

AMINOPOLYCARBOXYLATES AS RATE PROMOTERS FOR THE GLACIAL ACETIC ACID PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application is filed under the Patent Cooperation Treaty, which claims the benefit of priority to U.S. Provisional Patent Application No. 63/535,875 filed on August 31, 2023, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This disclosure relates to the production of glacial acetic acid (GAA). More particularly, the disclosure relates to rate promoter compounds in acetic acid production.

BACKGROUND OF THE INVENTION

[0003] A carbonylation process of methanol is a desirable commercial route for synthesis of acetic acid. In such a process, methanol, methyl acetate, or any mixture of the two, and carbon monoxide are reacted in the liquid phase in the presence of a homogeneous catalyst such as a rhodium (Rh)-based catalyst, at for instance 150 to 200°C and increased pressure to produce acetic acid with typically up to 95% selectivity and 5 % side products. Methyl iodide (CH_3I , or MeI) is typically used as a promoter for the carbonylation step in this process. The commercial reaction proceeds in the liquid phase with a solvent such as methyl acetate using the homogeneous catalyst. A controlled amount of water required for the reaction is added and/or generated *in situ* by reaction of methanol with HI or by esterification of methanol with acetic acid. Given that water must be separated from the acetic acid in recovery, it is desirable to use lower amounts of water in the carbonylation process.

[0004] In the carbonylation process, the homogeneous catalyst is preferably cycled between oxidative states. For example, for a (Rh)-based catalyst, the catalytically active species may be the four-coordinate anion $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, typically referred to as “Rh I”. The first organometallic step would be the oxidative addition of methyl iodide to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ to form the six-coordinate anion $[(\text{CH}_3)\text{Rh}(\text{CO})_2\text{I}_3]^-$. This anion rapidly transforms via the migration of a methyl group to an adjacent carbonyl (CO) ligand affording the five-coordinate acetyl anion $[(\text{CH}_3\text{CO})\text{Rh}(\text{CO})\text{I}_3]^-$. This five-coordinate complex then reacts with carbon monoxide to form the six-coordinate dicarbonyl complex, which then undergoes reductive elimination to yield acetyl iodide ($\text{CH}_3\text{C}(\text{O})\text{I}$). The catalytic cycle also involves two non-organometallic steps: conversion of methanol or methyl acetate to methyl iodide and the hydrolysis of acetyl iodide to acetic acid and hydrogen iodide. This reaction has been shown to be first-order with respect to methyl iodide and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. The first step of the catalytic cycle is oxidative addition of methyl iodide.

[0005] It would be desirable to improve this carbonylation process by accelerating or “promoting” the rate of formation of acetic acid, such as by promoting the rate of methyl iodide

oxidative addition. Methods that could suppress the undesirable oxidative addition of HI with $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and support a reduced amount of water in the process would be additionally desirable. For purposes of studying the potential benefits of rate promoter compounds (“promoters”) of the acetic acid process, it is this later rate-determining step that is beneficially studied.

[0006] In particular, the two oxidative addition reactions that control the pathways leading to desired methanol carbonylation (A) and undesired water gas shift (WGS) (B) are as shown below:



[0007] As such, any new GAA production method would desirably be capable of achieving acceleration of MeI oxidative addition and/or suppression of HI oxidative addition. Desirably the optimal production method will both accelerate MeI oxidative addition and suppress HI oxidative addition to Rh I. Suppression of HI oxidative addition to Rh I will free up additional Rh I for MeI oxidative addition.

SUMMARY OF THE INVENTION

[0008] A process for producing and recovering acetic acid in an acetic acid production system is disclosed, the process comprising contacting methanol and/or methyl acetate and carbon monoxide in the presence of a reaction mixture comprising iodide under carbonylation conditions sufficient to form acetic acid. The reaction mixture comprises a carbonylation catalyst, water, and one or more rate promoting compounds (“promoters”) selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof.

[0009] Embodiments of the disclosure include processes for producing acetic acid comprising (or consisting of, or consisting essentially of):

- a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising:
 - i) a carbonylation catalyst selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts;
 - ii) water in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and
 - iii) one or more promoters selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and
 - iv) iodide; and
- b) recovering acetic acid.

[0010] Embodiments of the disclosure also include methods for reducing water in an acetic acid production process comprising (or consisting of, or consisting essentially of):

- a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising iodide under carbonylation conditions sufficient to form acetic acid at a first rate, wherein the reaction mixture comprises:
 - i) a carbonylation catalyst, selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; and
 - ii) a first amount of water, where the water is present in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and
- b) combining one or more promoters to the reaction mixture at an iodide to promoter molar ratio of greater than 2, wherein the one or more promoters are selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and
- c) reducing the wt% of water in the reaction mixture to a second amount of water while maintaining a second rate of acetic acid production that is the same as or greater than the first rate of acetic acid production.

[0011] While the disclosed processes are susceptible to various modifications and alternative forms, the drawings illustrate specific embodiments herein described in detail by way of example. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular embodiments disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The claimed subject matter may be understood by reference to the following description taken in conjunction with the accompanying drawings, in which like reference numerals identify like elements, and in which:

[0013] **FIG. 1** is a schematic of an exemplary acetic acid production system in accordance with embodiments and/or techniques disclosed herein;

[0014] **FIG. 2** is a graphical representation of FTIR overlay spectra showing MeI oxidative addition to Rh I carbonylation catalyst at variable H₂O concentration as a function of time;

[0015] **FIG. 3** is a plot of first-order rate constants as a function of H₂O concentration for the data in **FIG. 2**;

[0016] **FIG. 4** is a plot of first-order rate constants as a function of promoter concentration;

[0017] **FIG. 5** is a graphical representation of FTIR overlay spectra showing MeI oxidative addition to Rh I carbonylation catalyst in the presence (separately) of LiOAc (top overlay spectra) and DTPA-Na₃Ca (bottom overlay spectra);

[0018] FIG. 6 is a graphical representation of comparison overlay FTIR spectra showing MeI oxidative addition to Rh I carbonylation catalyst in the presence (separately) of 0.5M LiOAc (bottom overlay spectra) and 0.033M DTPA-Na₃Ca (top overlay spectra) from 0 to 120 mins;

[0019] FIG. 7 is a graphical representation of FTIR overlay spectra demonstrating the effect of variable DTPA-Na₃Ca concentrations on MeI oxidative addition kinetics;

[0020] FIG. 8 is a plot of first-order rate constants for various common and novel promoters of oxidative addition rate constants;

[0021] FIG. 9 is a graphical representation of FTIR overlay spectra showing the oxidative addition of 0.25M HI to 0.015M Rh I at variable H₂O concentration from 0 to 60 mins;

[0022] FIG. 10 is a plot of associated rate constants for several of the kinetic runs in FIG. 9;

[0023] FIG. 11 is a plot of associated rate constants for several of relatively low water concentration kinetic runs;

[0024] FIG. 12 is a plot of associated rate constants for several of relatively high water concentration kinetic runs;

[0025] FIG. 13 is a plot of associated HI and MeI oxidative addition rate constants for the low rate, high H₂O runs being estimated, all rate constants are plotted as a function of H₂O concentration;

[0026] FIG. 14 is a graphical representation of FTIR overlay spectra in the presence of the novel promoter DTPA-Na₃Ca in the presence of HI;

[0027] FIG. 15 is a graphical representation of FTIR overlay spectra in the presence of the novel promoter DTPA-Na₃Ca in the presence of HI;

[0028] FIG. 16 is a plot of time profiles of data from FIG. 14 and FIG. 15;

[0029] FIG. 17 is a plot of time profiles of data from FIG. 14 and FIG. 15; and

[0030] FIG. 18 is a plot of first-order rate constants of HI oxidative addition to Rh I at various HI/promoter ratios.

DETAILED DESCRIPTION OF THE INVENTION

[0031] The designation of groups of the Periodic Table of the Elements as used herein is in accordance with the current IUPAC convention. The expression "MeI" is used herein as an abbreviation for methyl iodide. The expression "HI" is used herein as an abbreviation for hydrogen iodide. The expression "acac" is used herein as an abbreviation for acetoacetate anion, i.e., $\text{H}_3\text{CC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{O}^-$. Unless specifically indicated otherwise, the expression "wt%" as used herein refers to the percentage by weight of a particular component in the referenced composition. The expression "LiOAc" is an abbreviation for lithium acetate.

[0032] The term "alkyl" means a monovalent group of carbon and hydrogen (such as a C₁ to C₃₀, such as a C₁ to C₁₂ group). Alkyl groups in a compound are typically bonded to the compound

directly via a carbon atom. Unless otherwise specified, alkyl groups may be linear (*i.e.*, unbranched) or branched, be cyclic, acyclic, or part cyclic/acyclic. In an embodiment the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl.

[0033] Embodiments of the disclosed process and system involve the production of acetic acid by carbonylating methanol in a carbonylation reaction. The carbonylation reaction may be represented by: $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$.

[0034] FIG. 1 is a schematic of an exemplary acetic acid production system 100 implementing the carbonylation reaction. In some embodiments, the acetic acid system 100 may include a reaction area 102, a light-ends area 104, a purification area 106, and recycle area 108. The reaction area 102 may include a reactor 110, a flash vessel 120, and associated equipment. The reactor 110 is a reactor or vessel in which methanol is carbonylated in the presence of a catalyst to form acetic acid at elevated pressure and temperature. Note that the “streams” discussed herein may be part of more than one functional area. A “reaction mixture” is present in the reactor 110, from which a portion may be withdrawn, and to which components (such as catalysts, chemical reactants, promoters, diluent, etc.) may be introduced, combined and mixed to obtain a desirable concentration; and reacted and/or maintained at a desirable concentration.

[0035] The reaction area 102 may comprise a reactor 110, a flash vessel 120, equipment associated with the reactor 110 and flash vessel 120, and streams associated with the reactor 110 and flash vessel 120. For example, the reaction area 102 may comprise reactor 110, flash vessel 120, and streams (or portions of streams) 111, 112, 114, 121, 126, 131, 160, 138, 139, 148. The reactor 110 is a reactor or vessel in which methanol is carbonylated in the presence of a catalyst to form acetic acid at elevated pressure and temperature. The flash vessel 120 is a tank or vessel in which a reaction mixture obtained in the reactor, for example the reactor 110, is at least partially depressurized and/or cooled to form a vapor stream and a liquid stream. A vapor stream is a product or composition which comprises components in the gaseous state under the conditions of the processing step in which the stream is formed. A liquid stream may be a product or composition which comprises components in the liquid state under the conditions of the processing step in which the stream is formed.

[0036] The light-ends area 104 may comprise a separations column, for example a light-ends column 130, equipment associated with light-ends column 130, and streams associated with the light-ends column 130. For example, the light-ends area 104 may comprise light-ends column 130,

decanter **134**, and streams **126**, **131**, **132**, **133**, **135**, **136**, **138**, **139**. The light-ends column **130** is a fractioning or distillation column and includes any equipment associated with the column, including but not limited to heat exchangers, decanters, pumps, compressors, valves, and the like.

[0037] The purification area **106** may comprise a drying column **140**, optionally, a heavy-ends column **150**, equipment associated with drying column **140** and heavy-ends column **150**, and streams associated with the drying column **140** and heavy-ends column **150**. For example, the purification area **106** may comprise drying column **140**, heavy-ends column **150**, and streams **136**, **141**, **142**, **145**, **148**, **151**, **152**, **156**. The heavy-ends column **150** is a fractioning or distillation column and includes any equipment associated with the column, including but not limited to heat exchangers, decanters, pumps, compressors, valves, and the like.

[0038] The recycle area **108** may comprise process streams recycled to the reaction area **102** and/or light-ends area **104** (not shown). For example, in **FIG. 1**, the recycle area **108** may comprise streams **121**, **138**, **139**, **148**.

[0039] In an embodiment, the reactor **110** may be configured to receive a carbon monoxide feed stream **114** and a methanol feed stream **112**. The feed stream **112** may comprise a methanol feed stream, a methyl acetate feed stream or any mixture of the two. In the illustrated embodiment, the feed stream **112** is a mixed stream. A reaction mixture may be withdrawn from the reactor in stream **111**. Other streams may be included such as, for example, a stream that may recycle a bottoms mixture of the reactor **110** back into the reactor **110**, or a stream may be included to release a gas from the reactor **110**. Stream **111** may comprise at least a part of the reaction mixture.

[0040] In an embodiment, the flash vessel **120** may be configured to receive stream **111** from the reactor **110**. In the flash vessel **120**, stream **111** may be separated into a vapor stream **126** and a liquid stream **121**. The vapor stream **126** may be communicated to the light-ends column **130**, and the liquid stream **121** may be communicated to the reactor **110**. In an embodiment, stream **126** may have acetic acid, water, methyl iodide, methyl acetate, HI, mixtures thereof.

[0041] In an embodiment, the light-ends column **130** may be a distillation column and associated equipment such as a decanter **134**, pumps, compressors, valves, and other related equipment. The light-ends column **130** may be configured to receive stream **126** from the flash vessel **120**. In the illustrated embodiment, stream **132** is the overhead product from the light-ends column **130**, and stream **131** is bottoms product from the light-ends column **130**. As indicated, light-ends column **130** may include a decanter **134**, and stream **132** may pass into decanter **134**.

[0042] Stream **135** may emit from decanter **134** and recycle back to the light-ends column **130**. Stream **138** may emit from decanter **134** and may recycle back to the reactor **110** via, for example, stream **112** or be combined with any of the other streams that feed the reactor. Stream **139** may recycle a portion of the light phase of decanter **134** back to the reactor **110** via, for example, stream

112. Stream **136** may emit from the light-ends column **130**. Other streams may be included such as, for example, a stream that may recycle a bottoms mixture of the light-ends column **130** back into the light-ends column **130**. Streams received by or emitted from the light-ends column **130** may pass through a pump, compressor, heat exchanger, and the like as is common in the art.

[0043] In an embodiment, the drying column **140** may be a vessel and associated equipment such as heat exchangers, decanters, pumps, compressors, valves, and the like. The drying column **140** may be configured to receive stream **136** from the light-ends column **130**. The drying column **140** may separate components of stream **136** into streams **142** and **141**.

[0044] Stream **142** may emit from the drying column **140**, recycle back to the drying column **140** via stream **145**, and/or recycle back to the reactor **110** through stream **148** (via, for example, stream **112**). Stream **141** may emit from the drying column **140** and may include de-watered crude acetic acid product. Stream **142** may pass through equipment such as, for example, a heat exchanger or separation vessel before streams **145** or **148** recycle components of stream **142**. Other streams may be included such as, for example, a stream may recycle a bottoms mixture of the drying column **140** back into the drying column **140**. Streams received by or emitted from the drying column **140** may pass through a pump, compressor, heat exchanger, separation vessel, and the like as is common in the art.

[0045] The heavy-ends column **150** may be a distillation column and associated equipment such as heat exchangers, decanters, pumps, compressors, valves, and the like. The heavy-ends column **150** may be configured to receive stream **141** from the drying column **140**. The heavy-ends column **150** may separate components from stream **141** into streams **151**, **152**, and **156**. Streams **151** and **152** may be sent to additional processing equipment (not shown) for further processing. Stream **152** may also be recycled, for example, to light-ends column **130**. Stream **156** may have acetic acid product.

[0046] A single column (not depicted) may be used in the place of the combination of the light-ends distillation column **130** and the drying column **140**. The single column may vary in the diameter/height ratio and the number of stages according to the composition of vapor stream from the flash separation and the requisite product quality. For instance, U.S. Pat. No. 5,416,237, the teachings of which are incorporated herein by reference, discloses a single column distillation.

[0047] Alternative embodiments for the acetic acid production system **100** may also be found in U.S. Pat. Nos. 6,552,221, 7,524,988, and 8,076,512, which are fully incorporated herein by reference.

[0048] In an embodiment, the carbonylation reaction in reactor **110** of system **100** may be performed in the presence of a carbonylation catalyst. Catalysts may include, for example, rhodium catalysts and iridium catalysts.

[0049] Suitable rhodium catalysts are taught, for example, by U.S. Pat. No. 5,817,869, which is herein incorporated by reference. The rhodium catalysts may include rhodium metal and rhodium compounds. In an embodiment, the rhodium compounds may be selected from the group consisting of rhodium salts, rhodium oxides, rhodium acetates, organo-rhodium compounds, coordination compounds of rhodium, the like, and mixtures thereof. In an embodiment, the rhodium compounds may be selected from the group consisting of $\text{Rh}_2(\text{CO})_4\text{I}_2$, $\text{Rh}_2(\text{CO})_4\text{Br}_2$, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, $\text{Rh}(\text{CH}_3\text{CO}_2)_2$, $\text{Rh}(\text{CH}_3\text{CO}_2)_3$, $[\text{H}]\text{Rh}(\text{CO})_2\text{I}_2$, the like, and mixtures thereof. In an embodiment, the rhodium compounds may be selected from the group consisting of $[\text{H}]\text{Rh}(\text{CO})_2\text{I}_2$, $\text{Rh}(\text{CH}_3\text{CO}_2)_2$, the like, and mixtures thereof.

[0050] Suitable iridium catalysts are taught, for example, by U.S. Pat. No. 5,932,764, which is herein incorporated by reference. The iridium catalysts may include iridium metal and iridium compounds. Examples of suitable iridium compounds include IrCl_3 , IrI_3 , IrBr_3 , $[\text{Ir}(\text{CO})_2\text{I}]_2$, $[\text{Ir}(\text{CO})_2\text{Cl}]_2$, $[\text{Ir}(\text{CO})_2\text{Br}]_2$, $[\text{Ir}(\text{CO})_4\text{I}_2]\text{-H}^+$, $[\text{Ir}(\text{CO})_2\text{Br}_2]\text{-H}^+$, $[\text{Ir}(\text{CO})_2\text{I}_2]\text{-H}^+$, $[\text{Ir}(\text{CH}_3)_3\text{I}_3(\text{CO})_2]\text{-H}^+$, $\text{Ir}_4(\text{CO})_{12}$, $\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{IrBr}_3 \cdot 4\text{H}_2\text{O}$, $\text{Ir}_3(\text{CO})_{12}$, Ir_2O_3 , IrO_2 , $\text{Ir}(\text{acac})(\text{CO})_2$, $\text{Ir}(\text{acac})_3$, $\text{Ir}(\text{OAc})_3$, $[\text{Ir}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3][\text{OAc}]$, $\text{H}_2[\text{IrCl}_6]$, the like, and mixtures thereof. In an embodiment, the iridium compounds may be selected from the group consisting of acetates, oxalates, acetoacetates, the like, and mixtures thereof. In an embodiment, the iridium compounds may be one or more acetates.

[0051] In an embodiment, the catalyst may be used with a co-catalyst. In an embodiment, co-catalysts may include metals and metal compounds selected from the group consisting of osmium, rhenium, ruthenium, cadmium, mercury, zinc, gallium, indium, and tungsten, their compounds, the like, and mixtures thereof. In an embodiment, co-catalysts may be selected from the group consisting of ruthenium compounds and osmium compounds. In an embodiment, co-catalysts may be one or more ruthenium compounds. In an embodiment, the co-catalysts may be one or more acetates.

[0052] The reaction rate depends upon the concentration of the carbonylation catalyst in the reaction mixture in reactor **110**. In some embodiments the catalyst concentration is at least 2 mmol/l, or at least 3 mmol/l, or at least 5 mmol/l. In some embodiments the catalyst concentration is at most 150 mmol/l, or at most 100 mmol/l, or at most 25 mmol/l. In particular embodiments the catalyst concentration is from about 2 to about 150 mmol/l, or from about 3 to about 100 mmol/l, or from about 5 to about 25 mmol/l.

[0053] In an embodiment, the carbonylation reaction in reactor **110** of system **100** may be performed in the presence of a catalyst stabilizer. Suitable catalyst stabilizers include at least two types of catalyst stabilizers. The first type of catalyst stabilizer may be a metal iodide salt such as lithium iodide. The second type of catalyst stabilizer may be a non-salt stabilizer. In an

embodiment, non-salt stabilizers may be pentavalent Group 15 oxides, such as that disclosed in U.S. Pat. No. 9,790,159, which is herein incorporated by reference. The pentavalent Group 15 oxide is soluble in acetic acid and in an embodiment comprises a bidentate phosphine dioxide, tertiary arsine oxides, the like, or combinations thereof. Nonlimiting examples of suitable bidentate phosphine dioxide for use as a pentavalent Group 15 oxide include, but are not limited to, bis(diphenylphosphino)methane dioxide (bis-DPPMeO₂), bis(diphenylphosphino)propane dioxide (bis-DPPPrO₂), bis(diphenylphosphino)pentane dioxide (bis-DPPPeO₂), and combinations thereof. Nonlimiting examples of suitable phosphine oxides for use as a pentavalent Group 15 oxide include, but are not limited to, triphenyl arsine oxide (TPAsO), triethylarsine oxide (TEtAsO), and combinations thereof. In an embodiment, the catalyst stabilizer may be one or more phosphine oxides.

[0054] In an embodiment, hydrogen may also be fed into the reactor **110**. Addition of hydrogen can enhance the carbonylation efficiency. In an embodiment, the concentration of hydrogen may be in a range of from about 0.1 mol % to about 5 mol % of carbon monoxide in the reactor **110**. In an embodiment, the concentration of hydrogen may be in a range of from about 0.3 mol % to about 3 mol % of carbon monoxide in the reactor **110**.

[0055] In an embodiment, the carbonylation reaction in reactor **110** of system **100** may be performed in the presence of water. In an embodiment, the concentration of water is from about 0.1 wt% to about 10.0 wt%, about 0.2 wt% to about 6.0 wt%, about 0.3 wt% to about 4.5 wt%, or about 0.4 wt% to about 2 wt%, based on the total weight of the reaction mixture.

[0056] In an embodiment, the carbonylation reaction may be performed in the presence of methyl acetate. Methyl acetate may be formed *in situ*. In embodiments, methyl acetate may be added as a starting material to the reaction mixture. In an embodiment, the concentration of methyl acetate may be from about 2 wt% to about 20 wt% based on the total weight of the reaction mixture. In an embodiment, the concentration of methyl acetate may be from about 2 wt% to about 16 wt%. In an embodiment, the concentration of methyl acetate may be from about 2 wt% to about 8 wt%. Alternatively, methyl acetate or a mixture of methyl acetate and methanol from byproduct streams of the methanolysis of polyvinyl acetate or ethylene-vinyl acetate copolymers can be used for the carbonylation reaction.

[0057] In an embodiment, the carbonylation reaction may be performed in the presence of methyl iodide that is added to the reactor **110**, generated in the reactor, or both. In an embodiment, the concentration of MeI may be from about 0.6 wt% to about 36 wt% based on the total weight of the reaction mixture. In an embodiment, the concentration of MeI may be from about 4 wt% to about 24 wt%. In an embodiment, the concentration of MeI may be from about 6 wt% to about 20 wt%. Alternatively, MeI may be generated in the reactor **110** by adding HI.

[0058] As mentioned, methanol and carbon monoxide may be fed to the reactor 110 in stream 112 and stream 114, respectively. The methanol feed stream to the reactor 110 may come from a syngas-methanol facility or any other source. Methanol does not react directly with carbon monoxide to form acetic acid. It is converted to MeI by the HI present in the reactor 110 and then reacts with carbon monoxide and water to give acetic acid and regenerate the HI. Therefore, in any embodiment the concentration of HI present in the reactor is from about 0.1 wt% to about 10.0 wt%, about 0.2 wt% to about 6.0 wt%, about 0.3 wt% to about 4.5 wt%, or about 0.4 wt% to about 2 wt%, based on the total weight of the reaction mixture.

[0059] In any embodiment MeI reacts with the carbonylation catalyst in a rate limiting step in the acetic acid process to form an active catalyst species. While HI may be added to the reaction mixture to generate MeI, it is desirable to modulate the presence of the HI as it is believed to be a carbonylation catalyst inhibitor. Thus, in any embodiment a promoter compound is added to the reaction mixture in amounts that are beneficial to both ends.

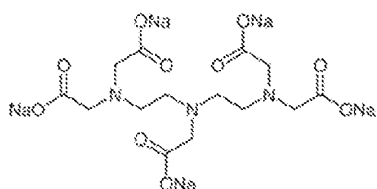
[0060] In any embodiment one or more promoters are combined and maintained in the reaction mixture, in any part of the acetic acid production system 100, preferably upstream of the purification area 106, wherein the one or more promoters are selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof. In any embodiment, the aminopolycarboxylate salts comprise 2, or 3 or more carboxylate groups. In another embodiment the aminopolycarboxylate salts comprise 2, or 3 to 5, or 8, or 10 carboxylate groups. In yet another embodiment the aminopolycarboxylate salts comprise at least one amine group and at least 3 or 4 carboxylate groups. In yet another embodiment the aminopolycarboxylate salts comprise at least 2 amine groups and at least 2 carboxylate groups.

[0061] In any embodiment the one or more promoters are selected from the group consisting of aminopolycarboxylate salts comprising at least one amine group and at least 3 or 4 carboxylate groups, and aminopolycarboxylate salts comprising at least 2 amine groups and at least 2 carboxylate groups.

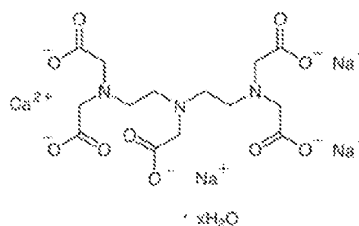
[0062] In any embodiment, the aminopolycarboxylate salts described herein may be represented by the general formula representing the anionic portion $[(\text{COO})\text{RNR}')_x]^-$, wherein a promoter compound may comprise "x" number of units, such as 2, 3, 4 or more; and wherein each R group can be the same or different can be a linear, branched, or cyclic alkyl or alkylene group, and is preferably an ethylene ($-\text{CH}_2-$) group; and wherein each R' group may be the same or different and can be a linear, branched, or cyclic alkyl or alkylene group; wherein when R' is an alkylene group it may be bound to another $[(\text{COO})\text{RNR}']$ unit, preferably "x" number of units.

[0063] Non-limiting examples of promoters are dialkyltriaminepentacarboxylate salts, such as diethylenetriaminepentaacetic acid pentasodium salts, diethylenetriaminepentaacetic acid calcium

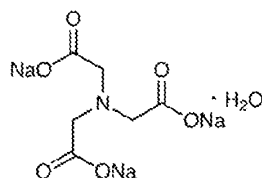
trisodium salt, trisodium nitrilotriacetate trisodium salt, tetrasodium N, N-bis(carboxymethyl)-L-glutamate, and carboxylate-substituted glutamate salts such as tetrasodium N, N-Bis(carboxymethyl)-L-glutamate (GLDA- Na_4), and trisodium nitrilotriacetate (NTA- Na_3). Exemplary structures are shown below in structures (1) to (4), where various molar equivalents of water of hydration may be present:



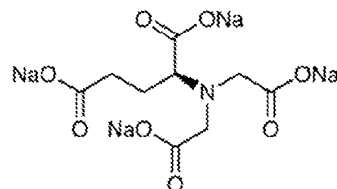
(1)



(2)



(3)



(4)

[0064] Wherein (1) is diethylenetriaminepentaacetic acid pentasodium salt (DTPA- Na_5), while (2) is diethylenetriaminepentaacetic acid calcium trisodium salt (DTPA- Na_3Ca). Structure (3) is trisodium nitrilotriacetate (NTA- Na_3), while (4) is tetrasodium N, N-bis(carboxymethyl)-L-glutamate salt. Other alkyl and carboxylate substituted versions of these, with any combination of Group I and Group II cations, are possible promoters as disclosed herein.

[0065] In any embodiment, the Group I and Group II aminopolycarboxylate salts may be completely ionized to form complete salts, or may be partially ionized as a mixture of the salt (e.g., Na^+ or Ca^{2+}) and acid (H^+).

[0066] In any embodiment, salts of glutamate ($\text{C}_5\text{H}_8\text{O}_4\text{N}$) and dicarboxymethyl alaninate ($\text{C}_7\text{H}_8\text{NO}_6$) are absent from the reaction mixture, meaning that they are not added to the reaction mixture and desirably absent (0 ppm), or if present, are present in an amount of less than 0.2 ppm, or 0.1 ppm. However, substituted versions of glutamate may be present as the one or more promoters as described herein such as tetrasodium N, N-Bis(carboxymethyl)-L-glutamate (GLDA- Na_4), and trisodium nitrilotriacetate (NTA- Na_3).

[0067] Thus in any embodiment is a process for producing acetic acid comprising (or consisting of, or consisting essentially of): a) combining methanol and carbon monoxide in the presence of a reaction mixture comprising: i) a carbonylation catalyst selected from the group consisting of

rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; ii) water in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and iii) one or more promoters selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and iv) iodide; and b) recovering acetic acid.

[0068] Also in any embodiment is a method for reducing water in an acetic acid production process comprising (or consisting of, or consisting essentially of): a) combining methanol and carbon monoxide in the presence of a reaction mixture comprising iodide under carbonylation conditions sufficient to form acetic acid at a first rate, wherein the reaction mixture comprises: i) a carbonylation catalyst, selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; and ii) a first amount of water, where the water is present in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and b) combining one or more promoters to the reaction mixture at an iodide to promoter ratio of greater than 2, wherein the one or more promoters are selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and c) reducing the wt% of water in the reaction mixture to a second amount of water while maintaining a second rate of acetic acid production that is the same as or greater than the first rate of acetic acid production.

[0069] In any embodiment the amount of promoter maintained in the reaction mixture is such that a molar ratio to carbonylation catalyst is greater than about 0.5:1. In some embodiments, the molar ratio of the promoter to rhodium is from about 0.5:1 to about 100:1. In some embodiments, from about 0.005 to about 2.0 M of the promoter may be in the reaction mixture. In some embodiments, from about 0.01 to about 1.5 M, or from 0.025 to 1.2 M, of the promoter may be in the reaction mixture.

[0070] In any embodiment the amount of promoter maintained in the reaction mixture is such that a molar ratio of iodide to promoter is greater than 2:1, or greater than 3:1, or greater than 4:1, or greater than 6:1. In some embodiments, the molar ratio of the iodide to promoter is from 2:1 to 40:1, or from 3:1 to 35:1, or from 4:1 to 30:1, or from 6:1 to 25:1. Also in any embodiment the one or more promoters are maintained at a promoter to carbonylation catalyst molar ratio of from 0.005:1 to 4:1, or from 0.01:1 to 3:1, or from 0.02:1 to 2:1.

[0071] In an embodiment, the rate at which promoter is introduced into the system **100** may be adjusted depending on the water, carbonylation catalyst, and/or HI content. In some embodiments, the promoter may be maintained in an amount of at least about 0.1 mol per mol HI. In some embodiments, at least about 0.5 mol promoter, or at least about 1 mol promoter, or at least about 1.5 mol promoter, per mol HI is maintained. In some embodiments, the promoter may be maintained in an amount of from about 0.1 to about 10 mol per mol HI. In some embodiments, the

amount of promoter is from about 0.25 to about 7.5 mol, or from about 0.5 to about 5 mol, or from about 0.75 to about 1.5 mol, per mol HI.

[0072] In other embodiments, the amount of promoter is from about 1 to about 10 mol, or from about 1 to about 7.5 mol, or from about 1 to about 5 mol, per mol HI. In some embodiments, the promoter may be maintained in an amount from about 0.1 to about 1.5 mol per mol HI. In some embodiments, the amount of promoter maintained may be from about 0.1 to about 1.3 mol, or from about 0.1 to about 1.1 mol, per mol HI. In further some embodiments, the amount of promoter is from about 0.5 to about 3 mol, or from about 0.5 to about 2 mol, or from about 0.5 to about 1.5 mol, per mol HI.

[0073] In an embodiment, the carbonylation reaction in reactor **110** of system **100** may occur at a temperature within the range of about 120°C to about 250°C, alternatively, about 150°C to about 250°C, alternatively, about 150°C to about 200°C. In an embodiment, the carbonylation reaction in reactor **110** of system **100** may be performed under a pressure within the range of about 200 psia (1.38 MPa-a) to 2,000 psia (13.8 MPa-a), alternatively, about 200 psia (1.38 MPa-a) to about 1,000 psia (6.9 MPa-a), alternatively, about 300 psia (2.1 MPa-a) to about 500 psia (3.4 MPa-a).

[0074] In an embodiment, the reaction mixture may be withdrawn from the reactor **110** through stream **111** and is flashed in flash vessel **120** to form a vapor stream **126** and a liquid stream **121**. The reaction mixture in stream **111** may include acetic acid, methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, water, HI, heavy impurities, catalyst, or combinations thereof. The flash vessel **120** may comprise any configuration for separating vapor and liquid components via a reduction in pressure. For example, the flash vessel **120** may comprise a flash tank, nozzle, valve, or combinations thereof.

[0075] The flash vessel **120** may have a pressure below that of the reactor **110**. In an embodiment, the flash vessel **120** may have a pressure of from about 10 psig (69 kPa-g) to 100 psig (689 kPa-g). In an embodiment, the flash vessel **120** may have a temperature of from about 100°C to 160°C.

[0076] The vapor stream **126** may include acetic acid and other volatile components such as methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, water, entrained HI, complexed HI, and mixtures thereof. The liquid stream **121** may include acetic acid, methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, water, complexed HI, HI, an azeotrope of HI and water, and mixtures thereof. In particular, the liquid stream may comprise the catalyst, complexed HI, HI, an azeotrope of HI and water, and mixtures thereof. The liquid stream **121** may further comprise sufficient amounts of water and acetic acid to carry and stabilize the catalyst, non-volatile catalyst stabilizers, or combinations thereof. The liquid stream **121** may

recycle to the reactor **110**. The vapor stream **126** may be communicated to light-ends column **130** for distillation.

[0077] In an embodiment, the vapor stream **126** may be distilled in a light-ends column **130** to form an overhead stream **132**, a crude acetic acid product stream **136**, and a bottoms stream **131**. In an embodiment, the light-ends column **130** may have at least 10 theoretical stages or 16 actual stages. In an alternative embodiment, the light-ends column **130** may have at least 14 theoretical stages. In an alternative embodiment, the light-ends column **130** may have at least 18 theoretical stages. In embodiments, one actual stage may equal approximately 0.6 theoretical stages. Actual stages can be trays or packing. The reaction mixture may be fed via stream **126** to the light-ends column **130** at the bottom or the first stage of the column **130**.

[0078] Overhead stream **132** may include acetaldehyde, water, carbon monoxide, carbon dioxide, methyl iodide, methyl acetate, methanol and acetic acid, one or more promoters and if present, catalyst stabilizer, and mixtures thereof. Bottoms stream **131** may have acetic acid, methyl iodide, methyl acetate, HI, water, and mixtures thereof. Stream **136** may have acetic acid, HI, water, heavy impurities, and mixtures thereof. Streams **132**, **131**, and **136**, as well as other streams discussed herein, may also comprise catalyst stabilizers and/or promoters at varying concentrations, depending on where the catalyst stabilizers and/or promoters are added to the system.

[0079] In an embodiment, the light-ends column **130** may be operated at an overhead pressure within the range of 20 psia (138 kPa-a) to 40 psia (276 kPa-a), alternatively, the overhead pressure may be within the range of 30 psia (207 kPa-a) to 35 psia (241 kPa-a). In an embodiment, the overhead temperature may be within the range of 95°C to 135°C, alternatively, the overhead temperature may be within the range of 110°C to 135°C, alternatively, the overhead temperature may be within the range of 125°C to 135°C. In an embodiment, the light-ends column **130** may be operated at a bottom pressure within the range of 25 psia (172 kPa-a) to 45 psia (310 kPa-a), alternatively, the bottom pressure may be within the range of 30 psia (207 kPa-a) to 40 psia (276 kPa-a).

[0080] In an embodiment, the bottom temperature of the light-ends column **130** may be within the range of 115°C to 155°C, alternatively, the bottom temperature is within the range of 125°C to 135°C. In an embodiment, crude acetic acid in stream **136** may be emitted from the light-ends column **130** as a liquid side-draw. Stream **136** may be operated at a pressure within the range of 25 psia (172 kPa-a) to 45 psia (310 kPa-a), alternatively, the pressure may be within the range of 30 psia (207 kPa-a) to 40 psia (276 kPa-a). In an embodiment, the temperature of stream **136** may be within the range of 110°C to 140°C, alternatively, the temperature may be within the range of

125°C to 135°C. Stream **136** may be taken between the fifth to the eighth actual stage of the light-ends column **130**.

[0081] The overhead vapor in stream **132** from the light-ends column **130** may be condensed and separated in a decanter **134** to form a light, aqueous phase and a heavy, organic phase. The heavy, organic phase may be recycled to the reactor **110** in stream **138** via stream **112**, for example. The stream **138** may comprise acetic acid, methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, water, HI, heavy impurities, the one or more promoters, a catalyst stabilizer (optionally), and mixtures thereof.

[0082] The light, aqueous phase may be recycled to the light-ends column **130** in stream **135** or may be recycled to the reactor **110** in stream **139** via stream **112**, for example. The stream **135** may comprise acetic acid, methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, water, HI, heavy impurities, the one or more promoters, a catalyst stabilizer (optionally), and mixtures thereof. The heavy, organic phase in stream **138** may comprise methyl iodide, and methyl acetate, and mixtures thereof. The light, aqueous phase in streams **136** and **139** may comprise water (greater than 50%), acetic acid, comprise methanol, methyl acetate, methyl iodide, carbon monoxide, carbon dioxide, heavy impurities, the one or more promoters, a catalyst stabilizer (optionally), and mixtures thereof. Make-up water may be introduced into the decanter **134** via stream **133**. Streams **139** and **138** may be considered to be in the light-ends area **104** and the recycle area **108**.

[0083] In one or more embodiments, the crude acetic acid in stream **136** may be optionally subjected to further purification, such as, but not limited to, drying-distillation, such as in drying column **140** to remove water and heavy-ends distillation in stream **141**. Stream **141** may be communicated to heavy-ends column **150** where heavy impurities such as propionic acid may be removed in stream **151** and final acetic acid product may be recovered in stream **156**.

[0084] In an embodiment, the promoter may be continually introduced into the system **100** via stream **160**, and may be added in any form such as a solid, liquid, or solution, such as in an acetic acid solution. In **FIG. 1**, stream **160** mixes with the flash vessel **120** vapors to continually introduce the promoter to the components of the flash vessel **120** vapor stream **126**. In an alternative embodiment (not illustrated), stream **160** may continually introduce the promoter into any equipment or streams in the reaction area **102**, light-ends area **104**, recycle area **108**, or combinations thereof. For example, stream **160** may continually introduce the promoter into the flash vessel **120**, light-ends column **130**, reactor **110**, streams **111**, **112**, **114**, **121**, **126**, **131**, **132**, **133**, **135**, **136**, **138**, **139**, or combinations thereof. Therefore, although stream **160** is shown in **FIG. 1** as mixing with the vapor stream emitted from the flash vessel **120**, it is contemplated that

alternative embodiments may include stream **160** as mixing with any equipment or stream in the reaction area **102**, light-ends area **104**, recycle area **108**, or combinations thereof.

[0085] In some embodiments, the one or more promoters disclosed herein may be continually introduced in stream **160** as a solution comprising the promoter and a solvent. In an embodiment, the promoter solution may comprise an acetic acid solution. The nature of the solvent or diluent generally may not be critical so long as the solvent or diluent does not interfere with the carbonylation reaction or the purification of the acetic acid in the purification area **106**.

[0086] Those skilled in the art of homogeneous processes having the benefit of this disclosure, and in particular those processes that require a flashing step to disengage involatile catalysts and promoter(s), will appreciate that attrition rates of catalysts and promoter(s) solely related to entrainment will be a function of several variables. Among these variables are reactor size, feed rate, flasher size, and flashing rate. They will also appreciate that a make-up solution of the one or more promoters disclosed herein in acetic acid could be as concentrated as the solubility limit of the promoters disclosed herein in acidic acid allows, which is about 50 wt% or as dilute as a few ppm.

[0087] A primary consideration is that the flow rate and concentration of the stream comprising the one or more promoters disclosed herein are matched such that there is a steady state concentration of one or more promoters in the reactor. This can normally vary from its high and low point between batch additions of up to 1.5 wt%, and in embodiments is controlled within a target range of ± 0.5 wt% or in another embodiment ± 0.2 wt%. Thus, for example in a process with an attrition rate of 1 wt% per month from the reactor, a monthly batch addition could be replaced by a continually metered stream corresponding to an average daily addition of the promoters disclosed herein of about 0.03 wt%.

[0088] In an embodiment, no solvent or diluent may be used. When a solvent or diluent is used in an embodiment, the solvent or diluent is one or more of the liquid constituents of the reaction mixture in reactor **110**, e.g., acetic acid, methanol, methyl iodide, water, or combinations thereof. In an embodiment, the solvent or diluent may be acetic acid, methanol, or both. Similarly, the amount of solvent or diluents used in this context is not critical and may be adjusted broadly depending on process economy. The use of a solvent or diluent may be advantageous to ensure fast and even distribution and contact of the promoter with HI.

[0089] In an embodiment, when the one or more promoters is introduced to the system **100** separately and independently from the reaction mixture and from any recycle stream it may be advantageous to employ a solvent or diluent. Such a "recycle stream" may be a product or composition which is recovered from a processing step downstream of the flash vessel and which is recycled to the reactor, flash vessel, or light-ends column. In an alternative embodiment, when

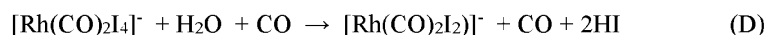
the one or more promoters is brought into contact with the reaction mixture in the flash vessel **120**, for example, by adding it to stream **131** prior to introducing the stream **131** to the flash vessel **120**, the promoters may be introduced in substance, i.e., in undiluted form, as the liquid constituents of the stream **131** act as solvents or diluents.

[0090] In any embodiment there is a greater than 5, or 10, or 16-fold rate increase in acetic acid production in the presence of (or, when combining) the one or more promoters disclosed herein. While not wishing to be bound by theory it is believed that there is some synergistic interaction associated with the amino groups in the promoters. These groups likely quaternize with MeI to form the corresponding ammonium iodides leading to an electronic environment likely significantly different to the parent molecule that promotes oxidative addition with the carbonylation catalyst.

[0091] Further, while not wishing to be bound by theory, it is believed that as the amount of water in the reaction mixture is advantageously lowered HI will increasingly exist in the covalent H-I form rather than the dissociated $\text{H}^+ \text{--} \text{I}^-$ or $\text{H}_3\text{O}^+ \text{--} \text{I}^-$ form, and that the promoters drive that equilibrium towards the dissociated form. Primarily only the covalent form is capable of oxidative addition in which the following initial reaction occurs (C):



The second part of the cycle involves interaction of the formed Rh III species with H_2O and CO (D):



At low water concentration with HI predominantly in the covalent form, the rate limiting step is likely to be the second step shown above, whereas at high water concentration the first step is likely to be rate limiting. Thus, it is believed that the one or more promoters suppresses the oxidative addition of HI to the carbonylation catalyst.

[0092] In an embodiment, continually introducing one or more promoters may comprise continually or alternately metering the promoter(s) in solution (e.g., an acetic acid solution) using a gas or liquid metering technology known in the art such as turbine meters, Coriolis meters, ultrasonic meters, positive displacement meters, or combinations thereof. Continuously or alternately metering may comprise uniformly injecting a known concentration of promoter in solution (e.g., an acetic acid solution), or adjusting up and down the injection rate to suit a desirable need.

[0093] In an embodiment, the reaction mixture in reactor **110** does not comprise promoter other than the promoter continually introduced into the system **100** and which has been recycled to the reactor **110**.

[0094] In an embodiment, the amount of promoter which is brought into contact with the HI, carbonylation catalyst, and/or water is generally not critical so long as the promoter is provided in an effective amount. An effective amount in this context is the amount of promoter which is capable of increasing the rate of producing acetic acid in the system **100**. The amount of promoter that is added is preferably governed by the attrition rate of the promoter from the reactor rather than the HI concentration.

[0095] Generally, it is not detrimental to the subsequent separation and purification of the final acetic acid product if the molar amount of the one or more promoters exceeds the molar amount needed to promote the acetic acid reaction, so long as the boiling point of the promoter is sufficiently higher than the boiling point of the vapor stream **126** which emits from the flash vessel **120** and/or the stream **136** which emits from the light-ends column **130**. For example, the boiling point of the promoter is sufficiently higher when the boiling point is at least 15°C., alternatively, at least 30°C., or alternatively, at least 50°C. above the boiling point of the crude acetic acid in stream **136**.

[0096] In any embodiment the one or more promoters may be maintained in the flash vessel **120** in an amount from about 0.1 to about 1.5 mol per mol HI. In some embodiments, the amount of promoter is from about 0.1 to about 1.3 mol, or from about 0.1 to about 1.1 mol, per mol HI. In some embodiments, the amount of promoter is from about 0.5 to about 3 mol, or from about 0.5 to about 2 mol, or from about 0.5 to about 1.5 mol, per mol HI.

[0097] In further embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a concentration of no more than about 20 wt% of the promoter in the liquid stream **121**. In other embodiments, the promoter may be maintained to establish a concentration of no more than about 15 wt%, or no more than about 12 wt%, or no more than about 10 wt%, of the promoter in the liquid stream **121**. In other embodiments, the promoter may be maintained in an amount sufficient to establish a concentration of at least about 0.5 wt% of the promoter in the liquid stream **121**. In some embodiments, the promoter may be maintained in an amount sufficient to establish a concentration of at least about 1 wt%, or at least about 2.5 wt%, or at least about 4 wt%, of the promoter in the liquid stream **121**. In particular embodiments, the promoter may be maintained in an amount sufficient to establish a concentration of from about 0.5 wt% to about 20 wt% of the promoter in the liquid stream **121**.

[0098] In yet other embodiments, the promoter may be maintained in an amount sufficient to establish a concentration of from about 1 wt% to about 20 wt%, or from about 2.5 wt% to about 20 wt%, or from about 4 wt% to about 20 wt%, of the promoter in the liquid stream **121**. In some embodiments, the promoter may be maintained in an amount sufficient to establish a concentration of from about 0.5 wt% to about 15 wt%, or from about 1 wt% to about 15 wt%, or from about 2.5

wt% to about 15 wt%, or from about 4 wt% to about 15 wt%, of the promoter in the liquid stream **121**. In some embodiments, the one or more promoters may be maintained in an amount sufficient to establish a concentration of from about 0.5 wt% to about 12 wt%, or from about 1 wt% to about 12 wt%, or from about 2.5 wt% to about 12 wt%, or from about 4 wt% to about 12 wt%, of the promoter in the liquid stream **121**.

[0099] The liquid stream **121** may be recycled to the reactor **110**. The recycled liquid stream **121** may introduce the one or more promoters into the reactor **110**, and consequently into the reaction mixture in reactor **110**.

[0100] In some embodiments, the amount of the one or more promoters which is maintained in the flash vessel **120** may be adjusted to establish a steady state concentration of no more than about 20 wt% of the promoter in the reaction mixture. In alternative embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of no more than about 17 wt%, or no more than about 15 wt%, or no more than about 12 wt%, of the promoter in the reaction mixture. In other embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of at least about 2 wt% of the promoter in the reaction mixture. In alternative embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of at least about 5 wt%, or at least about 7 wt%, of the promoter in the reaction mixture.

[0101] In particular embodiments, the one or more promoters may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration from about 2 wt% to about 20 wt% of the promoter in the reaction mixture. In alternative embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of from about 5 wt% to about 20 wt%, or from about 7 wt% to about 20 wt%, of the promoter in the reaction mixture. In alternative embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of from about 2 wt% to about 17 wt%, or from about 5 wt% to about 17 wt%, or from about 7 wt% to about 17 wt%, of the promoter in the reaction mixture.

[0102] In some embodiments, the one or more promoters may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of from about 2 wt% to about 15 wt%, or from about 5 wt% to about 15 wt%, or from about 7 wt% to about 15 wt%, of the promoter in the reaction mixture. In some embodiments, the promoter may be maintained in the flash vessel **120** in an amount sufficient to establish a steady state concentration of from about 2 wt% to about 12 wt%, or from about 5 wt% to about 12 wt%, or from about 7 wt% to about 12 wt%, of the promoter in the reaction mixture.

[0103] Residual HI which may reach the light-ends column **130** may be easily separated from as a bottom product stream **131** of the light-ends area **104**. Also, due to the removal of HI from the product stream in the earliest stage of the acetic acid work-up, side reactions which are caused by HI, i.e., the formation of undesirable long chain alkyl iodide contaminants in the product stream downstream from the flash vessel, are significantly reduced. Additionally, the reduced amounts of HI in the product streams downstream from the flash vessel **120** alleviate corrosion and engineering problems.

[0104] The beneficial effect of the one or more promoters is not restricted to the point of introduction into the system **100**. Rather, as the one or more promoters circulates in the system **100** by recycling the liquid stream **121** from the flash vessel **120** to the reactor **110**, its presence in the reaction mixture aids promoting the rate limiting step in the acetic acid process and/or suppressing the reaction of HI with the carbonylation catalyst. Therefore, upon continuous operation of the process, the amount of promoter which is brought into contact with the reaction mixture in the flash vessel **120** normally may be decreased as steady state conditions are achieved. Under steady state conditions, the amount of promoter which is brought into contact with the reaction mixture in the flash vessel **120** normally can be reduced to amounts necessary to maintain the desired steady state concentration of the promoter.

[0105] Having described the various aspects of the inventive process, stated here in numbered paragraphs (P) is:

P1. A process for producing acetic acid comprising: a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising: i) a carbonylation catalyst selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; ii) water in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and iii) one or more promoters selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and iv) iodide; and b) recovering acetic acid.

P2. The process of numbered paragraph 1, wherein the aminopolycarboxylate salts comprise 2, or 3 or more carboxylate groups.

P3. The process of numbered paragraphs 1 or 2, wherein the aminopolycarboxylate salts comprise 2, or 3 to 5, or 8, or 10 carboxylate groups.

P4. The process of any one of numbered paragraphs 1 to 3, wherein the aminopolycarboxylate salts comprise at least one amine group and at least 3 carboxylate groups.

P5. The process of any one of numbered paragraphs 1 to 4, wherein the aminopolycarboxylate salts comprise at least 2 amine groups and at least 2 carboxylate groups.

P6. The process of any one of numbered paragraphs 1 to 5, wherein the iodide is in the form

of HI, CH₃I, or both.

P7. The process of any one of numbered paragraphs 1 to 6, wherein the one or more promoters is continually added to the reaction mixture as an acetic acid solution.

P8. The process of any one of numbered paragraphs 1 to 6, wherein the process takes place in an acetic acid system comprising a reaction area, a light-ends area, a purification area, and a recycle area, wherein the reaction area comprises a reactor and a flash vessel.

P9. The process of numbered paragraph 8, wherein the one or more promoters are added to the flash vessel.

P10. The process of numbered paragraph 1, wherein the combining takes place in the reactor at a temperature within the range of about 120°C to about 250°C and a pressure within the range of about 200 psia (1.38 MPa-a) to 2,000 psia (13.8 MPa-a).

P11. The process of any one of numbered paragraphs 1 to 10, wherein the one or more promoters are maintained at an iodide to promoter molar ratio of 2:1 to 40:1.

P12. The process of any one of numbered paragraphs 1 to 11, wherein the one or more promoters are maintained at a promoter to carbonylation catalyst molar ratio of 0.005:1 to 4:1.

P13. The process of numbered paragraph 12, wherein as the molar ratio of the one or more promoters is increased the wt% of water can be decreased.

P14. The process of any one of numbered paragraphs 1 to 13, wherein salts of glutamate and dicarboxymethyl alaninate are absent.

P15. A method for reducing water in an acetic acid production process comprising: a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising iodide under carbonylation conditions sufficient to form acetic acid at a first rate, wherein the reaction mixture comprises: i) a carbonylation catalyst, selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; and ii) a first amount of water, where the water is present in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and b) combining one or more promoters to the reaction mixture at an iodide to promoter molar ratio of greater than 2, wherein the one or more promoters are selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and c) reducing the wt% of water in the reaction mixture to a second amount of water while maintaining a second rate of acetic acid production that is the same as or greater than the first rate of acetic acid production.

P16. The process of numbered paragraph 15, wherein the aminopolycarboxylate salts comprise 2, or 3 or more carboxylate groups.

P17. The process of numbered paragraphs 15 or 16, wherein the aminopolycarboxylate salts comprise 2, or 3 to 5, or 8, or 10 carboxylate groups.

P18. The process of any one of numbered paragraphs 15 to 17, wherein the aminopolycarboxylate salts comprise at least one amine group and at least 3 carboxylate groups.

P19. The process of any one of numbered paragraphs 15 to 18, wherein the aminopolycarboxylate salts comprise at least 2 amine groups and at least 2 carboxylate groups.

P20. The process of any one of numbered paragraphs 15 to 19, wherein the iodide is in the form of HI, CH₃I, or both.

P21. The process of any one of numbered paragraphs 15 to 20, wherein the one or more promoters is continually added to the reaction mixture as an acetic acid solution.

P22. The process of any one of numbered paragraphs 15 to 21, wherein the process takes place in an acetic acid system comprising a reaction area, a light-ends area, a purification area, and a recycle area, wherein the reaction area comprises a reactor and a flash vessel.

P23. The process of numbered paragraph 22, wherein the one or more promoters are added to the flash vessel.

P24. The process of numbered paragraph 12, wherein the combining takes place in the reactor at a temperature within the range of about 120°C to about 250°C and a pressure within the range of about 200 psia (1.38 MPa-a) to 2,000 psia (13.8 MPa-a).

P25. The process of any one of numbered paragraphs 15 to 24, wherein the one or more promoters are maintained at an iodide to promoter molar ratio of 2:1 to 40:1.

P26. The process of any one of numbered paragraphs 15 to 25, wherein the one or more promoters are maintained at a promoter to carbonylation catalyst molar ratio of 0.005:1 to 4.

P27. The process of any one of numbered paragraphs 15 to 26, salts of glutamate and dicarboxymethyl alaninate are absent.

EXAMPLES

[0106] The following investigations and examples are intended to be illustrative only, and are not intended to be, nor should they be construed as limiting the scope of the present invention in any way.

[0107] A 3,000 ppm stock solution of [Rh(CO)₂I₂Li (often referred to simply as “Rh I”) in glacial acetic acid (GAA) was prepared as follows: 0.12g of rhodium (I) dicarbonyl chloride dimer (CAS# 14523-22-9) was added to 20 mLs of previously N₂ purged glacial acetic acid in a 30 mL vial. The vial was septum sealed and lightly purged with N₂ at one atmosphere while being stirred at room temperature. After 10 minutes, the septum was removed, 0.21g of lithium iodide (LiI) was quickly added, the septum replaced and the mixture was stirred and purged for a further 10 minutes at which point full dissolution had occurred. The active Rh I catalyst has now formed and can be stored under an N₂ atmosphere indefinitely without decomposition. 100% formation of active catalyst was confirmed for each batch preparation by FTIR analysis of an aliquot. To start a kinetic

run, 1.5 mLs of this stock solution was syringed into a stirred, septum sealed, N₂ purged vial containing 1.5 mLs of other components (promoter, MeI or HI, H₂O, glacial acetic acid). The starting Rh concentration is therefore, 1500 ppm or 0.015M. Typical conditions for MeI oxidative runs are shown in Table 1. The high concentration of MeI used ensures pseudo first-order conditions in all experiments and it is to be understood that the use of the term “rate constant” in text, figures and tables refers to pseudo-first order rate constants. Comparative conditions for similar experiments reported in US 9,580,377 are also included in this Table 1.

Table 1. Conditions for Experiments

Conditions	US '377	Inventive examples
Rhodium, ppm	1200	1500
H ₂ O, M	1.3	1.3
MeI, M	1.6	2
Atmosphere	N ₂	N ₂
Temp, °C	22	22

[0108] Whenever possible, a constant H₂O concentration of about 1.3M (2 wt%) was maintained in kinetic experiments. For HI oxidative addition experiments, a concentration of 0.1M was chosen for most runs conducted. The 57% aqueous HI solution contributes 0.53M of H₂O to each kinetic experiment with the remainder, up to a total of 1.3M, being associated with H₂O content of concentrated promoter solutions. The various novel promoters that were investigated are listed in Table 2. DTPA-Na₅ was only available commercially as a 40 wt% (1M) aqueous solution. DTPA-Na₃Ca and NTA-Na₃ are available as solids. The various fully aqueous and GAA/H₂O solutions that were prepared are shown in the table. In all cases, density measurements were made such that molarities could be calculated. All materials were soluble in H₂O at > 40 wt% and in GAA/10wt% H₂O at >20 wt%.

Table 2. Characteristics and Concentrations of Exemplary Promoters

Promoter	MW, g/mole	Wt%	M	Density	Wt% H ₂ O	Wt% GAA
DTPA-Na ₃ Ca	497	22.9	0.53	1.194	7.5	69.6
DTPA-Na ₃ Ca	497	29.4	0.74	1.253	9.9	60.7
DTPA-Na ₃ Ca	497	44.4	1.15	1.284	55.6	0.0
DTPA-Na ₅	503	40.0	1.00	1.257	60.0	0.0
NTA-Na ₃	275	24.0	0.79	1.189	9.7	66.3
NTA-Na ₃	275	35.3	1.59	1.242	64.7	0.0
NTA-Na ₃	275	48.4	2.29	1.320	51.6	0.0

[0109] Because DTPA-Na₅ was only available as an aqueous solution, the highest molarity that could be used in kinetic runs while maintaining a 1.3M H₂O concentration, was 0.033M. For this reason, most kinetic studies were carried out with the analogous DTPA-Na₃Ca as in this case molarities up to about 0.15M could be used while not exceeding the target H₂O concentration.

[0110] FTIR spectroscopy was carried out as follows. An iS50 FTIR spectrometer equipped with a DTGS detector from Thermo Scientific was used for FTIR spectral acquisition. The sample compartment could optionally be fitted with a transmission cell accessory or with an attenuated total reflectance (ATR) accessory. The transmission cell, obtained from Harrick Scientific, was equipped with sapphire windows and was used with a pathlength of 0.1mm. The ATR cell was obtained from Pike Technologies and was equipped with a 3-bounce zinc selenide (ZnSe) crystal. For the FTIR measurements in this disclosure, measurements of rhodium carbonyl bands in the 1950-2100 cm^{-1} region were made and the two cells were largely interchangeable with regard to spectral acquisition time, quality of signal etc. The sample volume required for FTIR analysis was a function of cell being used. When the transmission cell was being used, a 1 mL syringe equipped with a needle was used to obtain about 0.3 mLs of sample from the septum sealed reaction vial (containing 3 mLs at outset). The sample was then loaded into the transmission cell, the cell was placed in the spectrometer sample compartment and a spectrum recorded. When the ATR cell was being used, the ATR accessory was fixed in the sample compartment and a much smaller sample volume (about 0.05 mLs obtained with a 100 μL microsyringe) was added to the ATR cell. For both cells, the sample was sealed to the atmosphere during spectral acquisition to avoid any trace air induced oxidation of the rhodium carbonyls.

Effect of H_2O Concentration on the Rate of MeI Oxidative Addition to Rh I

[0111] Glassware kinetic studies following the FTIR spectra of the Rh carbonylation catalyst were performed throughout these examples. While in most cases, H_2O concentration was maintained at 1.3M (about 2 wt%), certain instances with rate promoters led to a higher H_2O concentration up to a maximum of 3.9M (6 wt%). As such it was of interest to determine the effect of H_2O concentration (if any) on MeI oxidative addition with no other rate promoter present. Three runs were carried out in which H_2O was varied in 1.3M increments. Overlaid FTIR spectra for the three runs, each in a 0-240 minute time window, are shown in **FIG. 2**. Qualitatively it can be observed that there appears to be little difference in rate. This is confirmed by the first-order rate plots in **FIG. 3** and the rate constants (k) in Table 3. An increase of only 12% over this wide H_2O range is noted. This is consistent with measurements in US 9,580,377.

Table 3. First-order Rate Constants as a function of water concentration

Promoter	H_2O , M	$k \times 10^3 \cdot \text{min}^{-1}$
None	1.3	5.2
None	2.6	5.5
None	3.9	5.9

Effect of LiOAc, LiI & Cytop™ 503 on Rate of MeI Oxidative Addition to Rh I

[0112] A comparison of rate promotional effects of LiOAc with similar promotional effects of the exemplary novel promoters was performed, as well as with LiI and Cytop™ 503 (a liquid

phosphine-oxide based extractant obtained from Solvay S.A.) to confirm the trends observed by for LiOAc and LiI as disclosed in US 9,580,377 obtained in glassware under one atmosphere of N₂.

[0113] Kinetic data were obtained over a range of 0.17 to 0.93M for LiOAc, a range of 0.32 to 0.98M for LiI and a range of 0.25 to 0.75M for Cytop™ 503. The resulting pseudo first-order rate constants were first plotted as a function of promoter molarity with the zero point k (no promoter) of 4.0 min⁻¹ included. As the zero point tended to unduly weigh a linear fit, it was left out and the corresponding plots with linear fits are shown in **FIG. 4**. Good R² values were obtained and directional trends for LiOAc and LiI as disclosed in US 9,580,377, and for Cytop™ 503. It will be understood by those familiar with kinetic measurements that while directional and relative trends of rate constants are expected to remain consistent from lab to lab, absolute values may differ slightly due to quality of FTIR signal, lot of Rh I commercial precursor dimer used etc.

Effect of Potential New Promoters on Rate of MeI Oxidative Addition to Rh I

[0114] A novel class of potential rate promoters has its basis in the salts of amino acids. A limited selection of these compounds was investigated, and some relevant structures are shown in the detailed description above.

[0115] Several of the novel promoters led to exceedingly fast MeI oxidative addition rates. This is first shown visually in overlaid FTIR spectra in the next few figures. **FIG. 5** contains sets of spectra for 0.93M LiOAc over 0-180 minutes and for 0.16M DTPA-Na₃Ca over 0-60 minutes. Despite the almost 6-fold lower molarity of DTPA-Na₃Ca, MeI oxidative addition is essentially complete at 60 minutes compared to the 180 minute requirement for the solution containing LiOAc.

[0116] A similar comparison is shown in **FIG. 6**, this time for 0.5M LiOAc and 0.033M DTPA-Na₃ with spectra at 0 and 120 minutes being shown for each. Despite the 15-fold lower molarity of the DTPA-Na₃ solution, it can be visually observed that reaction has progressed to a greater extent than in the 0.5M LiOAc solution. The effect of variable concentration DTPA-Na₃Ca concentration on MeI oxidative addition rate is shown in **FIG. 7** in which sets of spectra associated with four different runs are overlaid. The full set of rate data obtained is shown in Tables 4 and 5.

Table 4. Common Promoter Rate Constants

Promoter	Molarity	H ₂ O, M	k x 10 ³ , min ⁻¹
None	NA	1.3	4.4
None	NA	1.3	4.0
None	NA	1.3	5.2
None	NA	2.6	5.5
None	NA	3.9	5.9
LiOAc	0.17	1.3	4.4

LiOAc	0.35	1.3	8.5
LiOAc	0.5	1.3	11.7
LiOAc	0.65	1.3	15.4
LiOAc	0.93	1.8	20.2
LiI	0.31	1.3	4.2
LiI	0.66	1.3	5.2
LiI	0.98	1.3	5.8
Cytop™ 503	0.25	1.3	3.7
Cytop™ 503	0.50	1.3	3.0
Cytop™ 503	0.75	1.3	2.5

Table 5. Exemplary Novel Promoter Rate Constants

Promoter	Molarity	H ₂ O, M	k x 10 ³ , min ⁻¹
DTPA-Na ₃ -Ca	0.03	1.3	8.4
DTPA-Na ₃ -Ca	0.06	1.3	18.5
DTPA-Na ₃ -Ca	0.12	1.3	38.0
DTPA-Na ₃ -Ca	0.14	1.3	47.0
DTPA-Na ₃ -Ca	0.16	1.5	51.8
DTPA-Na ₃ -Ca	0.20	1.8	61.3
DTPA-Na ₅	0.033	1.3	13.6
DTPA-Na ₅	0.066	2.6	25.2
DTPA-Na ₅	0.094	3.7	36.0
DTPA-Na ₅	0.102	4.0	38.5
NTA-Na ₃	0.069	1.3	12.2
NTA-Na ₃	0.08	1.3	15.7
NTA-Na ₃	0.088	2.6	15.7
NTA-Na ₃	0.099	1.6	17.2
NTA-Na ₃	0.16	2.6	22.8

[0117] The data in Tables 4 and 5 indicate that the target 1.3M H₂O (2 wt%) was largely maintained except for a few runs at high concentrations of new rate promoters. However, as described above and as shown in Table 4, there is only a minor effect of H₂O on rate. This is further demonstrated by NTA-Na₃ data in Table 5 in which essentially repeat runs were carried out with the exception that H₂O concentration was doubled in the second experiment. Within experimental error, similar rates were obtained. In any case, the data of Table 5 show very high rates with H₂O concentration at, or close to, 1.3M.

[0118] Selected corresponding plots associated with these tables are contained in **FIG. 8** and relative promotional effects are summarized in Table 6. The rate equations annotated in **FIG. 8** can be matched to the plot slopes in Table 6. The slopes of the plots are particularly informative. If one was to contend that the various new pentaacetate and triacetate salts should lead to a proportional rate increase over LiOAc associated with 5-fold or 3-fold higher acetate (carboxylate) molarity, then the pentaacetate plots should have a 5-fold steeper slope and the triacetate should have a 3-fold higher slope. Instead, an unexpected 16 to 18-fold and a 6-fold rate promotional increase were obtained for pentaacetate and triacetate salts respectively as shown in Table 6.

Table 6. Summary of Promotional Effects of Novel Promoters

Promoter	Slope	Acceleration Factor Relative to LiOAc	Number of carboxylate groups
DTPA-Na ₅	344	18	5
DTPA-Na ₃ Ca	306	16	5
NTA-Na ₃	119	6	3
LiOAc	19	1	1

Impact of H₂O Concentration on Rate of HI Oxidative Addition to Rh I

[0119] The effect of H₂O concentration on the rate of HI oxidative addition to Rh I and entry into the water gas shift (WGS) cycle is speculated to be an issue in the glacial acidic acid process. The theory is that as H₂O is lowered, HI will increasingly exist in the covalent H-I form rather than the dissociated H⁺--I⁻ or H₃O⁺--I⁻ form. It is believed, as discussed above, that the covalent form of HI is capable of the undesirable oxidative addition reaction with the carbonylation catalyst, thus suppressing the desirable MeI oxidative addition reaction. At low H₂O concentration with HI predominantly in the covalent form, the rate limiting step is likely to be the second step shown above, whereas at high H₂O concentration, the first step is likely to be rate limiting.

[0120] In order to verify and quantify this effect, a series of kinetic runs were carried out at room temperature in which starting HI concentration was 0.25M and H₂O concentration was varied from 1.3 to 3.9M (2 to 6 wt%). With the initial Rh I concentration at 0.015M, a 16-fold molar excess of HI was presumed sufficient to allow pseudo first-order conditions for easy rate constant determination. As 0.25M HI contains 1.3M H₂O, this was the highest HI concentration that could be used. While results were directionally as expected, the magnitude of the changes were surprising. Overlaid FTIR spectra for a 0-60 minute time window for four different H₂O concentrations are shown in **FIG. 9**. The overlaid spectra indicate a decreased rate of reaction over the 1.3 to 2.6M H₂O range shown in the figure.

[0121] Associated rate constant plots for several of these runs are shown in **FIG. 10**. While the reaction goes essentially to completion at 1.3M H₂O, almost no reaction takes place at 3.0M H₂O. A closer inspection of the data in **FIG. 10** was carried out in which rate plots for the three lowest H₂O runs are shown in **FIG. 11** and rate plots for higher H₂O runs are plotted in **FIG. 12**. The

three runs in **FIG. 11** obey pseudo first-order kinetics, though even over this narrow H₂O range of 1.3 to 2.1M (2 to 3.2 wt%), the R² can be observed to progressively decrease as pseudo first-order kinetics become more tenuous. In the higher H₂O runs shown in **FIG. 12**, it is apparent that kinetics are no longer pseudo first-order. The inference from these data is that a progressive decrease in % HI in the covalent form leads to a large decrease in rate and a switch from pseudo first-order to second or third-order kinetics.

[0122] With the rate constants for the low rate, high H₂O runs being estimated, all rate constants can be plotted as a function of H₂O concentration as shown in **FIG. 13**. Also included in this plot for comparison are the corresponding data for MeI oxidative addition to Rh I. An applied power fit tightly hugs all HI data points. From this plot, the effect of a change in H₂O concentration from 2 wt% to just 3 wt% can be observed and is in contrast to the minor dependence of MeI oxidative addition on H₂O concentration.

[0123] These data in **FIG. 13** would tend to confirm and quantify the working theory with regard to the undesirable WGS. The low H₂O conditions may represent an undesirable scenario where the HI oxidative addition step accelerates while the formed Rh III stalls out due to insufficient H₂O to drive the WGS to completion. Thus decreased shift is obtained at the expense of higher steady state Rh III, decreased catalyst stability and, without Rh addition, decreased carbonylation rate. These data indicate the criticality of tying up or ionizing covalent HI at low H₂O concentration in order to prevent its entry into the WGS cycle.

Suppression of the Rate of HI Oxidative Addition to Rh I

[0124] The surprisingly large rate promotional effect of aminopolycarboxylates described herein is encouraging from the point of view of carbonylation to glacial acidic acid. However, a similar rate promotional effect of undesired HI oxidative addition to start WGS would mute or possibly negate the carbonylation rate advantage. A similar kinetic study to that described above was therefore carried out except in this case 0.1M HI was used instead of 2M MeI. In all cases, 1.3M H₂O was maintained.

[0125] In a first study, side-by-side runs were carried out with 0.1M HI in which one of the vials also contained 0.007M DTPA-Na₃Ca. Overlaid spectra for both runs over a 5-hour monitoring period are shown in **FIG. 14**. Even at a 14-fold molar deficiency of promoter to HI, the oxidative addition is largely shut down compared to the run with no rate promoter. These initial data prompted an in-depth investigation of HI kinetics at even lower promoter concentrations.

[0126] Spectroscopic data associated with three 0.1M HI kinetic runs are shown in **FIG. 15**. Each run was tracked for a period of 5 hours. The top set of overlaid spectra are for a 0.1M HI/0.0037M DTPA-Na₃Ca combination. The DTPA-Na₃Ca concentration is doubled for the run associated with the middle set of spectra and then doubled again for run associated with the bottom

set of spectra. In this way the molar equivalency of HI to DTPA-Na₃Ca was varied from a low of 6 to a high of 27. The suppression of HI addition to Rh I can be noted and in fact, at 0.016M DTPA-Na₃Ca, the highest molarity tested, there is essentially no HI reaction taking place.

[0127] Spectroscopic data for another set of three 0.1M HI runs were carried out with LiOAc was the promoter. The molar equivalency of HI relative to LiOAc was much reduced compared to those for DTPA-Na₃Ca with the three molar equivalencies being 1, 2 and 6. The quantitative data associated with the FTIR spectra obtained are trended in time profile format in **FIG. 16** and **FIG. 17**. A qualitative visual comparison of **FIG. 16** and **FIG. 17** indicates that reaction of HI with Rh I is suppressed at several fold lower concentration of added DTPA-Na₃Ca compared to LiOAc. In terms of a rate equation, it is likely that this is quite complex and no attempt was made to determine rate constants.

[0128] HI oxidative addition to Rh I was investigated in the presence of variable Cytop™ 503 concentration. Over the 3-hour monitoring period, only in the case of a four-fold molar excess of HI was significant Rh III formation observed. As an alternative to rate constants as a tool for comparison, % Rh I remaining unreacted at 250 minutes was used to compare extent of HI oxidative addition across all runs. The full data set is shown in Table 7.

Table 7. Relative oxidative addition of HI with or without the novel promoters

HI/Promoter, M	Promoter	H ₂ O, M	% Rh I @ 250 mins
N/A	None	1.3	41
1	LiOAc	1.3	91
2	LiOAc	1.3	73
6.3	LiOAc	1.3	56
N/A	None	1.3	41
6.3	DTPA-Na ₃ -Ca	1.3	93
6.7	DTPA-Na ₃ -Ca	1.3	92
13.3	DTPA-Na ₃ -Ca	1.3	88
14.5	DTPA-Na ₃ -Ca	1.3	85
25	DTPA-Na ₃ -Ca	1.3	67
27	DTPA-Na ₃ -Ca	1.3	58
N/A	None	1.3	41
1	Cytop™ 503	1.3	100
1.3	Cytop™ 503	1.3	98
2	Cytop™ 503	1.3	94
4	Cytop™ 503	1.3	79
N/A	None	1.3	41
1.3	NTA-Na ₃	1.3	96

2	NTA-Na ₃	1.3	95
3	NTA-Na ₃	1.3	94
6.3	NTA-Na ₃	1.3	81
14.3	NTA-Na ₃	1.3	70

[0129] Data from this table are plotted in **FIG. 18** in which reasonable linear fits are obtained for all four sets of data. While the comparative equations are likely only semi-quantitative, the data would suggest that Cytop™ 503 has a 2-fold superiority over LiOAc with regard to suppression of HI oxidative addition. A further 3 to 5-fold suppression is achieved with the two new promoters that were tested.

[0130] The slopes and corresponding relative rates of suppression of HI oxidative addition are shown in Table 8. As in Table 5 for corresponding rates of MeI oxidative addition promotion, the ability of these aminopolycarboxylates to advantageously impact a reaction rate is demonstrated. To summarize, the data as disclosed above demonstrate a dual effect of a new class of promoter compounds in promoting the first step of MeOH carbonylation and in suppressing the undesired first step of WGS. The magnitude of these effects are up to 20-fold and 11-fold respectively greater than those observed for LiOAc for experiments performed under the same conditions.

Table 8. Suppression of WGS with novel promoters

Promoter	Slope	Suppression Relative to LiOAc
DTPA-Na ₃ -Ca	1.6	10.9
NTA-Na ₃	2.1	8.4
Cytop™ 503	7	2.5
LiOAc	17.5	1

[0131] A summary table of novel oxidative addition rate promoter compounds is provided in Table 7 of the concurrently filed patent application titled “Polyphosphates and Polyphosphonates as Rate Promoters for the Glacial Acetic Acid Process”. While not wishing to be bound by theory, it is postulated that there are at least two properties of these new rate accelerators that lead to their ability to induce a novel and unexpected increase in MeI oxidative addition rate. The first of these is the high intramolecular concentration of salt groups (phosphonates or phosphates) which are not present in salts such as LiI and LiOAc. In these new promoters, salt group proximity coupled with their known chelating ability may play a role in their rate promotional effect. The second property of these promoters is associated with the presence, in most, of an amino backbone. In a GAA medium rich in iodide (MeI or HI), quaternization to the corresponding ammonium acetate, ammonium iodide or a mixture of both will almost certainly take place, even at room temperature.

[0132] The scope of the present application is not intended to be limited to the particular embodiments of the promoters, processes, means, methods, and/or steps described in the specification. The particular embodiments disclosed above are illustrative only, as the process and

system may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein.

[0133] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, in addition to recited ranges, any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0134] All patents, test procedures, and other documents cited in this application are fully incorporated herein by reference for all jurisdictions in which such incorporation is permitted. In the event of conflict between one or more of the incorporated patents or publications and the present disclosure, the present specification, including definitions, controls.

CLAIMS

What is claimed is:

1. A process for producing acetic acid comprising:
 - a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising:
 - i) a carbonylation catalyst selected from rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts;
 - ii) water in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and
 - iii) one or more promoters selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and
 - iv) iodide; and
 - b) recovering acetic acid.
2. The process of claim 1, wherein the aminopolycarboxylate salts comprise 2 or more carboxylate groups.
3. The process of claim 1, wherein the aminopolycarboxylate salts comprise 2 to 10 carboxylate groups.
4. The process of claim 1, wherein the aminopolycarboxylate salts comprise at least one amine group and at least 3 carboxylate groups.
5. The process of claim 1, wherein the aminopolycarboxylate salts comprise at least 2 amine groups and at least 2 carboxylate groups.
6. The process of claim 1, wherein the iodide is in the form of HI, CH₃I, or both.
7. The process of claim 1, wherein the one or more promoters is continually added to the reaction mixture as an acetic acid solution.
8. The process of claim 1, wherein the process takes place in an acetic acid system comprising a reaction area, a light-ends area, a purification area, and a recycle area, wherein the reaction area comprises a reactor and a flash vessel.
9. The process of claim 8, wherein the one or more promoters are added to the flash vessel.
10. The process of claim 1, wherein the combining takes place in the reactor at a temperature within the range of about 120°C to about 250°C and a pressure within the range of about 200 psia (1.38 MPa-a) to 2,000 psia (13.8 MPa-a).
11. The process of claim 1, wherein the one or more promoters are maintained at an iodide to promoter molar ratio of 2:1 to 40:1.
12. The process of claim 1, wherein the one or more promoters are maintained at a promoter to carbonylation catalyst molar ratio of 0.005:1 to 4:1.

13. The process of claim 11, wherein as the molar ratio of the one or more promoters is increased the wt% of water can be decreased.
14. The process of claim 1, wherein salts of salts of glutamate and dicarboxymethyl alaninate are absent.
15. A method for reducing water in an acetic acid production process comprising:
 - a) combining methanol, methyl acetate or any mixture of the two, and carbon monoxide in the presence of a reaction mixture comprising iodide under carbonylation conditions sufficient to form acetic acid at a first rate, wherein the reaction mixture comprises:
 - i) a carbonylation catalyst, selected from the group consisting of rhodium catalysts, iridium catalysts, palladium catalysts, and cobalt catalysts; and
 - ii) a first amount of water, where the water is present in the range of from 0.1 wt% to 10 wt%, based on the weight of the reaction mixture; and
 - b) combining one or more promoters to the reaction mixture at an iodide to promoter molar ratio of greater than 2, wherein the one or more promoters are selected from the group consisting of Group I and Group II aminopolycarboxylate salts and mixtures thereof; and
 - c) reducing the wt% of water in the reaction mixture to a second amount of water while maintaining a second rate of acetic acid production that is the same as or greater than the first rate of acetic acid production.
16. The process of claim 15, wherein the aminopolycarboxylate salts comprise 2 or more carboxylate groups.
17. The process of claim 15, wherein the aminopolycarboxylate salts comprise 2 to 10 carboxylate groups.
18. The process of claim 15, wherein the aminopolycarboxylate salts comprise at least one amine group and at least 3 carboxylate groups.
19. The process of claim 15, wherein the aminopolycarboxylate salts comprise at least 2 amine groups and at least 2 carboxylate groups.
20. The process of claim 15, wherein the iodide is in the form of HI, CH₃I, or both.
21. The process of claim 15, wherein the one or more promoters is continually added to the reaction mixture as an acetic acid solution.
22. The process of claim 15, wherein the process takes place in an acetic acid system comprising a reaction area, a light-ends area, a purification area, and a recycle area, wherein the reaction area comprises a reactor and a flash vessel.
23. The process of claim 22, wherein the one or more promoters are added to the flash

vessel.

24. The process of claim 12, wherein the combining takes place in the reactor at a temperature within the range of about 120°C to about 250°C and a pressure within the range of about 200 psia (1.38 MPa-a) to 2,000 psia (13.8 MPa-a).
25. The process of claim 15, wherein the one or more promoters are maintained at an iodide to promoter molar ratio of 2:1 to 40:1.
26. The process of claim 15, wherein the one or more promoters are maintained at a promoter to carbonylation catalyst molar ratio of 0.005:1 to 4:1.
27. The process of claim 15, salts of glutamate and dicarboxymethyl alaninate are absent.