel. Further separation of the glycolaldehyde from the water, catalyst and unreacted formaldehyde can be effected through known separation methods (*e.g.*, distillation, chromatography, and the like). The glycolaldehyde selectivity can be at least, equal to, or between any two of 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, and 100%, including all values and ranges there between. In some embodiments, the glycolaldehyde selectivity is 60% to 100%, 80% to 100%, and 90% to 100%. In some embodiments, methanol and/or ethylene glycol is produced as a by-product. The methanol selectivity can be less than, equal to, or between any two of 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%. The ethylene glycol selectivity can be less than, equal to, or between any two of 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%.

EXAMPLES

[0041] 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 Glycolaldehyde with Amine Ligand)

[0042] A PARR reactor (60 mL, Parr Instrument Company, USA) was charged with tetrahydrofuran solvent (15 mL, 13.185 g, S D Fine-Chem Limited (INDIA)), (acetylacetonato)dicarbonylrhodium catalyst precursor (Rh(CO)₂acac, 0.008 g, MilliporeSigma (U.S.A.)), tribenzylamine coordinating ligand (0.103 g, MilliporeSigma), and of formalin solution (5 mL, 5.761 g 37% aqueous formaldehyde, S D Fine-Chem Limited) The catalyst: formaldehyde molar ratio was 1:2000. CO and H₂ gas (789 psig (5 MPa) of 1:1

molar ratio) was added to the reactor and the reactor is heated to 100 °C. After 6 hours the reactor was allowed to cool overnight and the gases were vented. Gas Chromatographic (Agilent 6890N, Agilent Scientific Instruments, U.S.A.) analysis of the resultant product mixture showed 95.13% glycolaldehyde and 4% methanol, with formaldehyde conversion of 1.5%.

Example 2

(Production of Glycolaldehyde with Amine Ligand)

[0043] The reaction conditions and ingredients were the same as Example 1, except that the amount of THF was increased to 17.5 mL (16.8 g) and the formalin was changed to 2.5 mL (2.52 g) to provide a catalyst to formaldehyde ratio of 1:1000. Gas Chromatographic analysis of the resultant product mixture showed 62% glycolaldehyde, and 38% methanol, with formaldehyde conversion of 7%.

Example 3

(Production of Glycolaldehyde with Amine Ligand)

[0044] The reaction conditions and ingredients were the same as Example 1, except that the amount of THF was change to 10 mL (8.6 g) and formalin was changed to 10 mL (10.8 g) to provide a catalyst to formaldehyde ratio of 1:4000. Gas Chromatographic analysis of the resultant product mixture showed 100% glycolaldehyde, with formaldehyde conversion of 0.6%

Example 4

(Production of Glycolaldehyde with Amine Ligand)

[0045] The reaction conditions and ingredients were the same as Example 1, except that the amount of THF was change to 17 mL (15.5 g) and formalin was changed to 0.5 mL (0.53 g) to provide a catalyst to formaldehyde ratio of 1:200. Gas Chromatographic analysis of the resultant product mixture showed 65.8% glycolaldehyde, 34.2% methanol, with formaldehyde conversion of 8.1%.

Example 5**(Production of Glycolaldehyde with Water-Soluble Phosphine Ligand)**

[0046] The PARR reactor was charged with dimethylacetamide solvent (19.5 mL, 12.45 g, MilliporeSigma, U.S.A.) [Rh(COD)Cl]₂ catalyst precursor (0.0108 g), sodium salt of triphenylphosphine trisulfonate coordinating ligand (0.106 g), and of formalin solution (0.5 mL, 0.56 g, 37% aqueous formaldehyde, catalyst:formaldehyde ratio of 1:150). CO and H₂ gas (789 psig (5 MPa) of 1:1 molar ratio) was added to the reactor and the reactor is heated to 100 °C. After 3 hours the reactor was allowed to cool overnight and the gases were vented. Gas Chromatographic analysis of the resultant product mixture showed 74.4% glycolaldehyde, 1.49% ethylene glycol (EG) and 24.1% methanol, with 70.30% formaldehyde conversion.

Example 6**(Comparative Example Based On Use of Phosphine and Amine Ligands)**

[0047] The PARR reactor was charged with THF solvent (15 ml, 13.6969 g), Rh(CO)₂acac catalyst precursor (0.008 g), tribenzylamine ligand (0.103 g), triphenyl phosphine (0.008 g), and formalin solution (5.3 g 37% aqueous formaldehyde catalyst: substrate ratio of 1:2000). CO and H₂ gas (789 psig (5 MPa) of 1:1 molar ratio) was added to the reactor and the reactor is heated to 100 °C. After 6 hours the reactor was allowed to cool overnight and the gases were vented. Gas Chromatographic analysis of the resultant product mixture showed 4.32% glycolaldehyde, 95.1% methanol with formaldehyde conversion of 36%.

[0048] Although embodiments of the present application and their advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the embodiments as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the above disclosure, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein can be utilized.

Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

CLAIMS

1. A method of producing glycolaldehyde, the method comprising:
contacting a homogeneous aqueous solution comprising a water-miscible organic solvent, formaldehyde, water, and a catalytic rhodium metal complex with a gas comprising hydrogen (H₂) and carbon monoxide (CO), the catalytic rhodium metal complex comprising at least one water soluble phosphine-containing ligand or at least one amine-containing ligand, and
catalytically reacting the H₂, CO, and the formaldehyde to form glycolaldehyde.
2. The method of claim 1, wherein the selectivity of glycolaldehyde is at least 60%, preferably at least 70%, or more preferably 90% to 100%.
3. The method of any one of claims 1 to 2, wherein the homogenous solution comprises 0 wt. % to 30 wt. % water.
4. The method of any one of claims 1 to 3, wherein the catalytic rhodium metal complex includes the at least one phosphine-containing ligand and does not include the at least one amine-containing ligand.
5. The method of claim 4, wherein the at least one water soluble phosphine-containing ligand is a substituted aryl phosphine ligand, preferable a substituted triphenyl phosphine ligand, or an alkyl phosphine ligand, preferably, a trialkylphosphine ligand.
6. The method of claim 5, wherein the at least one water soluble phosphine-containing ligand is a substituted triphenyl phosphine ligand, preferably, a triphenylphosphine trisulfonate ligand.
7. The method of any one of claims 1 to 3, wherein the catalytic rhodium metal complex includes the at least one amine-containing ligand and does not include the at least one phosphine-containing ligand.
8. The method of claim 7, wherein the at least one amine-containing ligand is an aryl amine ligand, preferably a tribenzylamine ligand, or an alkyl amine ligand, preferably, a trialkyl amine ligand.

9. The method of claim 8, wherein the at least one amine-containing ligand is a tribenzylamine ligand.
10. The method of any one of claims 1 to 9, wherein the catalytic rhodium metal complex is formed *in situ* from a rhodium metal precursor and at least one water soluble phosphine-containing compound or at least amine-containing compound.
11. The method of claim 10, wherein the rhodium metal precursor is (acetylacetonato)dicarbonylrhodium(I) or chloro(1,5-cyclooctadiene)rhodium(I) dimer.
12. The method of any one of claims 10 to 11, wherein the at least one water soluble phosphine-containing compound is a substituted triphenyl phosphine compound, preferably, triphenylphosphine trisulfonate.
13. The method of any one of claims 10 to 11, wherein the at least one amine-containing compound is substituted tribenzylamine.
14. The method of any one of claims 1 to 13, wherein the reaction temperature is 90 °C to 150 °C and/or the reaction pressure is 0.1 MPa to 15 MPa.
15. The method of any one of claims 1 to 14, wherein the molar ratio of CO:H₂ is 10:1 to 1:10, preferably 5:1 to 1:5, or more preferably 1:1.
16. The method of any one of claims 1 to 15, wherein the catalyst to formaldehyde molar ratio is 1:25 to 1:10,000.
17. The method of any one of claims 1 to 16, wherein the formaldehyde is an aqueous solution of formaldehyde, paraformaldehyde, or gaseous formaldehyde.
18. The method of claim 17, wherein the formaldehyde is the aqueous solution of formaldehyde.
19. The method of any one of claims 1 to 18, wherein the water-miscible organic solvent is tetrahydrofuran (THF), N,N-dimethyl acetamide, N,N-dimethyl formamide, a higher alcohol, or a diol, preferably THF.
20. A method of producing glycolaldehyde, the method comprising:

contacting a composition comprising an ionic liquid solvent, formaldehyde, and a catalytic rhodium metal complex with a gas comprising hydrogen (H_2) and carbon monoxide (CO), the rhodium metal complex comprising at least one phosphine-containing ligand or at least one amine-containing ligand, and catalytically reacting the gas and the formaldehyde to form glycolaldehyde.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/059244

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C47/19 C07C45/68
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

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 4 405 821 A (GOETZ RICHARD W [US]) 20 September 1983 (1983-09-20) abstract examples 1-52 -----	1-4,7-9, 13-20 10-12
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Y	WO 2005/058788 A1 (SHELL INT RESEARCH [NL]; ALMEIDA LENERO KARINA QUETZALY [NL] ET AL.) 30 June 2005 (2005-06-30) examples 1-6 -----	10-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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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

Delanghe, Patrick

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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