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(54) **Title:** RUTHENIUM-BISMUTH MIXED OXIDE HYDROGENATION CATALYSTS AND PROCESSES FOR PRODUCING ETHANOL

(57) **Abstract:** A process is disclosed for producing ethanol, comprising contacting acetic acid and hydrogen in a reactor in the presence of a catalyst comprising a binder, a mixed oxide, and at least two promoter metals comprising ruthenium and bismuth. The mixed oxide preferably also comprises cobalt and tin.



**RUTHENIUM-BISMUTH MIXED OXIDE HYDROGENATION CATALYSTS AND  
PROCESSES FOR PRODUCING ETHANOL**

**FIELD OF THE INVENTION**

**[0001]** The present invention relates generally to processes for hydrogenating acetic acid to form ethanol and to novel catalysts comprising ruthenium and bismuth, and a mixed oxide for use in such processes.

**BACKGROUND OF THE INVENTION**

**[0002]** Ethanol for industrial use is conventionally produced from petrochemical feed stocks, such as oil, natural gas, or coal, from feed stock intermediates, such as syngas, or from starchy materials or cellulosic materials, such as corn or sugar cane. Conventional methods for producing ethanol from petrochemical feed stocks, as well as from cellulosic materials, include the acid-catalyzed hydration of ethylene, methanol homologation, direct alcohol synthesis, and Fischer-Tropsch synthesis. Instability in petrochemical feed stock prices contributes to fluctuations in the cost of conventionally produced ethanol, making the need for alternative sources of ethanol production all the greater when feed stock prices rise. Starchy materials, as well as cellulosic material, are converted to ethanol by fermentation. However, fermentation is typically used for consumer production of ethanol, which is suitable for fuels or human consumption. In addition, fermentation of starchy or cellulosic materials competes with food sources and places restraints on the amount of ethanol that can be produced.

**[0003]** As an alternative to fermentation, ethanol may be produced by hydrogenating acetic acid and esters thereof. Ethanol production via the reduction of acetic acid generally uses a hydrogenation catalyst. The reduction of various carboxylic acids over metal oxides has been proposed.

**[0004]** EP0175558 describes the vapor phase formation of carboxylic acid alcohols and/or esters such as ethanol and ethyl acetate from the corresponding mono and di-functional carboxylic acid, such as acetic acid, in the presence of a copper oxide-metal oxide supported catalyst, such as  $\text{CuO}/\text{ZnAl}_2\text{O}_4$ . A disadvantage with copper oxide catalysts in carboxylic acid hydrogenation reactions is the lack of long-term catalyst stability.

**[0005]** US Pat. No. 4,398,039 describes a process for the vapor phase hydrogenation of carboxylic acids to yield their corresponding alcohols in the presence of steam and a catalyst

comprising the mixed oxides of ruthenium, at least one of cobalt and nickel, and optionally one of cadmium, zinc, copper, iron, rhodium, palladium, osmium, iridium and platinum. The total loading of active metals is 5%. A process is further provided for the preparation of carboxylic acid esters from carboxylic acids in the absence of steam utilizing the above-identified catalysts.

**[0006]** US Pat. No. 4,517,391 describes preparing ethanol by hydrogenating acetic acid under superatmospheric pressure and at elevated temperatures by a process wherein a predominantly cobalt-containing catalyst is used and acetic acid and hydrogen are passed through the reactor, at from 210 to 330°C, and under 10 to 350 bar, under conditions such that a liquid phase is not formed during the process. The cobalt-containing catalyst contains, as active components, from 50 to 80% by weight of Co, from 10 to 30% by weight of Cu, from 0 to 10% by weight of Mn, from 0 to 5% by weight of Mo and from 0 to 5% by weight of phosphoric acid, the percentages being based on the metal content. However, the productivity as reported in the examples of US Pat. No. 4,517,391 is 89.8 grams of ethanol per kilogram of catalyst per hour, which is too low for commercial production.

**[0007]** US Pat. No. 4,918,248 describes producing an alcohol by catalytically reducing an organic carboxylic acid ester with hydrogen in the presence of a catalyst obtained by reducing a catalyst precursor comprising (A) copper oxide and (B) titanium oxide and/or titanium hydroxide at a weight ratio of (A) to (B) in the range between 15/85 and 65/35. The component (A) may alternatively be a composite metal oxide comprising copper oxide and up to 20 wt. % of zinc oxide.

**[0008]** CN103785418 discloses a catalyst containing at least cobalt and tin and its application in the preparation of alcohol by carboxylic acid hydrogenation. The disclosed catalyst contains 10 wt.% to 50 wt.% cobalt and 0.1 wt.% to 50 wt.% tin in the total weight of catalyst, in addition to other metals such as silver, zinc, and zirconium. CN103785418 prepares the hydrogenation through the co-precipitation, deposition-precipitation, steamed ammonia precipitation, sol-gel, and being dissolved as alloy, then combined with one type or multiple types of suction filtration and ball milling methods.

**[0009]** CN103785415 discloses a method to prepare alcohol by selective hydrogenation of carboxylic acid. The disclosed catalyst contains 10 wt.% to 50 wt.% cobalt and 0.1 wt.% to 50 wt.% bismuth in the total weight of catalyst.

[0010] CN103787827 discloses a method to prepare alcohol by selective hydrogenation of carboxylic acid. The disclosed hydrogenation catalyst contains at least cobalt and a trace amount of precious metal additives of platinum, palladium or rhenium.

[0011] Other hydrogenation catalysts that are not metal oxides have also been proposed. US Pat. No. 6,495,730 describes a process for hydrogenating carboxylic acid using a catalyst comprising activated carbon to support active metal species comprising ruthenium and tin. US Pat. No. 6,204,417 describes another process for preparing aliphatic alcohols by hydrogenating aliphatic carboxylic acids or anhydrides or esters thereof or lactones in the presence of a catalyst comprising platinum and rhenium. US Pat. No. 5,149,680 describes catalytic hydrogenation of carboxylic acids and their anhydrides to alcohols and/or esters in the presence of a catalyst containing a Group VIII metal, such as palladium, a metal capable of alloying with the Group VIII metal, and at least one of the metals rhenium, tungsten or molybdenum. US Pat. No. 4,777,303 describes the production of alcohols by the hydrogenation of carboxylic acids in the presence of a catalyst that comprises a first component which is either molybdenum or tungsten and a second component which is a noble metal of Group VIII on a high surface area graphitized carbon. US Pat. No. 4,804,791 describes another production process of alcohols by the hydrogenation of carboxylic acids in the presence of a catalyst comprising a noble metal of Group VIII and rhenium.

[0012] Thus, further improvements to hydrogenation catalysts that demonstrate high stability, conversion of acetic acid, and other oxygenates, with high selectivity to ethanol are needed.

#### SUMMARY OF THE INVENTION

[0013] In a first embodiment of the present invention, there is provided a process for producing ethanol, comprising contacting acetic acid in a reactor in the presence of a catalyst comprising a binder, a mixed oxide comprising cobalt and tin, and at least two promoter metals comprising ruthenium and bismuth. The total ruthenium loading may be from 0.05 to 3 wt.%, e.g., from 0.1 to 0.6 wt.%, and the total bismuth loading of the catalyst may be from 0.1 to 10 wt.%, e.g., 0.25 to 3 wt.%, based on the total weight of the catalyst. The molar ratio of ruthenium to bismuth may be from 5:1 to 0.2:1, e.g., from 1:1 to 0.4:1. In one embodiment, the total ruthenium loading is less than the total loading of bismuth. The catalyst may further comprise a promoter metal selected from the group consisting of rhenium, rhodium, palladium, osmium, iridium, platinum, and combinations thereof, wherein the total loading of the

additional promoter metal is from 0.01 to 1 wt.%, based on the total weight of the catalyst. In a preferred embodiment, the mixed oxide comprises cobalt (II)-stannate.

**[0014]** The combined metal amount of the mixed oxide may be from 40 to 90 wt.%, based on the total weight of the catalyst. The mixed oxide may be present in an amount from 40 to 90 wt.%, from 60 to 90 wt.%, e.g., from 70 to 85 wt.%, based on the total weight of the catalyst. The mixed oxide loading is determined prior to reducing any of the metals of the mixed oxide. The total tin loading of the catalyst is from 10 to 60 wt.%, e.g., from 40 to 55 wt.%, based on the metal content of the catalyst. The total cobalt loading of the catalyst may be from 10 to 60 wt.%, e.g., 25 to 45 wt.%, based on the metal content of the catalyst. The catalyst has a molar ratio of cobalt to tin from 2:1 to 0.75:1. In one embodiment, the mixed oxide further comprises nickel and the total nickel loading of the catalyst is from 2 to 40 wt.%, based on the metal content of the catalyst. In another embodiment, the catalyst is substantially free of metals selected from the group consisting of silver, zinc, zirconium, cadmium, copper, manganese, and molybdenum. The binder is selected from the group consisting of silica, aluminum oxide, and titania. The binder loading may be from 5 to 40 wt.%, e.g., 10 to 35 wt.%, based on the total weight of the catalyst.

**[0015]** The contacting of the catalyst comprising the mixed oxide with acetic acid may be performed in a vapor phase at a temperature of 200°C to 350°C, an absolute pressure of 101 kPa to 3000 kPa, and a hydrogen to acetic acid mole ratio of greater than 4:1. In one embodiment, the catalyst comprising the mixed oxide may be contacted with a feed stream comprising from 50 to 95 wt.% acetic acid and from 5 to 50 wt.% ethyl acetate.

**[0016]** In a second embodiment, there is provided a process for producing ethanol comprising contacting acetic acid in a reactor in the presence of a catalyst comprising a binder, ruthenium, bismuth, and a mixed oxide comprising tin. The total tin loading of the catalyst is from 10 to 60 wt.%, based on the total metal content of the catalyst, wherein the catalyst is substantially free of metals selected from the group consisting of silver, zinc, zirconium, cadmium, copper, manganese, and molybdenum. The mixed oxide may further comprise cobalt, nickel, or combinations thereof. In one embodiment, the total ruthenium loading is less than the total loading of bismuth. In a preferred embodiment, the mixed oxide comprises cobalt (II)-stannate. The mixed oxide may be present in an amount from 40 to 90 wt.%, e.g., from 60 to 90 wt.% or from 70 to 85 wt.%, based on the total weight of the catalyst.

**[0017]** In a third embodiment, there is provided a catalyst comprising a binder, a mixed oxide comprising cobalt and tin, and at least two promoter metals comprising ruthenium and bismuth. The total ruthenium loading may be from 0.05 to 3 wt.%, and the total bismuth loading of the catalyst may be from 0.1 to 10 wt.%, e.g., 0.25 to 3 wt.%, based on the total weight of the catalyst. The molar ratio of ruthenium to bismuth may be from 5:1 to 0.2:1, e.g., from 1:1 to 0.4:1. In one embodiment, the total ruthenium loading is less than the total loading of bismuth. The catalyst may further comprise a promoter metal selected from the group consisting of rhenium, rhodium, palladium, osmium, iridium, platinum, and combinations thereof, wherein the total loading of the additional promoter metal is from 0.01 to 1 wt.%, based on the total weight of the catalyst. In one embodiment, the catalyst is substantially free of metals selected from the group consisting of silver, zinc, zirconium, cadmium, copper, manganese, and molybdenum. The combined metal amount of the mixed oxide may be at least 40 wt.%, based on the total weight of the catalyst. The mixed oxide may be present in an amount from 40 to 90 wt.%, 60 to 90 wt.%, e.g., from 70 to 85 wt.%, based on the total weight of the catalyst.

**[0018]** In a fourth embodiment, there is provided a catalyst comprising a binder, ruthenium, bismuth, and a mixed oxide comprising tin. The total tin loading of the catalyst is from 10 to 60 wt.%, based on the total metal content of the catalyst, wherein the catalyst is substantially free of metals selected from the group consisting of silver, zinc, zirconium, cadmium, copper, manganese, and molybdenum. The mixed oxide may further comprise cobalt, nickel, or combinations thereof. The total ruthenium loading may be less than the total loading of bismuth. The total ruthenium loading is from 0.05 to 3 wt.%, based on the total weight of the catalyst. In a preferred embodiment, the mixed oxide comprises cobalt (II)-stannate. The mixed oxide may be present in an amount from 40 to 90 wt.%, e.g., from 60 to 90 wt.% or from 70 to 85 wt.%, based on the total weight of the catalyst.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0019]** FIG. 1 shows the acetic acid conversion for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}(1.0)$  (4 mm extrudate) over 4,700 hours of time-on-stream (TOS) at 280°C.

**[0020]** FIG. 2 shows the crude product selectivity for ethanol and ethyl acetate for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}(1.0)$  (4 mm extrudate) over 4,700 hrs of TOS at 280°C.

[0021] FIG. 3 shows the ethanol productivity (g/kg/hr) for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$  (1.0)(4 mm extrudate) over 4,700 hrs of TOS at 280°C.

[0022] FIG. 4 shows the ethanol to ethyl acetate weight ratio (wt/wt) for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (1.0) (4 mm extrudate) over 4,700 hrs of TOS at 280°C.

[0023] FIG. 5 shows the acetic acid conversion for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)(4 mm extrudate) and  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)Bi(1.0) (4 mm extrudate) over 140 hrs of TOS at 280°C.

[0024] FIG. 6 shows the crude product selectivity for ethanol and ethyl acetate for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5) (4 mm extrudate) and  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)Bi(1.0)(4 mm extrudate) over 140 hrs of TOS at 280°C.

[0025] FIG. 7A shows the conversion and selectivity for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5), and  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)Bi(1.0) (4 mm extrudates) at 280°C.

[0026] FIG. 7B shows the conversion and selectivity for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5), and  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)Bi(1.0) (4 mm extrudates) at 275°C.

[0027] FIG. 7C shows the conversion and selectivity for  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5), and  $[\text{Co}_{1.35}\text{SnO}_x]\text{Ru}$ (0.5)Bi(1.0) (4 mm extrudates) at 270°C.

#### DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention relates to processes for producing ethanol by hydrogenating acetic acid in the presence of a catalyst comprising a binder, at least two promoter metals comprising ruthenium and bismuth, and a mixed oxide comprising tin and/or cobalt. The promoter metal may enhance the catalytic activity and in addition advantageously improve ethyl acetate conversion so that the crude ethanol produce contains lower amounts of ethyl acetate. In addition, other impurity formation, e.g., diethyl ether, may be reduced by using a catalyst comprising a mixed oxide comprising a promoter metal, and tin and/or cobalt of the present invention. Low byproduct formation reduces the separation requirements to obtain ethanol.

[0029] A mixed oxide refers to an oxide having cations of more than one chemical element. For purposes of the present invention, mixed oxides include the reduced metals of the mixed oxide. In one embodiment, the mixed oxide may comprise one or more promoter metals, such as ruthenium and bismuth. In addition to the promoter metal, the mixed oxide may also comprise tin and/or cobalt, preferably both. In another embodiment of the present invention, the

catalyst may comprise a mixed oxide comprising at least two promoter metals comprising ruthenium and bismuth, cobalt, tin, and nickel. The catalyst may also comprise a binder, such as an inert material. Silica may be a preferred binder.

**[0030]** In one embodiment, the catalysts of the present invention have a high total loading of metals in the mixed oxide, which includes the promoter metals, such as ruthenium and bismuth, and tin and/or cobalt. The combined metal amount of the mixed oxide, which comprises the promoter metal and tin and/or cobalt, may be at least 40 wt.%, based on the total weight of the catalyst, e.g., at least 45 wt.% or at least 50 wt.%. In terms of ranges, the combined metal amount of the mixed oxide may be from 40 to 90 wt.%, based on the total weight of the catalyst, e.g., from 45 to 80 wt.% or from 50 to 70 wt.%. Unless otherwise stated, all ranges disclosed herein include both endpoints and all numbers between the endpoints.

**[0031]** The catalysts of the invention comprise at least ruthenium and bismuth as promoter metals. The total ruthenium loading may be from 0.05 to 3 wt.%, e.g., from 0.1 to 1 wt.%, and the total bismuth loading of the catalyst may be from 0.1 to 10 wt.%, e.g., 0.25 to 3 wt.%, based on the total weight of the catalyst. The molar ratio of ruthenium to bismuth may be from 5:1 to 0.2:1, e.g., from 1:1 to 0.4:1. Advantageously the presence of bismuth may help reduce the ruthenium loading without decreasing catalyst performance. This can lower the cost of the catalysts. In one embodiment, the total ruthenium loading is less than the total loading of bismuth. The catalysts of the invention may also comprise an additional promoter metal that is selected from the group consisting of rhenium, rhodium, palladium, osmium, iridium, platinum, and combinations thereof and the total loading of the additional promoter metal is from 0.01 to 1 wt.%, based on the total weight of the catalyst.

**[0032]** Without being bound by theory, a promoter metal of the catalyst preferably has a potential activity on acid hydrogenation and ethyl acetate hydrolysis.

**[0033]** In one embodiment, the mixed oxide is present in an amount from 40 to 90 wt.%, e.g., 60 to 90 wt.%, based on the total weight of the catalyst. This amount is determined prior to reducing any of the metals of the mixed oxide. Preferably, the mixed oxide may be present in an amount from 70 to 85 wt.%, based on the total weight of the catalyst. The mixed oxides comprise tin and the total tin loading of the catalyst may be from 10 to 60 wt.%, e.g., from 35 to 55 wt.%, based on the total metal content of the catalyst. In one embodiment, the mixed oxide further comprises cobalt, nickel or combinations thereof. The total cobalt loading of the

catalyst may be from 10 to 60 wt.%, e.g., from 25 to 45 wt.% or from 30 to 40 wt.%, based on the total metal content of the catalyst. Lower loadings of cobalt and tin of less than 10 wt.% are to be avoided since this may decrease the conversion of acetic acid and/or selectivity to ethanol.

**[0034]** In one embodiment, when cobalt and tin are both used, the mixed oxide of the present invention has been found to be effective with a molar ratio of cobalt to tin that is from 2:1 to 0.75:1, e.g., from 1.5:1 to 1:1 or from 1.4:1 to 1.1:1. A molar excess of cobalt may improve the selectivity to ethanol in the catalyst. In addition, it is preferred that there is a molar excess of tin to promoter metal.

**[0035]** Without being bound by theory, the promoter metals, tin and/or cobalt are predominately present on the catalyst as a mixed oxide. However, the catalyst may contain some discrete regions of oxides of the promoter metals, cobalt oxide and tin oxide. In addition, the metallic promoter metals, cobalt or tin, i.e. as reduced metals, may also be present on the catalyst.

**[0036]** In an alternative embodiment, the catalyst may comprise at least two promoter metals comprising ruthenium and bismuth, a binder, and a mixed oxide comprising cobalt and tin, wherein the promoter metals are in a reduced state and not part of the mixed oxide.

**[0037]** The mixed oxide, and thus catalyst, is preferable anhydrous.

**[0038]** The binder of the catalyst may be an inert material which is used to enhance the crush strength of the final catalyst. Suitable inert materials comprise silica, aluminum oxide, and titania. The binder may be present in an amount from 5 to 40 wt.%, e.g. from 10 to 35 wt.% or from 10 to 20 wt.%, based on the total weight of the catalyst. Thus, in one embodiment, the catalyst may comprise a silica binder and a mixed oxide comprising at least two promoter metals comprising ruthenium and bismuth, cobalt and tin.

**[0039]** In one embodiment, in addition to the promoter metal, the mixed oxide may further comprise nickel. The total nickel loading of the catalyst may be from 0.5 to 40 wt.%, e.g., 1 to 20 wt.%, based on the total metal content of the catalyst. Without being bound by theory, nickel may improve the activity of the catalysts to convert acetic acid. In addition, nickel may be useful for converting other oxygenates in the feed, such as ethyl acetate. The other oxygenates may also be formed in the reactor as by-products.

**[0040]** In some embodiments, the mixed oxide may comprise tertiary promoter metals. These tertiary promoter metals may be present in minor amounts from 0 to 5 wt.%. The tertiary

promoter metals may include titanium, vanadium, chromium, manganese, iron, copper, zinc, zirconium, molybdenum, tungsten, rhenium, or cadmium. In other embodiments, the mixed oxide may be substantially free of tertiary promoter metals, such as, silver, zinc, zirconium, cadmium, copper, manganese, or molybdenum. Substantially free means that the catalyst does not contain secondary promoter metals beyond trace amounts of less than 0.0001 wt.%. When the mixed oxide is substantially free of these secondary promoter metals, it is preferred that the binder, and thus catalyst are also substantially free of these secondary promoter metals.

**[0041]** The surface area of the catalyst comprising a mixed oxide comprising promoter metal, tin, and/or cobalt may be from 100 to 250 m<sup>2</sup>/g, e.g., from 150 to 180 m<sup>2</sup>/g. Pore volumes are between 0.18 and 0.35 mL/g, with average pore diameters from 6 to 8 nm. The morphology of the catalyst may be pellets, extrudates, spheres, spray dried microspheres, rings, pentarings, trilobes, quadrilobes, multi-lobal shapes, or flakes. The shape of the catalyst may be determined by hydrogen process conditions to provide a shape that can withstand pressure drops in the reactor.

**[0042]** The catalyst comprising a binder and a mixed oxide of the present invention has an on-stream stability for at least 200 hours at constant reaction conditions. Stability refers to a catalyst that has a change of less than 2% in conversion and less than 2% selectivity to ethanol, after initial break-in. In addition, stability refers to a catalyst that does not demonstrate any increase in by-product formation while on-stream. This greatly improves the industrial usefulness of a catalyst for continuous production. Also, this reduces the need to change the catalyst and reduces reactor down time for continuous processes.

**[0043]** The catalyst comprising a mixed oxide of the present invention may be made by the following method. Other suitable methods may also be used in conjunction with the present invention. In one embodiment, at least two solutions containing a metal precursor are prepared. Suitable metal precursors may include metal halides, metal halide hydrates, metal acetates, metal hydroxyls, metal oxalates, metal nitrates, metal alkoxides, metal sulfates, metal carboxylates and metal carbonates. A promoter metal precursor may be included in one of the solutions or prepared as a separate solution.

**[0044]** For purposes of the present invention, there is at least one precursor comprising a promoter metal, and at least one precursor comprising cobalt, and/or at least one precursor comprising tin. The precursors may be prepared in the same solution or in different solutions.

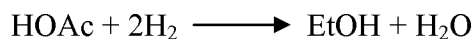
In one embodiment, a solution comprising the promoter metal precursor and cobalt precursor is prepared. Each solution may be an aqueous solution that comprises water. In some embodiments, when the mixed oxide comprises a molar excess of cobalt, at least one of the solutions may comprise an alkali hydroxide, such as sodium hydroxide. The solutions are combined and a binder, preferably in solid form, is added thereto while mixing. When a halide precursor is used, the mixture may be filtered and washed to remove halide anions. The mixed solution may be aged for a sufficient period of time at a temperature from 5°C to 60°C, e.g., from 15°C to 40°C. To obtain an anhydrous catalyst, the mixture may be dried at a temperature from 50°C to 150°C, e.g. from 75°C to 125°C, for 1 to 24 hours. Next, the material may be calcined in air at a temperature from 300°C to 700°C, e.g., from 400°C to 600°C, for 0.5 to 12 hours.

**[0045]** When additional metals, such as nickel or a secondary promoter metal disclosed herein, are included in the catalyst, a metal precursor thereto may be added to either the cobalt precursor solution or the tin precursor solution. In some embodiments, a separate solution may be prepared and combined once the cobalt precursor solution and tin precursor solution are combined.

**[0046]** In one embodiment, the present invention comprises a method of making a catalyst comprising a binder and a mixed oxide comprising at least two promoter metals comprising ruthenium and bismuth, cobalt and tin, the method comprising preparing a first solution comprising water, a cobalt precursor and a promoter metal precursor, wherein the cobalt precursor is selected from the group consisting of cobalt halides, cobalt halide hydrates, cobalt acetates, cobalt hydroxyls, cobalt oxalates, cobalt nitrates, cobalt alkoxides, cobalt sulfates, cobalt carboxylates and cobalt carbonates and the promoter metal precursor is selected from the group consisting of promoter metal halides, promoter metal halide hydrates, promoter metal acetates, promoter metal hydroxyls, promoter metal oxalates, promoter metal nitrates, promoter metal alkoxides, promoter metal sulfates, promoter metal carboxylates and promoter metal carbonates, and preparing a second solution comprising water, sodium hydroxide, and a tin precursor, wherein the tin precursor is selected from the group consisting of tin halides, tin halide hydrates, tin acetates, tin hydroxyls, tin oxide dispersion (such as ammonia, amine dispersed dispersion or hydrated dispersion), tin oxalates, tin nitrates, tin alkoxides, tin sulfates, tin carboxylates and tin carbonates. The second solution is added to the first solution and then

silica gel is added, in solid form, to the mixture with stirring. The mixture may be dried and calcined to form a catalyst comprising a binder and a mixed oxide comprising cobalt and tin of the present invention. Sodium hydroxide may be added to the second solution when there is a molar excess of cobalt.

[0047] The hydrogenation reaction of a carboxylic acid, acetic acid in this example, may be represented as follows:



[0048] It has surprisingly and unexpectedly been discovered that the catalysts of the present invention provide high conversion of acetic acid and high selectivities to ethanol, when employed in the hydrogenation of carboxylic acids such as acetic acid. In addition, due to the promoter metal, the catalysts of the present invention demonstrate a favorable conversion of ethyl acetate. Embodiments of the present invention beneficially may be used in industrial applications to produce ethanol on an economically feasible scale.

[0049] The feed stream to the hydrogenation process preferably comprises acetic acid. In some embodiments, pure acetic acid may be used as the feed. In other embodiments, the feed stream may contain some other oxygenates, such as ethyl acetate, acetaldehyde, or diethyl acetal, or higher acids, such as propanoic acid or butanoic acid. Minor amounts of ethanol may also be present in the feed stream. In one embodiment, the feed stream may comprise from 50 to 95 wt.% acetic acid, and from 5 to 50 wt.% oxygenates. More preferably, the feed stream may comprise from 60 to 95 wt.% acetic acid and from 5 to 40 wt.% ethyl acetate. The other oxygenates may originate from recycle streams that are fed to the hydrogenation reactor. In other embodiments, the feed stream may comprise from 0 to 15 wt.% water, e.g., from 0.1 to 10 wt.% water. An exemplary feed stream, e.g., a mixed feed stream, may comprise from 50 to 95 wt.% acetic acid, from 5 to 50 wt.% ethyl acetate, from 0.01 to 10 wt.% acetaldehyde, from 0.01 to 10 wt.% ethanol, and from 0.01 to 10 wt.% diethyl acetal.

[0050] The process of hydrogenating acetic acid to form ethanol according to one embodiment of the invention may be conducted in a variety of configurations using a fixed bed reactor or a fluidized bed reactor as one of skill in the art will readily appreciate. In many embodiments of the present invention, an “adiabatic” reactor can be used; that is, there is little or no need for internal plumbing through the reaction zone to add or remove heat.

Alternatively, a shell and tube reactor provided with a heat transfer medium can be used. In many cases, the reaction zone may be housed in a single vessel or in a series of vessels with heat exchangers therebetween. It is considered significant that acetic acid reduction processes using the catalysts of the present invention may be carried out in adiabatic reactors as this reactor configuration is typically far less capital intensive than tube and shell configurations.

**[0051]** Typically, the catalyst is employed in a fixed bed reactor, e.g., in the shape of an elongated pipe or tube where the reactants, typically in the vapor form, are passed over or through the catalyst. Other reactors, such as fluid or ebullient bed reactors, can be employed, if desired. In some instances, the hydrogenation catalysts may be used in conjunction with an inert material to regulate the pressure drop of the reactant stream through the catalyst bed and the contact time of the reactant compounds with the catalyst particles.

**[0052]** The hydrogenation reaction may be carried out in either the liquid phase or vapor phase. Preferably the reaction is carried out in the vapor phase under the following conditions. The reaction temperature may range from 200°C to 350°C, e.g., from 200°C to 325°C, from 225°C to 300°C, or from 250°C to 300°C. The pressure may range from 101 kPa to 3000 kPa (about 1 to 30 atmospheres), e.g., from 101 kPa to 2700 kPa, or from 101 kPa to 2300 kPa. The reactants may be fed to the reactor at a gas hourly space velocities (GHSV) of greater than 500 hr<sup>-1</sup>, e.g., greater than 1000 hr<sup>-1</sup>, greater than 2500 hr<sup>-1</sup> and even greater than 5000 hr<sup>-1</sup>. In terms of ranges the GHSV may range from 50 hr<sup>-1</sup> to 50,000 hr<sup>-1</sup>, e.g., from 500 hr<sup>-1</sup> to 30,000 hr<sup>-1</sup>, from 1000 hr<sup>-1</sup> to 10,000 hr<sup>-1</sup>, or from 1000 hr<sup>-1</sup> to 8000 hr<sup>-1</sup>.

**[0053]** In another aspect of the process of this invention, the hydrogenation is carried out at a pressure just sufficient to overcome the pressure drop across the catalytic bed at the GHSV selected, although there is no bar to the use of higher pressures, it being understood that considerable pressure drop through the reactor bed may be experienced at high space velocities, e.g., 5000 hr<sup>-1</sup> or 8000 hr<sup>-1</sup>.

**[0054]** Although the reaction consumes two moles of hydrogen per mole of acetic acid to produce one mole of ethanol, the actual molar ratio of hydrogen to acetic acid in the feed stream may vary from 100:1 to 1:100, e.g., from 50:1 to 1:50, from 20:1 to 1:2, or from 12:1 to 1:1. Most preferably, the molar ratio of hydrogen to acetic acid is greater than 4:1, e.g., greater than 5:1 or greater than 8:1.

[0055] Contact or residence time can also vary widely, depending upon such variables as amount of acetic acid, catalyst, reactor, temperature and pressure. Typical contact times range from a fraction of a second to more than several hours when a catalyst system other than a fixed bed is used, with preferred contact times, at least for vapor phase reactions, from 0.1 to 100 seconds, e.g., from 0.3 to 80 seconds or from 0.4 to 40 seconds.

[0056] The acetic acid may be vaporized at the reaction temperature, and then the vaporized acetic acid can be fed along with hydrogen in undiluted state or diluted with a relatively inert carrier gas, such as nitrogen, argon, helium, carbon dioxide and the like. For reactions run in the vapor phase, the temperature should be controlled in the system such that it does not fall below the dew point of acetic acid.

[0057] In particular, using catalysts and processes of the present invention may achieve favorable conversion of acetic acid and favorable selectivity and productivity to ethanol. For purposes of the present invention, the term conversion refers to the amount of acetic acid in the feed that is converted to a compound other than acetic acid. Conversion is expressed as a mole percentage based on acetic acid in the feed.

[0058] The conversion of acetic acid (AcOH) is calculated from gas chromatography (GC) data using the following equation:

$$AcOH\ Conv. (\%) = 100 * \frac{mmol\ AcOH\ (feed\ stream) - mmol\ AcOH\ (product)}{mmol\ AcOH\ (feed\ stream)}$$

[0059] For purposes of the present invention, the conversion may be at least 70%, e.g., at least 80% or at least 90%. Although catalysts that have high conversions are desirable, such as at least 90%, a lower conversion may be acceptable at high selectivity for ethanol. In addition to converting acetic acid, the catalysts of the present invention may also convert ethyl acetate at a rate sufficient to keep the ethyl acetate amounts low in the crude ethanol product. The conversion of ethyl acetate may be at least 0%, meaning there is no net production of ethyl acetate, or more preferably at least 5%.

[0060] To achieve a desirable catalyst performance, it is valuable to maintain the conversion for a long period of time under reaction conditions, i.e. when exposed to hydrogen and acetic acid. In one embodiment, the conversion of the catalyst is stable, i.e. does not vary by more

than 2%, for a period of at least 200 total hours on stream (TOS), e.g., at least 500 TOS or at least 750 TOS.

**[0061]** “Selectivity” is expressed as a mole percent based on converted acetic acid, and any ethyl acetate if present. It should be understood that each compound converted from acetic acid has an independent selectivity and that selectivity is independent from conversion. For example, if 50 mole % of the converted acetic acid and ethyl acetate is converted to ethanol, we refer to the ethanol selectivity as 50%. Selectivity to ethanol (EtOH) is calculated from GC data using the following equation:

$$EtOH\ Sel.(\%) = 100 * \frac{mmol\ EtOH\ (product)}{(mmol\ Converted\_AcOH) + 2 * (mmol\ Converted\_EtAc)}$$

**[0062]** This equation is used when ethyl acetate is present in the feed stream and there is conversion on ethyl acetate. If pure acid is used as feed, the equation can be simplified to the following equation:

$$EtOH\ Sel.(\%) = 100 * \frac{mmol\ EtOH\ (product)}{mmol\ AcOH\ (feed\ stream) - mmol\ AcOH\ (product)}$$

**[0063]** For purposes of the present invention, the selectivity to ethanol of the catalyst is at least 70%, e.g., at least 80% or at least 90%. During the startup or catalyst aging period, there may be a net make of ethyl acetate, but the selectivity to ethyl acetate may be less than 10%, e.g., less than 6%. The selectivity to acetaldehyde and/or diethyl acetate may vary depending on conversion and may be from 0 to 20%, e.g., from 0.1 to 10% or from 0.5 to 10%. At higher conversions of acetic acid, the selectivity to acetaldehyde and diethyl acetal may decrease as more of these compounds are converted to ethanol. In addition, the selectivity to diethyl ether should be low, less than 5%, e.g. less than 3% or less than 1%.

**[0064]** In one embodiment of the present invention, it is also desirable to have low selectivity to undesirable products, such as methane, ethane, and carbon dioxide. The selectivity to these undesirable products is less than 5%, e.g., less than 3% or less than 1.5%. Preferably, no detectable amounts of these undesirable products are formed during hydrogenation. In several embodiments of the present invention, formation of alkanes is low, usually under 2%, often under 1%, and in many cases under 0.5% of the acetic acid passed over the catalyst is converted to alkanes, which have little value other than as fuel.

**[0065]** Productivity refers to the grams of a specified product, e.g., ethanol, formed during the hydrogenation based on the kilogram of catalyst used per hour. In one embodiment of the present invention, a productivity of at least 200 grams of ethanol per kilogram catalyst per hour, e.g., at least 400 grams of ethanol or least 600 grams of ethanol, is preferred. In terms of ranges, the productivity preferably is from 200 to 4,000 grams of ethanol per kilogram catalyst per hour, e.g., from 400 to 3,500 or from 600 to 3,000.

**[0066]** In another embodiment, the invention is to a crude ethanol product formed by processes of the present invention. The crude ethanol product produced by the hydrogenation process of the present invention, before any subsequent processing, such as purification and separation, typically comprises ethanol, water, and unreacted acetic acid, as shown in Table 1. The amount of impurities and byproducts such as ethyl acetate, acetaldehyde, diethyl acetal and acetone may vary. The others may include alkanes, ethers, other acids and esters, other alcohols, etc. The alcohols may be n-propanol and iso-propanol. Exemplary crude ethanol compositional ranges, excluding hydrogen and other non-condensable gases, in various embodiments of the invention are provided below in Table 1.

**TABLE 1**  
**CRUDE ETHANOL PRODUCT COMPOSITIONS**

| Component      | Conc.<br>(wt.%) | Conc.<br>(wt.%) | Conc.<br>(wt.%) |
|----------------|-----------------|-----------------|-----------------|
| Ethanol        | 25 to 70        | 30 to 60        | 40 to 55        |
| Acetic Acid    | 0 to 30         | 5 to 25         | 10 to 20        |
| Ethyl Acetate  | 0 to 20         | 0.1 to 15       | 1 to 10         |
| Acetaldehyde   | 0 to 20         | 0.5 to 10       | 1 to 5          |
| Diethyl Acetal | 0 to 35         | 0.5 to 20       | 1 to 15         |
| Water          | 5 to 35         | 5 to 30         | 5 to 25         |
| Acetone        | 0 to 10         | 0 to 5          | 0 to 1          |
| Other          | 0 to 10         | 0 to 5          | 0 to 1          |

**[0067]** An ethanol product may be recovered from the crude ethanol product produced by the reactor using the catalyst of the present invention using several different techniques, such as distillation columns, adsorption units, membranes, or molecular sieves. For example, multiple columns may be used to remove impurities and concentration ethanol to an industrial grade ethanol or an anhydrous ethanol suitable for fuel applications. Exemplary separation and recovery processes are disclosed in U.S. Pat. Nos. 8,309,773; 8,304,586; and 8,304,587; and

U.S. Pub. Nos. 2012/0010438; 2012/0277490; and 2012/0277497, the entire contents and disclosure of which are hereby incorporated by reference.

**[0068]** In one embodiment, the process may comprise hydrogenating an acetic acid feed stream in a reactor in the presence of a catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt to form a crude ethanol product, separating at least a portion of the crude ethanol product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, separating at least a portion of the first distillate in a second column into a second distillate comprising ethyl acetate and a second residue comprising ethanol and water, wherein the second column is an extractive distillation column, feeding an extraction agent to the second column, and separating at least a portion of the second residue in a third column into a third distillate comprising ethanol and a third residue comprising water. Water from the third residue may be used as the extraction agent. Also, a fourth column may be used to separate acetaldehyde and acetone from the second distillate.

**[0069]** In another embodiment, the process may comprising hydrogenating acetic acid and/or an ester thereof in a reactor in the presence of a catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt to form a crude ethanol product, separating a portion of the crude ethanol product in a first distillation column to yield a first distillate comprising acetaldehyde and ethyl acetate, and a first residue comprising ethanol, acetic acid, ethyl acetate and water, separating a portion of the first residue in a second distillation column to yield a second residue comprising acetic acid and an vapor overhead comprising ethanol, ethyl acetate and water, removing water, using a membrane or pressure swing absorption, from at least a portion of the vapor overhead to yield an ethanol mixture stream having a lower water content than the at least a portion of the vapor overhead, and separating at least a portion of the ethanol mixture stream in a third distillation column to yield a third distillate comprising ethyl acetate and a third residue comprising ethanol and less than 8 wt.% water.

**[0070]** The raw materials used in connection with the process of this invention may be derived from any suitable source including natural gas, petroleum, coal, biomass and so forth. It is well known to produce acetic acid through methanol carbonylation, acetaldehyde oxidation, ethane oxidation, oxidative fermentation, and anaerobic fermentation. As petroleum and natural gas prices fluctuate becoming either more or less expensive, methods for producing

acetic acid and intermediates such as methanol and carbon monoxide from alternate carbon sources have drawn increasing interest. In particular, when petroleum is relatively expensive compared to natural gas, it may become advantageous to produce acetic acid from synthesis gas (“syngas”) that is derived from any available carbon source. U.S. Pat. No. 6,232,352 the disclosure of which is incorporated herein by reference, for example, teaches a method of retrofitting a methanol plant for the manufacture of acetic acid. By retrofitting a methanol plant, the large capital costs associated with CO generation for a new acetic acid plant are significantly reduced or largely eliminated. All or part of the syngas is diverted from the methanol synthesis loop and supplied to a separator unit to recover CO and hydrogen, which are then used to produce acetic acid. In addition to acetic acid, the process can also be used to make hydrogen which may be utilized in connection with this invention.

**[0071]** U.S. Pat. No. RE 35,377, also incorporated herein by reference, provides a method for the production of methanol by conversion of carbonaceous materials such as oil, coal, natural gas and biomass materials. The process includes hydrogasification of solid and/or liquid carbonaceous materials to obtain a process gas which is steam pyrolyzed with additional natural gas to form synthesis gas. The syngas is converted to methanol which may be carbonylated to acetic acid. The method likewise produces hydrogen which may be used in connection with this invention as noted above. *See also*, U.S. Pat. No. 5,821,111, which discloses a process for converting waste biomass through gasification into synthesis gas as well as U.S. Pat. No. 6,685,754, the disclosures of which are incorporated herein by reference.

**[0072]** Alternatively, acetic acid in vapor form may be taken directly as crude product from the flash vessel of a methanol carbonylation unit of the class described in U.S. Pat. No. 6,657,078, the entirety of which is incorporated herein by reference. The crude vapor product, for example, may be fed directly to the ethanol synthesis reaction zones of the present invention without the need for condensing the acetic acid and light ends or removing water, saving overall processing costs.

**[0073]** In one embodiment, the process may comprise a process for the formation of ethanol comprising, converting a carbon source into acetic acid, and contacting a feed stream containing the acetic acid and hydrogen with a catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt of the present invention. In another embodiment, the process may comprise a process for the formation of ethanol comprising

converting a carbon source, such as biomass, into a first stream comprising syngas, catalytically converting at least some of the syngas into a second stream comprising methanol, separating some of the syngas into hydrogen and carbon monoxide, catalytically converting at least some of the methanol with some of the carbon monoxide into a third stream comprising acetic acid; and reducing at least some of the acetic acid with some of the hydrogen in the presence of a catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt of the present invention into a fourth stream comprising ethanol.

**[0074]** Ethanol, obtained from hydrogenation processes of the present invention, may be used in its own right as a fuel or subsequently converted to ethylene which is an important commodity feedstock as it can be converted to polyethylene, vinyl acetate and/or ethyl acetate or any of a wide variety of other chemical products. Any known dehydration catalyst, such as zeolite catalysts or phosphotungstic acid catalysts, can be employed to dehydrate ethanol to ethylene, as described in copending U.S. Pub. Nos. 2010/0030002 and 2010/0030001 and WO2010146332, the entire contents and disclosures of which are hereby incorporated by reference.

**[0075]** Ethanol may also be used as a fuel, in pharmaceutical products, cleansers, sanitizers, hydrogenation transport or consumption. Ethanol may also be used as a source material for making ethyl acetate, aldehydes, and higher alcohols, especially butanol. In addition, any ester, such as ethyl acetate, formed during the process of making ethanol according to the present invention may be further reacted with an acid catalyst to form additional ethanol as well as acetic acid, which may be recycled to the hydrogenation process.

**[0076]** The catalysts of the present invention may be used with one or more other hydrogenation catalysts in a stacked bed reactor or in a multiple reactor configuration. A stacked bed reactor is particular useful when one catalyst is suitable for high selectivity to ethanol at low conversions. The catalyst comprising the mixed oxide of the present invention may be used in combination with another hydrogenation catalyst to increase the acetic acid conversion and thus improve the overall yield to ethanol. In other embodiment, the catalyst comprising the mixed oxide of the present invention may be used to convert unreacted acetic acid in a recycle stream.

**[0077]** In one embodiment, the catalyst comprising a binder and mixed oxide comprising a promoter metals comprising ruthenium and bismuth, and tin and/or cobalt of the present

invention may be used in the second reactor bed of a stacked bed configuration. The first reactor bed may comprise a different hydrogenation catalyst. Suitable hydrogenation catalysts are described in US Pat. Nos. 7,608,744; 7,863,489; 8,080,694; 8,309,772; 8,338,650; 8,350,886; 8,471,075; 8,501,652; 8,865,609; 8,975,200; and US Pub. No. 2013/0178663; the entire contents and disclosure of which are hereby incorporated by reference. In general, the different hydrogenation catalyst in the first bed may comprise a Group VIII metal and at least one promoter metal on a supported catalyst. Suitable Group VIII metals may include rhodium, rhenium, ruthenium, platinum, palladium, osmium, and iridium. Suitable promoter metals may include copper, iron, cobalt, vanadium, nickel, titanium, zinc, chromium, molybdenum, tungsten, tin, lanthanum, cerium, and manganese. Combinations of Pt/Sn, Pt/Co, Pd/Sn, Pt/Co, and Pd/Co may be preferred for the different catalyst. The metal loadings may be from 0.1 to 20 wt.%, e.g., from 0.5 to 10 wt.%, based on the total weight of the catalyst. The support may be any suitable support such as silica, alumina, titania, silica/alumina, pyrogenic silica, silica gel, high purity silica, zirconia, carbon (e.g., carbon black or activated carbon) zeolites and mixtures thereof. The supported catalyst may comprise a modified support that changes the acidity or basicity of the support. The support modified may be present in an amount from 0.5 to 30 wt.%, e.g., from 1 to 15 wt.%, based on the total weight of the catalyst. Acidic modifiers may include tungsten, molybdenum, vanadium, or oxides thereof. Suitable basic modifiers may include magnesium or calcium, such as calcium metasilicate.

**[0078]** The first bed may operate under similar hydrogenation conditions as the mixed oxide catalyst of the present invention. The reaction temperature of the first bed may range from 200°C to 350°C, e.g., from 250°C to 300°C. The pressure may range from 101 kPa to 3000 kPa, e.g., from 101 kPa to 2300 kPa. The reactants may be fed to the reactor at a gas hourly space velocities (GHSV) of greater than 500 hr<sup>-1</sup>, e.g., greater than 1000 hr<sup>-1</sup>. In one embodiment, fresh hydrogen may be fed to the first bed and the unreacted hydrogen from the first bed is passed along to the second bed with the reaction effluent. In other embodiments, each bed may receive a fresh hydrogen feed.

**[0079]** Exemplary catalysts for the first reactor bed may comprise one or more the following catalysts. One exemplary catalyst comprises 0.1 to 3 wt.% platinum and 0.5 to 10 wt.% tin on a silica support having from 5 to 20 wt.% calcium metasilicate. Another exemplary catalyst comprises 0.1 to 3 wt.% platinum and 0.5 to 10 wt.% tin on a silica support having from 5 to 20

wt.% calcium metasilicate and from 0.5 to 10 wt.% cobalt. Another exemplary catalyst comprises 0.1 to 3 wt.% platinum, 0.5 to 10 wt.% tin, and 0.5 to 10 wt.% cobalt on a silica support having from 5 to 20 wt.% tungsten. Another exemplary catalyst comprises 0.1 to 3 wt.% platinum and 0.5 to 10 wt.% tin on a silica support having from 5 to 20 wt.% tungsten, and 0.5 to 10 wt.% cobalt. Another exemplary catalyst comprises 0.1 to 3 wt.% platinum, 0.5 to 10 wt.% tin, and 0.5 to 10 wt.% cobalt on a silica support having from 5 to 20 wt.% tungsten, 0.5 to 10 wt.% tin, and 0.5 to 10 wt.% cobalt.

**[0080]** In one embodiment, the stack bed process may comprise introducing a feed stream of acetic acid and hydrogen into a stacked bed reactor that comprises a first bed and a second bed to produce a crude ethanol product, wherein the first bed comprises a first catalyst comprising platinum and tin on a first support and the second bed comprises a second catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt and tin of the present invention, recovering ethanol from the crude ethanol product in one or more columns. The acetic acid feed stream may comprise from 5 to 50 wt.% ethyl acetate and from 50 to 95 wt.% acetic acid.

**[0081]** Various other combinations of hydrogenation catalyst may be readily employed with the catalyst comprising the mixed oxide of the present invention. In addition, the order of the catalyst beds in the stack bed configuration may be arranged as needed to achieve ethanol production at high yields.

**[0082]** In addition, the catalyst comprising the mixed oxide of the present invention may be used in a first reactor with a copper containing catalyst in a second reactor that is suitable for converting ethyl acetate to ethanol. The second reactor may comprise a second catalyst that comprises copper or an oxide thereof. In one embodiment, the second catalyst may further comprise zinc, aluminum, chromium, cobalt, or oxides thereof. A copper-zinc or copper-chromium catalyst may be particularly preferred. Copper may be present in an amount from 35 to 70 wt.% and more preferably 40 to 65 wt.%. Zinc or chromium may be present in an amount from 15 to 40 wt.% and more preferably 20 to 30 wt.%.

**[0083]** The second bed that contains a copper catalyst may operate with a reaction temperature from 125°C to 350°C, e.g., from 180°C to 345°C, from 225°C to 310°C, or from 290°C to 305°C. The pressure may range from 700 to 8,500 kPa, e.g., from 1,500 to 7,000 kPa, or from 2,000 to 6,500 kPa. The reactants may be fed to the reactor at a gas hourly space

velocities (GHSV) of greater than  $500 \text{ hr}^{-1}$ , e.g., greater than  $1000 \text{ hr}^{-1}$ , greater than  $2500 \text{ hr}^{-1}$  and even greater than  $5000 \text{ hr}^{-1}$ .

**[0084]** In one embodiment, the stack bed process may comprise introducing a feed stream of acetic acid and hydrogen into a stacked bed reactor that comprises a first bed and a second bed to produce a crude ethanol product, wherein the first bed comprises a first catalyst comprising a binder and mixed oxide comprising a promoter metal, and tin and/or cobalt of the present invention and the second bed comprises a second catalyst comprising copper-containing catalyst of the present invention, recovering ethanol from the crude ethanol product in one or more columns. The acetic acid feed stream may comprise from 5 to 50 wt.% ethyl acetate and from 50 to 95 wt.% acetic acid.

**[0085]** The invention is described in detail below with reference to numerous embodiments for purposes of exemplification and illustration only. Modifications to particular embodiments within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to those of skill in the art.

**[0086]** The following examples describe the procedures used for the preparation of various catalysts employed in the process of this invention.

#### **Example 1**

**[0087]** To prepare the bulk CoSn catalyst, 4.60 g of  $\text{SiO}_2$  (silica gel) was added to 150 mL of deionized  $\text{H}_2\text{O}$  with stirring. An aqueous solution of cobalt(II) acetate tetrahydrate was prepared by adding 27.449 g (0.1102 mol) to the suspension. Separately, an aqueous solution of sodium stannate and sodium hydroxide was prepared by dissolving 21.765 g (0.0816 mol) of  $\text{Na}_2\text{SnO}_3 \cdot 3 \text{H}_2\text{O}$ , and 2.288 g (0.0572 mol) of NaOH in ~150 mL of deionized  $\text{H}_2\text{O}$ . The  $\text{Na}_2\text{SnO}_3/\text{NaOH}$  solution was then added to the cobalt acetate solution using a drop funnel over ~10 min with stirring (10-12 mL/min) at room temperature, and the final suspension was then aged with stirring for 2 hrs at room temperature. The material was then collected on a Buchner funnel (Watman #541 filter paper), and washed with 500 mL of deionized  $\text{H}_2\text{O}$ . The solid was then transferred into a porcelain dish, and dried overnight at  $120^\circ\text{C}$  under circulating air. Yield: 26.8 g of the dried cobalt-tin hydroxo precursor. The material was calcined at  $550^\circ\text{C}$  under air for 6 hrs using a heating rate of 3 degree/min. Yield: 22.3 g of the calcined silica-cobalt(II) stannate. The material contains 80 wt.% of the mixed oxide and is represented by the formula

[SiO<sub>2</sub>-Co<sub>1.35</sub>SnO<sub>3.70</sub>(80)]. The surface area of the calcined material was 166 m<sup>2</sup>/g, with a pore volume of 0.27 cm<sup>3</sup>/g, and an average pore diameter of 6.5 nm.

**[0088]** To prepare the ruthenium promoted CoSn catalyst, an aqueous solution of ruthenium(III) nitrosyl nitrate (31.3 wt.% Ru) was prepared by dissolving 0.64 g (1.0 wt.% Ru) or 0.32 g (0.5 wt.% Ru) in 13 mL of deionized H<sub>2</sub>O. The homogeneous, dark-brown solution was used to impregnate 19.8 g of the bulk CoSn catalyst (4 mm pellets) by incipient wetness. The material was then dried at 120°C, and calcined at 500°C for 6 hrs under air using a heating rate of 3 degree/min. The material produced is represented by the formula [SiO<sub>2</sub>-Co<sub>1.35</sub>SnO<sub>3.70</sub>(80)]Ru(1.0), and [SiO<sub>2</sub>-Co<sub>1.35</sub>SnO<sub>3.70</sub>(80)]Ru(0.5).

**[0089]** To prepare ruthenium and bismuth promoted CoSn catalyst, a metal impregnation solution was prepared by first adding 0.32 g of ruthenium(III) nitrosyl nitrate (31.3 wt.% Ru) to 10 mL of deionized H<sub>2</sub>O and 1.5 mL of 1.0 M HNO<sub>3</sub>. Next, 0.465 g (0.96 mmol) of solid bismuth(III) nitrate pentahydrate, Bi(NO<sub>3</sub>)<sub>3</sub> · 5 H<sub>2</sub>O was added to the solution, and dissolved with stirring. The homogeneous, dark-brown solution was used to impregnate 19.8 g of the bulk CoSn catalyst (4 mm pellets) by incipient wetness. The material was dried at 120°C, and then calcined at 500°C for 6 hrs under air using a heating rate of 3 degree/min. The material produced is represented by the formula [SiO<sub>2</sub>-Co<sub>1.35</sub>SnO<sub>3.70</sub>(80)]Ru(0.5)Bi(1.0).

## Example 2

**[0090]** Two exemplary reactor systems may be used to test the performance of the catalysts: the MX4-I reactor system and the LTR-C reactor system. The reactor effluent was periodically collected, and product analysis is carried out using an authentic sample calibrated GC off-line analysis method. Temperature program: T<sub>init</sub> = 60 °C (hold 2.5 min); ramp (20 deg/min) to 245 °C (hold 5.5 min). Total run time 17.25 min (Oven maximum temperature 280 °C).

**[0091]** [MX4-I] Reactor System & Catalytic Testing Conditions. Test unit consists of four independent tubular fixed bed reactor systems with common temperature control, pressure and gas and liquid feeds. The reactors are made of 3/8" 316 SS tubing, and are 12 1/8 inches in length. The vaporizers are made of 3/8" 316 SS tubing and are 12 3/8 inches in length. The reactors, vaporizers, and their respective effluent transfer lines are electrically heated (heat tape). The reactor effluents are routed to chilled water condensers and knock-out pots. Condensed liquids are collected automatically, and then manually drained from the knock-out pots as needed. None-condensed gases are passed through a manual back pressure regulator

(BPR) and then scrubbed through water and vented to the fume hood. A volume of 6 - 10 mL of catalyst (4 mm pellets) is loaded to reactor. Both inlet and outlet of reactor are filled with glass beads (3mm) to form the fixed bed. The following running conditions for catalyst screening were used: [HOAc], 0.092 g/mL; [H<sub>2</sub>], 342 sccm ([H<sub>2</sub>]/[HOAc] = 9.5); 280°C; 2169.7 kPa (300 psig); 6 to 10 mL of heterogeneous catalyst (4 mm pellets); 24 - 50 hrs of reaction time.

**[0092]** [LTR-C] Reactor System & Catalytic Testing Conditions. Test unit (life time reactor) consists of a tubular reactor made of 1" OD (0.834" ID) X 12.25" L 316 SS tubing. The reactor has three separate heat bands. A 1/8" thermocouple with six-points was installed inside of reactor. The vaporizer is made of 0.50" Hastelloy C tubing and is approximately 17.5 in. in length. A volume of 30 mL of catalyst (4 mm pellets) was loaded to reactor. Both inlet and outlet of reactor are filled with 50 mL of Denstone® 57 (3mm) to form the fixed bed. The following running conditions for catalyst screening were used: [HOAc], 0.276 g/mL; [H<sub>2</sub>], 1026 sccm ([H<sub>2</sub>]/[HOAc] = 9.5); 280°C; 2169.7 kPa (300 psig); 30 mL of heterogeneous catalyst (4 mm pellets); TOS: 4,700 hrs of reaction time.

### **Example 3**

**[0093]** The catalyst activity and product selectivity of the Ru (1.0) promoted CoSn catalyst was tested. A catalyst sample running in LTR-C (NorPro extrudate 2101 with 1.0 wt.% Ru) was removed from the reactor after a total time on stream of ~4,700 hrs at 280 °C. The testing results, i.e., the final conversion of acetic acid, the crude product selectivity for ethanol and ethyl acetate, and the productivity of ethanol, the ethanol to ethyl acetate ratio are shown in FIGS. 1-4, respectively. The results show that after a total time on stream of 4,700 hrs at 280°C, the final conversion of acetic acid was still in excess of 97%, the selectivity towards ethanol and ethyl acetate remained at 54 wt.%, and 11 wt.%, respectively. An average ethanol productivity was observed with 505 g/kg/hr.

### **Example 4**

**[0094]** The catalytic activity and the product selectivity of the Ru (0.5) promoted catalyst [Co<sub>1.35</sub>SnO<sub>x</sub>]Ru(0.5)), and Ru(0.5)Bi (1.0) modified catalysts [Co<sub>1.35</sub>SnO<sub>x</sub>]Ru(0.5)Bi(1.0) were tested after the catalysts had been running in the reactor after 140 hours under three different temperatures, 280°C, 275°C, and 270°C. FIGS.5 and 6 shows acetic acid conversion and product selectivity of the two catalysts after running in the reactor for over 140 hrs at 280°C.

The same data are also represented in FIG. 7a. FIGS. 7b and 7c show the catalytic activity and the product selectivity of the two catalysts at two other temperatures, 275°C, and 270°C.

**[0095]** The results indicate that the both catalysts had sufficient catalytic activity and stability, as indicated by a high acetic acid conversion and sufficient product selectivity under the above conditions. It also shows that the presence of Bi (1.0 wt%) can provide additional stability and activity in performance to catalysts having lower amount of Ru (0.5 wt.%), as indicated by an even higher acetic acid conversion, especially at a lower temperatures, such as 275°C and 270°C. No significant difference in the product selectivity for either ethanol or ethyl acetate was observed between the Ru (0.5) promoted catalyst and the Ru(0.5) Bi(1.0) promoted catalyst.

**[0096]** While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited below and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

**We claim:**

1. A process for producing ethanol, comprising contacting acetic acid and hydrogen in a reactor in the presence of a catalyst comprising a binder, a mixed oxide comprising cobalt and tin, and at least two promoter metals comprising ruthenium and bismuth.
2. The process of claim 1, wherein the molar ratio of ruthenium to bismuth is from 5:1 to 0.2:1.
3. The process of any one of claims 1 or 2, wherein the total ruthenium loading is less than the total loading of bismuth.
4. The process of any one of the preceding claims, wherein the total ruthenium loading is from 0.05 to 3 wt.%, and the total bismuth loading is from 0.1 to 10 wt.%, based on the total weight of the catalyst.
5. The process of any one of the preceding claims, wherein the mixed oxide is from 40 to 90 wt.%, based on the total weight of the catalyst.
6. The process of any one of the preceding claims, further comprising a promoter metal selected from the group consisting of rhenium, rhodium, palladium, osmium, iridium, platinum, and combinations thereof, wherein the total loading of the additional promoter metal is from 0.01 to 1 wt.%, based on the total weight of the catalyst.
7. The process of any one of the preceding claims, wherein the total tin loading of the catalyst is from 10 to 60 wt.%, based on the metal content of the catalyst.
8. The process of any one of the preceding claims, wherein the total cobalt loading of the catalyst is from 10 to 60 wt.%, based on the metal content of the catalyst.
9. The process of any one of the preceding claims, wherein the catalyst has a molar ratio of cobalt to tin from 2:1 to 0.75:1.

10. The process of any one of the preceding claims, wherein the mixed oxide further comprises nickel and wherein the total nickel loading of the catalyst is from 2 to 40 wt.%, based on the metal content of the catalyst.
11. The process of any one of the preceding claims, wherein the catalyst is substantially free of silver, zinc, zirconium, cadmium, copper, manganese, and molybdenum.
12. The process of any one of the preceding claims, wherein the binder is selected from the group consisting of silica, aluminum oxide, and titania.
13. The process of any one of the preceding claims, wherein the binder is present in an amount from 5 to 40 wt.%, based on the total weight of the catalyst.
14. The process of any one of the preceding claims, wherein the contacting is performed in a vapor phase at a temperature of 200°C to 350°C, an absolute pressure of 101 kPa to 3000 kPa, and a hydrogen to acetic acid mole ratio of greater than 4:1.
15. The process of any one of the preceding claims, wherein a feed stream is contacted with hydrogen and the feed stream comprises from 50 to 95 wt.% acetic acid and from 5 to 50 wt.% ethyl acetate.

1/4

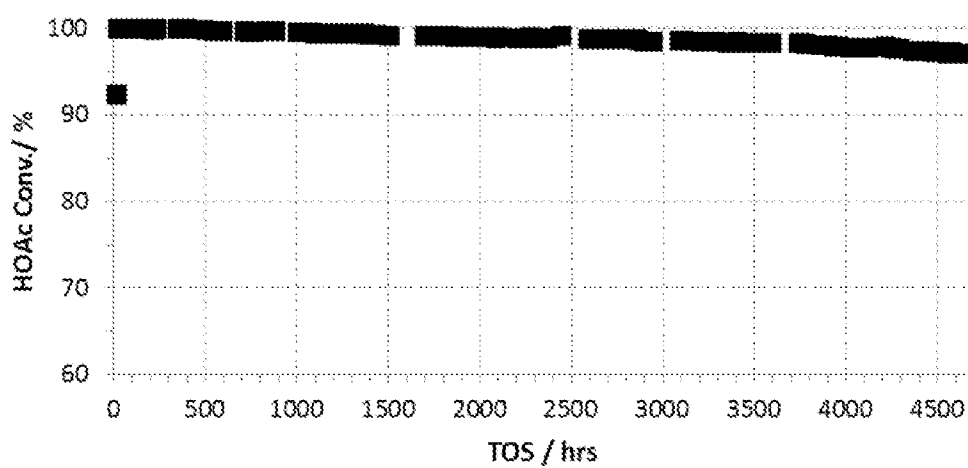


FIG. 1

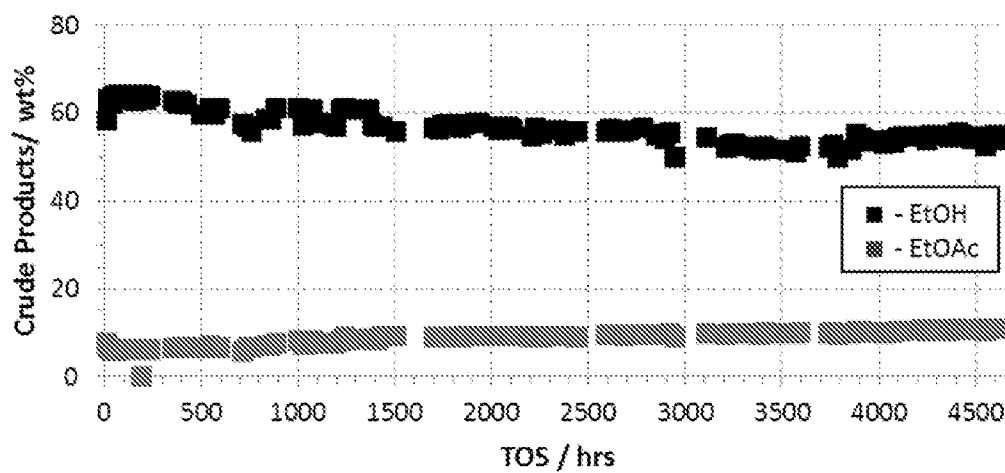


FIG. 2

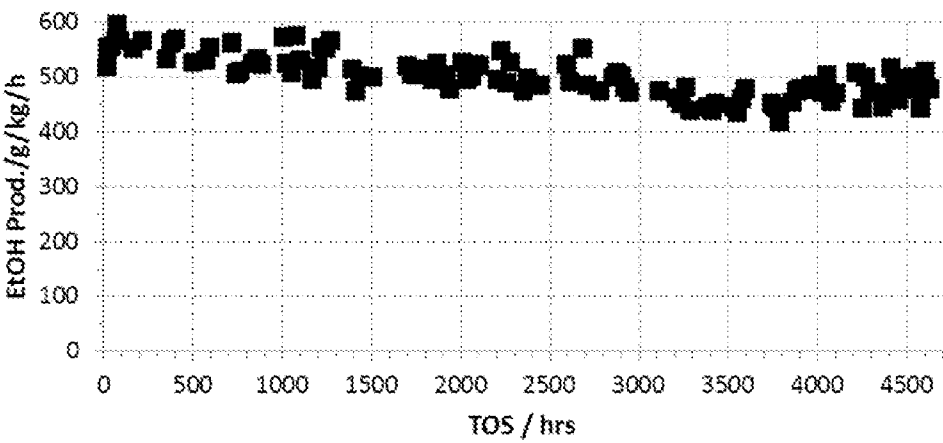


FIG. 3

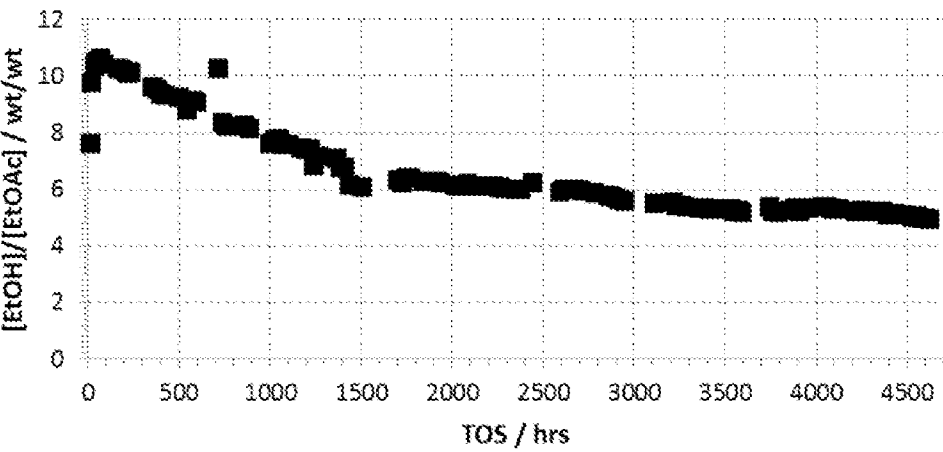


FIG. 4

3/4

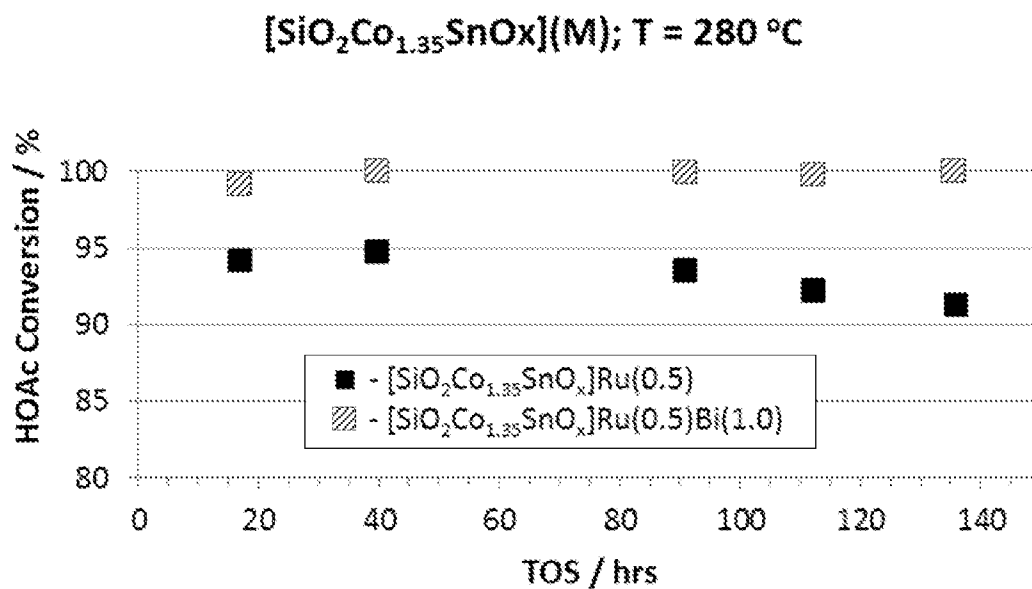


FIG. 5

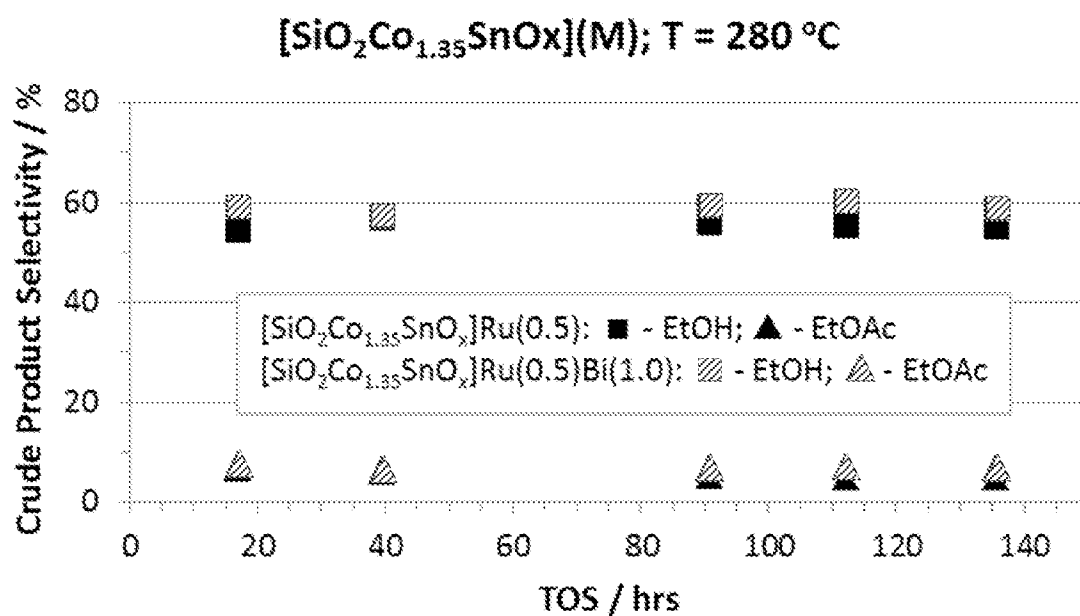


FIG. 6

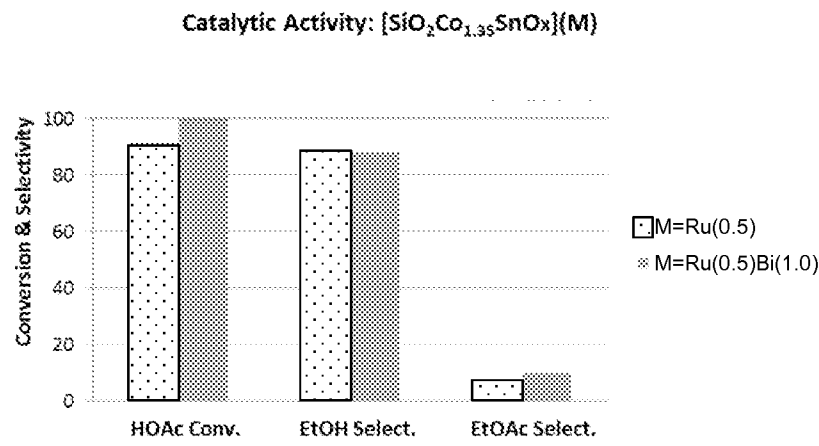


FIG. 7A

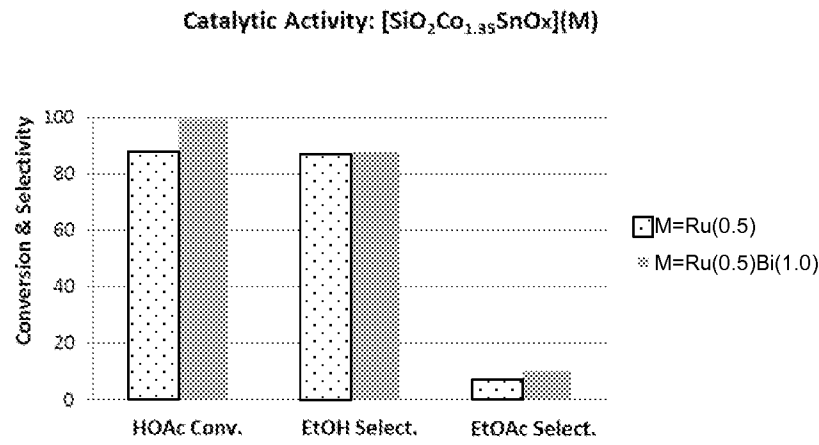


FIG. 7B

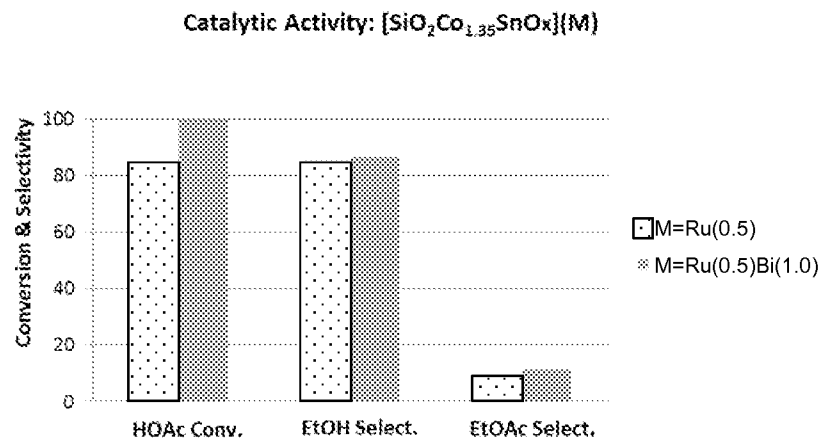


FIG. 7C

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2015/027818

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07C29/149 C07C31/08  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                      | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 2013/178663 A1 (ZHOU ZHENHUA [US] ET AL) 11 July 2013 (2013-07-11)<br>cited in the application<br>the whole document | 1                     |
| A         | US 2013/190527 A1 (ZHOU ZHENHUA [US] ET AL) 25 July 2013 (2013-07-25)<br>the whole document                             | 1                     |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

4 January 2016

Date of mailing of the international search report

11/02/2016

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Authorized officer

de Nooy, Arjan

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/027818

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date         |
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| US 2013190527                             | A1                  | 25-07-2013                 | NONE                        |
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