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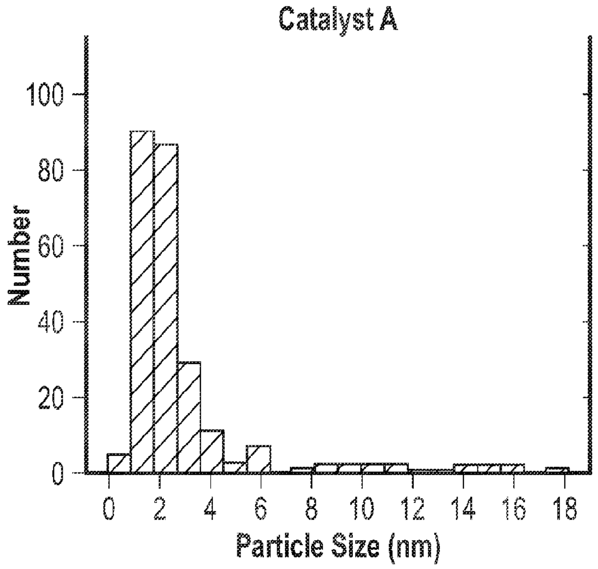
(54) Title: SUGAR OXIDATION CATALYST WITH IMPROVED SELECTIVITY

FIG. 1A


Catalyst A

(57) **Abstract:** A method comprising contacting a support material with a platinum salt and alkali aurate to form a metallated support; heat treating the metallated support to form a heat-treated metallated support; and reducing the heat treated metallated support to form a selective oxidation catalyst. A method comprising contacting a polyol with a catalyst comprising an alkali metal aurate and platinum salt on a support under conditions suitable for the formation of an oxidized product.

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[Continued on next page]

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SUGAR OXIDATION CATALYST WITH IMPROVED SELECTIVITY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Serial No. 63/592,429 filed October 23, 2023 and entitled "Metal Precursor for the Production of Sugar Oxidation Catalysts with Improved Performance," which is hereby incorporated herein by reference in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

TECHNICAL FIELD

[0003] The present disclosure generally relates to catalysts. More particularly, the present disclosure relates to the oxidation catalysts with improved performance.

BACKGROUND

[0004] Transition metal catalysts for the selective oxidation of platform chemicals such as sugars are desired. One such transition metal catalyst combines the properties of both gold and platinum. Gold catalysts have potential for both selective and nonselective oxidation of hydrocarbons, for methanol synthesis by hydrogenation of carbon monoxide or dioxide, for the water–gas shift, and for the reduction of nitric oxide by hydrogen, propene, or carbon monoxide. Supported gold chloride is the most active catalyst for the hydrochlorination of ethyne, the activity being correlated with the metal's high standard electrode potential. The remarkable catalytic behavior shown by gold depends on forming it into very small particles.

[0005] Platinum catalysts have demonstrated the selective oxidation of glucose to glucaric acid. However, these processes suffer from economic shortcomings resulting from, among other matters, process yield limitations, low conversion rates, and limited selectivity due to shortcomings in the performance of existing catalysts. None of these catalysts or the processes employing them are used industrially for the selective oxidation of glucose-containing carbohydrates to manufacture specialty or industrial carboxylic acids or derivatives thereof. Additionally, the type of transition metal salt used in the preparation of gold-platinum catalysts may detrimentally impact the final catalyst preparation. For example, use of transition metal halide salts, such as chloride salts, used in the production of these gold-platinum catalysts generate increased halide ions in the final catalyst composition. Chloride can poison transition metal catalysts, which are used in many reactions, including the oxidation of volatile organic through a variety of mechanisms such as by strongly adsorbing onto metal sites or forming salt deposits that foul or poison catalysts.

SUMMARY

[0006] Disclosed herein is a method comprising contacting a support material with a platinum salt and alkali aurate to form a metallated support; heat treating the metallated support to form a heat-treated metallated support; and reducing the heat treated metallated support to form a selective oxidation catalyst.

[0007] Also disclosed herein is a method comprising contacting a polyol with a catalyst comprising an alkali metal aurate and platinum salt on a support under conditions suitable for the formation of an oxidized product.

BRIEF DESCRIPTION OF DRAWINGS

[0008] For a detailed description of the aspects of the disclosed processes and systems, reference will now be made to the accompanying drawings in which:

[0009] Figure 1A is a graph of the particle size distribution for Catalyst A of example 1

[0010] Figure 1B is a graph of the particle size distribution for Catalyst B of example 1.

[0011] Figure 2 is a graph of catalytic activity for the indicated catalysts.

[0012] Figure 3 is a plot of gluconic acid throughput as a function of reactor pass for the indicated catalysts.

[0013] Figure 4 is a plot of glucaric acid throughput as a function of reactor pass for the indicated catalysts.

[0014] Figure 5 is a graph of the conversion of glucodialdose as a function of catalyst type.

[0015] Figure 6A is a graph of the product distribution for the reaction product of glucodialdose using a control catalyst.

[0016] Figure 6B is a graph of the product distribution for the reaction product of glucodialdose and catalyst of the type disclosed herein.

DETAILED DESCRIPTION

[0017] The following discussion is directed to various exemplary aspects. However, one of ordinary skill in the art will understand that the examples disclosed herein have broad application, and that the discussion of any aspect is meant only to be exemplary of that aspect, and not intended to suggest that the scope of the disclosure, including the claims, is limited to that aspect.

[0018] The figures are not necessarily to scale. Certain features and components herein may be shown exaggerated in scale or in somewhat schematic form and some details of conventional elements may not be shown in interest of clarity and conciseness.

[0019] In the following discussion and in the claims, the terms “including” and “comprising” are used in an open-ended fashion, and thus should be interpreted to mean “including, but not limited to… .” As used herein, the terms “approximately,” “about,” “substantially,” and the like mean within 10% (i.e., plus or minus 10%) of the recited value. Thus, for example, a recited angle of “about 80 degrees” refers to an angle ranging from 72 degrees to 88 degrees.

[0020] Unless the context dictates the contrary, all ranges set forth herein should be interpreted as being inclusive of their endpoints, and open-ended ranges should be interpreted to include only commercially practical values. Similarly, all lists of values should be considered as inclusive of intermediate values unless the context indicates the contrary.

[0021] For the reasons previously described, there remains a need for new, industrially scalable catalysts for the selective and commercially-meaningful oxidation carbohydrates or polyols lacking some of the aforementioned challenges. Disclosed herein are transition metal precursors that may be converted into oxidation catalysts. These transition metal catalyst precursors can be utilized in the formation of selective oxidation catalysts having a final catalyst formulation with a reduced halide content. For example, the final catalyst formulation may have a halide concentration (e.g., chloride concentration) in the range of from about 10 ppm to about 1000 ppm or from about 50 ppm to about 750 ppm or about 100 ppm to about 500 ppm. In some aspects, the catalyst formulation excludes halides. Hereinafter these low halide selective oxidation catalysts are designated LH-SOC. In one or more aspects, a LH-SOC of the present disclosure comprises at least two transition metals and a support material.

[0022] In an aspect, the LH-SOC comprises gold. In one or more aspects, a reagent for the preparation of the LH-SOC is an alkali metal salt of a gold hydroxide complex. For example, the gold hydroxide comprises gold (III) hydroxide, $Au(OH)_3$. In one or more aspects, the alkali metal salt of an aurate is formed by reaction of an alkali metal hydroxide and gold (III) trihydroxide. The product may be characterized by the general chemical formula $MAu(OH)_4$ where M is a Group 1 element such as lithium (Li), sodium

(Na), potassium (K),rubidium (Rb), caesium (Cs),and francium (Fr). In an aspect, M is sodium. In another aspect M is potassium.

[0023] In one or more aspects, a method of the present disclosure comprises contacting an alkali hydroxide with gold (III) trihydroxide under conditions suitable for the formation of an alkali aurate characterized by the general formula $MAu(OH)_4$ which is typically hydrated. In general, hydrated M aurate may be produced by dissolving $Au(OH)_3$ in aqueous alkali hydroxide. For example, potassium hydroxide can be contacted with gold (III) trihydroxide to form $KAu(OH)_4$ or sodium hydroxide can be contacted with gold (III) trihydroxide to form $NaAu(OH)_4$. These reactions are shown in equations (1) and (2).

$$KOH + Au(OH)_3 \rightarrow KAu(OH)_4 \quad (1)$$

$$NaOH + Au(OH)_3 \rightarrow NaAu(OH)_4 \quad (2)$$

[0024] In one or more aspects, the LH-SOC comprises a Group 10 metal. For example, the LH-SOC may comprise nickel (Ni), palladium (Pd), platinum (Pt), darmstadtium (Ds), or combinations thereof. In an aspect, the LH-SOC comprises platinum.

[0025] Platinum used in the preparation of the LH-SOC may be in the form of any suitable salt. Nonlimiting examples of platinum salts for use in preparation of the LH-SOC include oxides, nitrates, nitrites, formates, propionates, oxalates, acetates, hydroxides, hydrogen carbonates, amine complexes or organic complexes, for example triphenylphosphine complexes or acetylacetonate complexes, of these metals.

[0026] In one or more aspects, the total amount of transition metals present in the LH-SOC (e.g., amount of platinum and gold) ranges from about 0.1 weight percent (wt.%) to about 5 wt.% or from about 0.25 wt.% to about 5 wt.% or about 0.5 wt.% to about 5 wt.% or from about 1 wt.% to about 4 wt.% or from about 1 wt.% to about 3 wt.% based on the total weight of the LH-SOC or about 0.1 wt.%, about 0.25 wt.%, about 0.5 wt.%, about 0.75 wt.%, about 1 wt.%, about 1.25 wt.%, about 1.5 wt.%, about 1.75 wt.%, about 2 wt.%, about 2.25 wt.%, about 2.5 wt.%, about 2.75 wt.%, about 3 wt.%, about 3.25 wt.%, about 3.5 wt.%, about 3.75 wt.%, about 4 wt.%, about 4.25 wt.%, about 4.5 wt.%, about 4.75 wt.%, or about 5 wt. In such aspects, the amount of either metal may take a value within any of the disclosed ranges provided the total amount of transition metal also falls within the disclosed ranges.

[0027] In one or more aspects, the LH-SOC comprises a material onto which the transition metals are supported. It is to be understood the support may provide one or more surfaces with which the transition metals may become associated. Any suitable support may be used in preparation of the LH-SOC. For example, the support may comprise any suitable type of carbon (carbon black, graphite, or activated carbon), various types of ceramics, silica, alumina, titania, zirconia, zeolites, metal organic frameworks, glass, and mixtures thereof. The support can be in any suitable form such as powder, granules, beads, extrusion, pellets, or tablets. In some aspects, the support is in the form of powder or granules and the final product may be formed into one of the aforementioned shapes.

[0028] In one or more aspects, the LH-SOC comprises a carbon-containing support, hereinafter referred to as the "carbon support". The carbon support may be characterized by a specific surface area ranging from about 100 m^2/g to about 1000 m^2/g or from about 100 m^2/g to about 900 m^2/g or about 100 m^2/g to about 800 m^2/g or about 100 m^2/g to about 700 m^2/g or about 100 m^2/g to about 500 m^2/g or about 250 m^2/g to about 500 m^2/g or from about 300 m^2/g to about 500 m^2/g. The specific surface area may be determined using any suitable methodology such as by the BET method.

[0029] The carbon support material may be microporous, macroporous or a combination thereof. For example, the carbon support material may be characterized by a micropore area of from about 10 m^2/g to about 100 m^2/g, or from about 25 m^2/g to about 100m^2/g or from about 40 m^2/g to about 90 m^2/g. Herein the micropore area refers to the surface area associated with the micropores, where a micropore is defined as a pore of internal width less than 2 nm. Micropore area may be determined using any suitable methodology such as a t-plot, generated from a nitrogen adsorption isotherm. In some aspects, the carbon support material may be mesoporous and have pore diameters ranging from about 2 nm to about 100 nm or from about 10 nm to about 80 nm or from about 10 nm to about 50 nm.

[0030] In one or more aspects, association of the metal salts with the support material to form a catalyst precursor may be carried out using any suitable methodology. For example, the metal salts may be deposited onto the support using methods such as incipient wetness impregnation, wet impregnation, ion exchange, and spray coating.

[0031] In one aspect, a method of preparing a LH-SOC comprises preparation of (i) a solution comprising the alkali aurate; and (ii) a solution comprising a platinum salt. The alkali aurate solution, platinum salt solution or both may be prepared using any suitable solvent such as an aqueous solvent. The support (e.g., carbon) may be associated (e.g., impregnated) with the transition metal solutions sequentially, for example the support may be impregnated with the alkali aurate solution followed by impregnation with the platinum salt solution to allow for gold deposition on the support followed by platinum deposition. In the alternative, the support may be prepared by impregnation with a platinum salt solution followed by impregnation with the alkali aurate solution to allow for platinum deposition on the support followed by gold deposition. In some aspects, a single solution comprising both the alkali aurate and platinum salt is prepared used to impregnate the support and allows for codeposition of the gold and platinum on the support.

[0032] In any aspect, the transition metal salt solutions may comprise solvents such as aqueous fluids. In one or more aspects, the solvents used in preparation of the transition metal solutions exclude halides such as chloride. The resulting material having gold and platinum deposited on the support (either through sequential deposition or codeposition) is termed the metallated support.

[0033] In one or more aspects, preparation of the LH-SOC further comprises heat treating the metallated support. Heat treatment of the metallated support may involve subjecting the metallated support to a temperature of from about 50 °C to about 200 °C or from about 60 °C to about 150 °C or from about 60 °C to about 130 °C for a time period of from about 1 hour (hr) to about 12 hours or from about 1 hour (hr) to about 4 hrs or from about 4 hrs to about 8 hrs or from about 8 hrs to about 12 hrs. The resulting material is termed a heat-treated metallated support.

[0034] A method of preparing an LH-SOC may further comprise reducing the heat-treated metallated support. Reduction of the heat-treated metallated support may be carried out under one or more of the following reaction conditions: a hydrogen-nitrogen stream having a hydrogen percentage ranging from about 1% to about 20% or about 2% to about 15% or about 1% to about 14 %; a temperature of from about 100 °C to about 700 °C or from about 100 °C to about 600 °C or from about 200 °C to about 500 °C; and a time period of from about 1 hour to about 12 hours or from about 2 hours to about 10 hours or from about 1 hour to about 5 hours. The resultant material is the LH-SOC.

[0035] A LH-SOC prepared as disclosed herein may be characterized by the formation of a platinum-gold clusters dispersed on at least a portion of the support material. The platinum-gold clusters refer to areas on the support material where platinum and gold are colocalized. Pt/Au clusters formed as prepared herein may be characterized by a cluster size ranging from about 1 nm to about 25 nm or from about 2 nm to about 20 nm or from about 1 nm to about 10 nm or from about 5 nm to about 10 nm. Without wishing to be limited by theory, at least some portion of the colocalized metals may interact electronically in a manner that beneficially affects the catalytic activity of the LH-SOC.

[0036] In one or more aspects, the LH-SOC is used to catalyze the oxidation of a sugar or sugar-based compound. For example, the LH-SOC may be contacted with a sugar under reaction conditions such as one or more of the following: a sugar or sugar containing product present in an amount of from about 10 wt.% to about 90 wt.% based on the total weight of the reaction mixture or form about 15 wt.% to about 75 wt.% or from about 20 wt.% to about 50 wt.%; air at a pressure ranging from about 200 pounds per square inch absolute (psia) to about 1200 psia or from about 300 psia to about 1000 psia or from about 400 psia to about 900 psia; and temperatures ranging from about 60 °C to about 300 °C or from about 75 °C to about 250 °C or from about 100 °C to about 200 °C. In one or more aspects, the reaction is carried out in the presence of an aqueous solvent.

[0037] In one or more aspects, glucose is oxidized in the presence of LH-SOC and results in equal to or greater than 90% conversion of glucose to the corresponding aldose, or from about 90% to about 99% or from about 95% to about 99%. In one or more aspects, the LH-SOC results in the selective oxidation of glucose to gluconic acid where gluconic acid comprises from about 1% to about 40% of the final product or from about 5% to about 30% of the final product or from about 10% to about 20%.

[0038] In one or more aspects the sugar oxidation products comprise a glucose oxidation product, a gluconic acid oxidation product, a gluconate, or a combination thereof. The glucose oxidation product, gluconic acid oxidation product, or combination thereof may be buffered to a suitable pH.

[0039] Additionally or alternatively, the one or more sugar oxidation products comprise glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products or a combination thereof.

[0040] Additionally or alternatively, the one or more sugar oxidation products comprise galactonic acid, galactaric acid, an oxidation product comprising predominantly (e.g., greater than about 50 weight percent) galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C2 to C6 diacids or a combination thereof. Additionally or alternatively, in one or more aspects, the one or more sugar oxidation products comprise glutamic acid. Additionally or alternatively, the one or more sugar oxidation products comprise glucodialdose, 2-ketoglucose or a combination thereof.

[0041] In an aspect, the one or more one or more sugar oxidation products comprise less than about 5 wt.% maltose, maltotriose, fructose, higher molecular weight polysaccharides, oxidation products thereof or a combination thereof based on the total weight of the sugar-derived carboxylic acid.

[0042] Disclosed herein are methods that may potentially improve the properties of an oxidation catalyst. Without wishing to be limited by theory, the methodologies disclosed herein may result in improved performance characteristics of the oxidation catalyst such as increased catalyst selectivity, improved percent conversion of substrate in the oxidation reaction, and improved time-on-stream of the catalyst.

[0043] These improvements may be attributable in part to advantageous catalyst characteristics such as gold/platinum dispersion, gold/platinum alloy formation, gold/platinum spatial distribution, gold/platinum cluster size in the catalyst, or a combination thereof. In one or more aspects, the methods disclosed herein may exclude the hazards associated with the use of tetrachloroauric acid in the catalyst preparation. Advantageously the presently disclosed methodologies may result in the elimination of hazardous gas (chlorine) generated during the conventional process, providing the possibility to apply basic solutions in the carrier impregnation and adjusting the loaded metal characteristics thereof as alternative methods for the production of sugar acids.

ADDITIONAL DISCLOSURE

[0044] A first aspect which is a method comprising contacting a support material with a platinum salt and alkali aurate to form a metallated support; heat treating the metallated support to form a heat-treated metallated support; and reducing the heat treated metallated support to form a selective oxidation catalyst.

[0045] A second aspect which is the method of the first aspect wherein the alkali metal aurate is characterized by the general formula $MAu(OH)_4$ where M is a Group 1 element.

[0046] A third aspect which is the method of the second aspect wherein M comprises potassium.

[0047] A fourth aspect which is the method of the second aspect wherein M comprises sodium.

[0048] A fifth aspect which is the method of any of the first through fourth aspects wherein the platinum salt, alkali aurate or combination thereof is present in an amount ranging from about 0.1 wt.% to about 5 wt.%.

[0049] A sixth aspect which is the method of any of the first through fifth aspects wherein the platinum salt excludes chloride.

[0050] A seventh aspect which is the method of any of the first through sixth aspects wherein the support comprises carbon, carbon black, graphite, activated carbon, ceramics, silica, alumina, titania, zirconia, zeolites, metal organic frameworks, glass, or combinations thereof.

[0051] An eighth aspect which is the method of any of the first through seventh aspects wherein the support comprises carbon.

[0052] A ninth aspect which is the method of any of the first through eighth aspects wherein the support is characterized by a specific surface area ranging from about 100 m^2/g to about 1000 m^2/g.

[0053] A tenth aspect which is the method of any of the first through ninth aspects wherein the support is characterized by a micropore area of from about 10 m^2/g to about 100 m^2/g.

[0054] An eleventh aspect which is the method of any of the first through tenth aspects wherein heat treatment occurs in a temperature range of from about 50 °C to about 200 °C.

[0055] A twelfth aspect which is the method of any of the first through eleventh aspects wherein the reducing occurs in the presence of a hydrogen-nitrogen mixture comprising from about 1% to about 20% hydrogen.

[0056] A thirteenth aspect which is the method of any of the first through twelfth aspects wherein the catalyst is characterized by gold-platinum clusters.

[0057] A fourteenth aspect which is the method of the thirteenth aspect wherein the gold-platinum clusters have a cluster size ranging from about 1 nm to about 25 nm.

[0058] A fifteenth aspect which is a method comprising contacting a polyol with a catalyst comprising an alkali metal aurate and platinum salt on a support under conditions suitable for the formation of an oxidized product.

[0059] A sixteenth aspect which is the method of the fifteenth aspect wherein the polyol comprises a sugar, a sugar oxidation product or combination thereof.

[0060] A seventeenth aspect which is the method of any of the fifteenth through sixteenth aspects wherein the catalyst excludes chloride.

[0061] An eighteenth aspect which is the method of any of the fifteenth through seventeenth aspects wherein the sugar comprises glucose.

[0062] A nineteenth aspect which is the method of eighteenth aspect wherein the oxidized product comprises glucaric acid, gluconic acid, glucuronic acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose or combinations thereof.

[0063] A twentieth aspect which is the method of any of the fifteenth through nineteenth aspects wherein the oxidized product comprises glucaric acid, gluconic acid, glucodialdose or combinations thereof

EXAMPLE

[0064] The subject matter having been generally described, the following examples are given as particular aspects of the disclosure and are included to demonstrate the practice and advantages thereof, as well as aspects and features of the presently disclosed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the present subject matter, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific aspects which are disclosed and still obtain a like or similar result without departing from the scope of the instant disclosure. It is understood that the examples are given by way of illustration and are not intended to limit the specification of the claims to follow in any manner.

EXAMPLE 1

[0065] LH-SOCs of the present disclosure were synthesized and evaluated. Specifically, a first sample was synthesized by impregnating a carbon support with $Pt(NO_3)_4$ followed by impregnation with $NaAu(OH)_4$. The sample was then dried and reduced as described herein to produce the LH-SOC catalyst A. The second sample, L H-SOC catalyst B was prepared by impregnation of a carbon support with $NaAu(OH)_4$ followed by impregnation with $Pt(NO_3)_4$ and subsequently dried and reduced. Both catalysts had a target metal loading for gold of 0.3 wt.% and platinum of 0.2 wt.%.

[0066] Transmission electron micrographs of different portions of catalyst samples indicated that for large particles, Au was growing on the Pt particle. However, for small particles, Au and Pt distribution was relatively uniform but the Au:Pt ratio varied in different particles.

[0067] The particle size distributions for Catalysts A and B are presented in Figures 1A and 1B, respectively. With reference to Figures 1A and 1B, the majority of catalyst particles had a particle size of less than 5 nm.

[0068] The catalytic activity of both catalysts were evaluated for the oxidation of glucose. Specifically, the catalysts were reacted with glucose under the following conditions: air pressure of 600 pounds per square inch gauge (psig) to 900 psig, temperature of 80 °C to 160 °C for a reaction time of approximately 30 minutes, with a flow rate of 10 mL/min to 30 mL/min. The control catalyst was prepared by codeposition of the transition metals onto the support. Each parameter was evaluated by for weight percentage of desired products, based on purpald assays designated AX, or by high performance liquid chromatography (HPLC), designated BX. The extent of glucose oxidation was also measured after the substrate had completed a first pass over the catalyst and then again after a seventh pass over the catalyst. Selectivity of the catalyst for gluconic acid and glucaric acid production was also evaluated. The results are depicted in Figure 2.

[0069] With reference to Figure 2, Catalyst A prepared by impregnation of the carbon support with platinum followed by gold had the greatest improvement in activity and selectivity when compared to the control catalyst.

EXAMPLE 2

[0070] The behavior of the catalysts as a function of reaction pass was investigated. The throughput of gluconic acid and glucaric acid as a function reaction pass was determined for each catalyst and the results are presented in Figures 3 and 4, respectively. The results demonstrate that for gluconic acid throughput all three catalyst are at their lowest levels after seven reactor passes. For gluconic acid throughput, catalysts A and B display a monotonically linear decrease in catalytic activity however the control catalyst displays a large increase in activity on the fifth pass. For glucaric acid throughput, glucaric acid throughput increased as the number of passes increased and was still significant after seven passes. The reaction was repeated and similar results were observed.

EXAMPLE 3

[0071] Catalyst activity in the oxidation of the aldehyde glucodialdose (GDA) was evaluated. Specifically, GDA was reacted by introducing 500 mL of a 10 wt.% GDA solution to a reactor bed having either a control catalyst which was a Au-Pt on carbon prepared using a platinum chloride salt, Catalyst A1 and A2 which were duplicate samples that contained 0.3 wt.% aurate and 0.2 wt.% $Pt(NO_3)_4$, prepared by sequential addition onto carbon and LH-SOC; Catalyst C which contained 0.6 wt.% aurate and 0.6 wt.% of a $PtCl_4$ on a carbon support and Catalyst D which is similar to Catalyst C with the addition of 0.1 wt.% Sr. Reactions of GDA with the catalysts were carried using an air pressure of 900 psig at a temperature of 140 °C for a reaction time of approximately 28 minutes. The results are presented in Figure 5 and demonstrate that catalysts containing chloride and or with an increased metal loading had a conversion rate that was slower than the LH-SOCs of the present disclosure.

[0072] The individual components of the reaction product prepared using glucodialdose and an LH-SOC, specifically Catalyst A LH-SOC and a control Au-Pt on carbon was determined. The results are presented in Figure 6A for the control and Figure 6B for Catalyst A. With reference to Figures 6A and 6B, the product distribution observed with an LH-SOC differs substantively from the product distribution using the control Au-Pt/carbon which was prepared without an aurate salt.

[0073] The subject matter having been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the subject matter. The aspects described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the subject matter disclosed herein are possible and are within the scope of the disclosed subject matter. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0074] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an aspect of the present disclosure. Thus, the claims are a further description and are an addition to the aspects of the present invention. The discussion of a reference herein is not an admission that it is prior art to the presently disclosed subject matter, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A method comprising:

contacting a support material with a platinum salt and alkali aurate to form a metallated support;

heat treating the metallated support to form a heat-treated metallated support; and

reducing the heat treated metallated support to form a selective oxidation catalyst.

2. The method of claim 1, wherein the alkali metal aurate is characterized by the general formula $MAu(OH)_4$ where M is a Group 1 element.

3. The method of claim 2. wherein M comprises potassium.

4. The method of claim 2, wherein M comprises sodium.

5. The method of claim 1, wherein the platinum salt, alkali aurate or combination thereof is present in an amount ranging from about 0.1 wt.% to about 5 wt.%.

6 The method of claim 1, wherein the platinum salt excludes chloride.

7. The method of claim 1, wherein the support comprises carbon, carbon black, graphite, activated carbon, ceramics, silica, alumina, titania, zirconia, zeolites, metal organic frameworks, glass, or combinations thereof.

8. The method of claim 1, wherein the support comprises carbon.

9. The method of claim 1, wherein the support is characterized by a specific surface area ranging from about 100 m^2/g to about 1000 m^2/g.

10. The method of claim 1, wherein the support is characterized by a micropore area of from about 10 m^2/g to about 100 m^2/g.

11. The method of claim 1, wherein heat treatment occurs in a temperature range of from about 50 °C to about 200 °C.

12. The method of claim 1, wherein the reducing occurs in the presence of a hydrogen-nitrogen mixture comprising from about 1% to about 20% hydrogen.

13. The method of claim 1, wherein the catalyst is characterized by gold-platinum clusters.

14. The method of claim 13, wherein the gold-platinum clusters have a cluster size ranging from about 1 nm to about 25 nm.

15. A method, comprising:

contacting a polyol with a catalyst comprising an alkali metal aurate and platinum salt on a support under conditions suitable for the formation of an oxidized product.

16. The method of claim 15, wherein the polyol comprises a sugar, a sugar oxidation product or combinations thereof.

17. The method of claim 15, wherein the catalyst excludes chloride.

18. The method of claim 18, wherein the sugar comprises glucose.

19. The method of claim 18, wherein the oxidized product comprises glucaric acid, gluconic acid, glucuronic acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose or combinations thereof.

20. The method of claim 18, wherein the oxidized product comprises glucaric acid, gluconic acid, glucodialdose or combinations thereof.

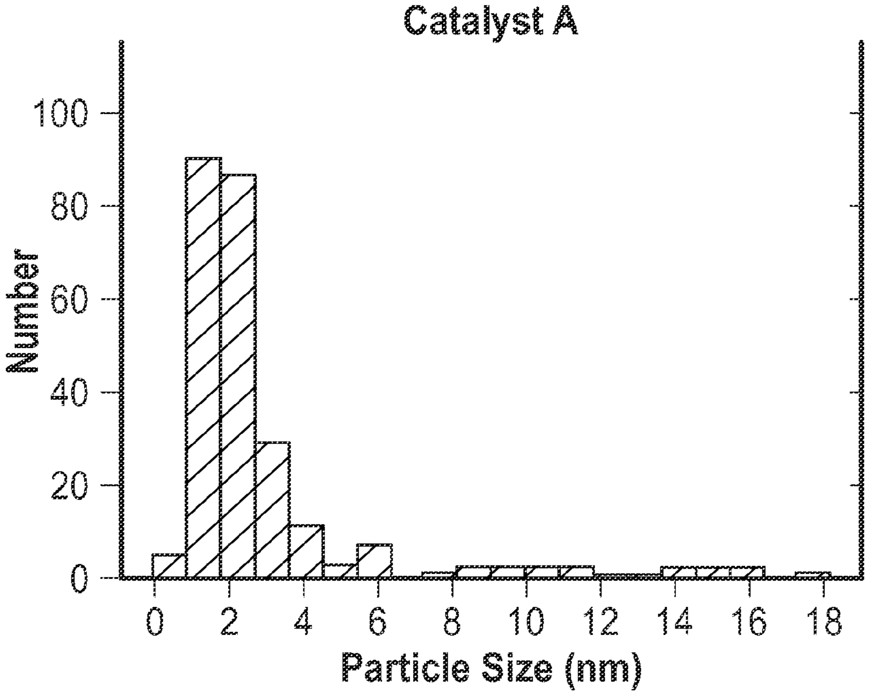
Catalyst A
Number
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
Particle Size (nm)

FIG. 1A

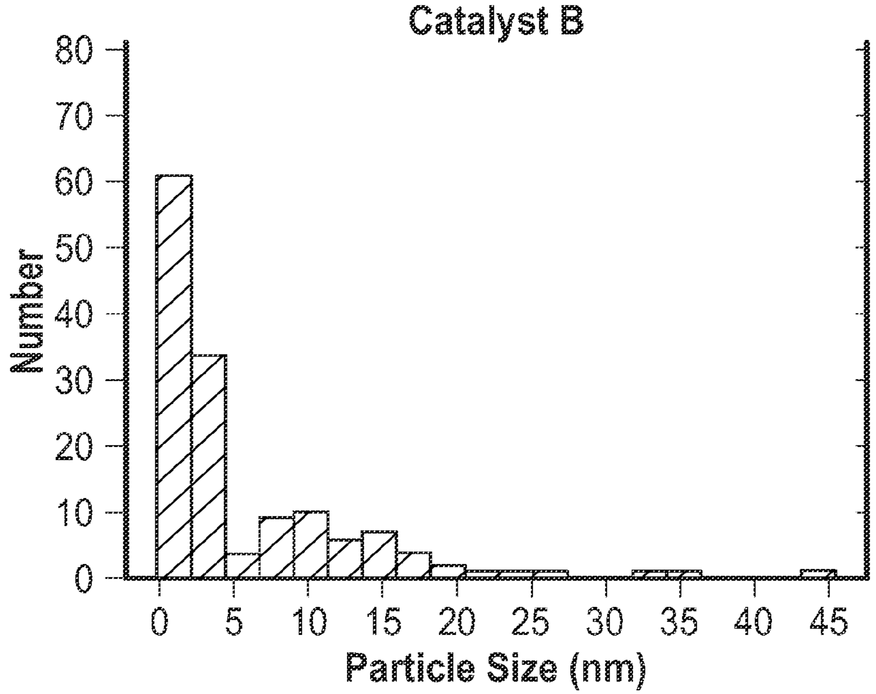
Catalyst B
Number
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
Particle Size (nm)

FIG. 1B

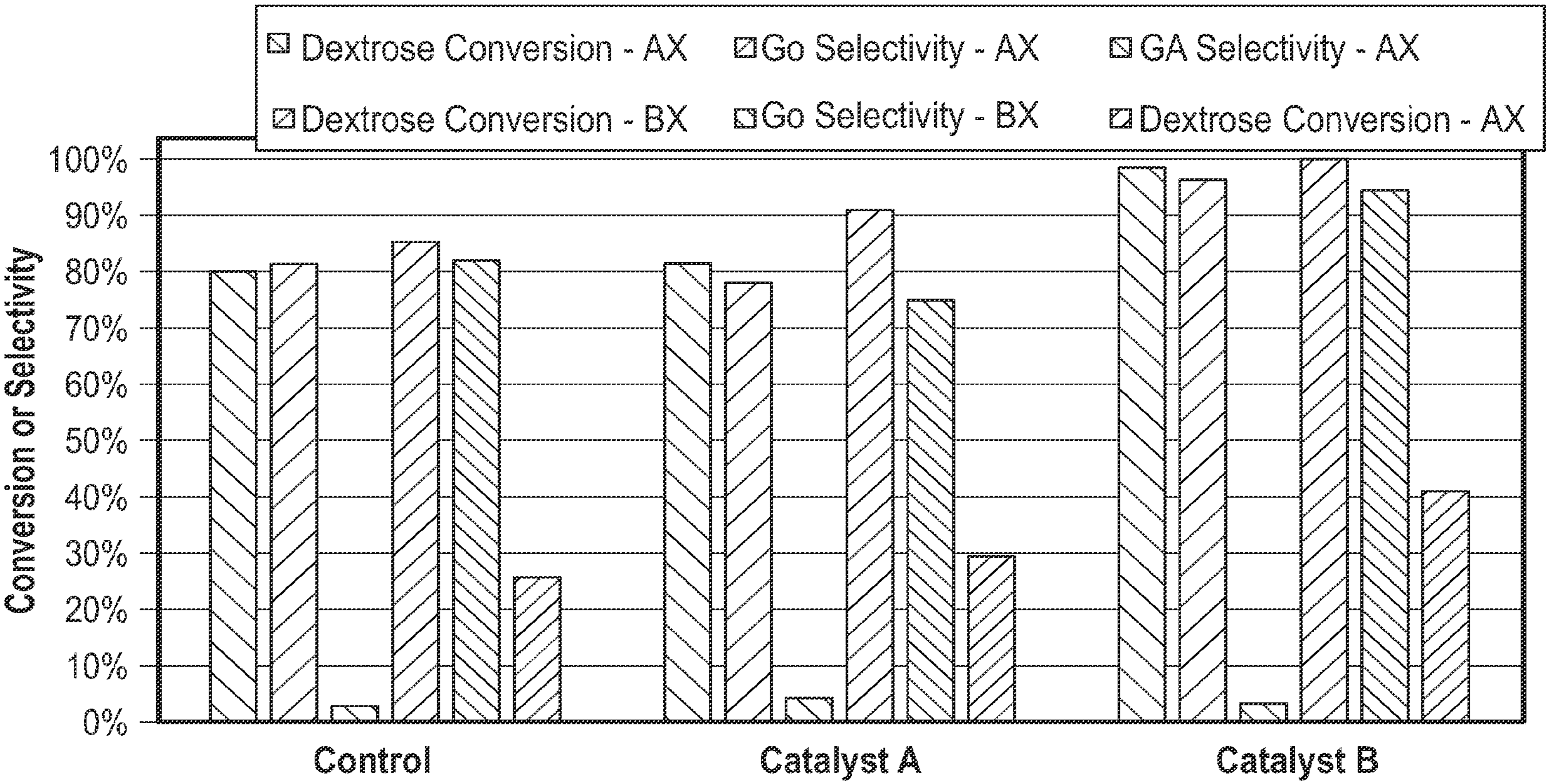
▧ Dextrose Conversion - AX
▨ Go Selectivity - AX
▧ GA Selectivity - AX
▨ Dextrose Conversion - BX
▧ Go Selectivity - BX
▨ Dextrose Conversion - AX
Conversion or Selectivity
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Control
Catalyst A
Catalyst B

FIG. 2

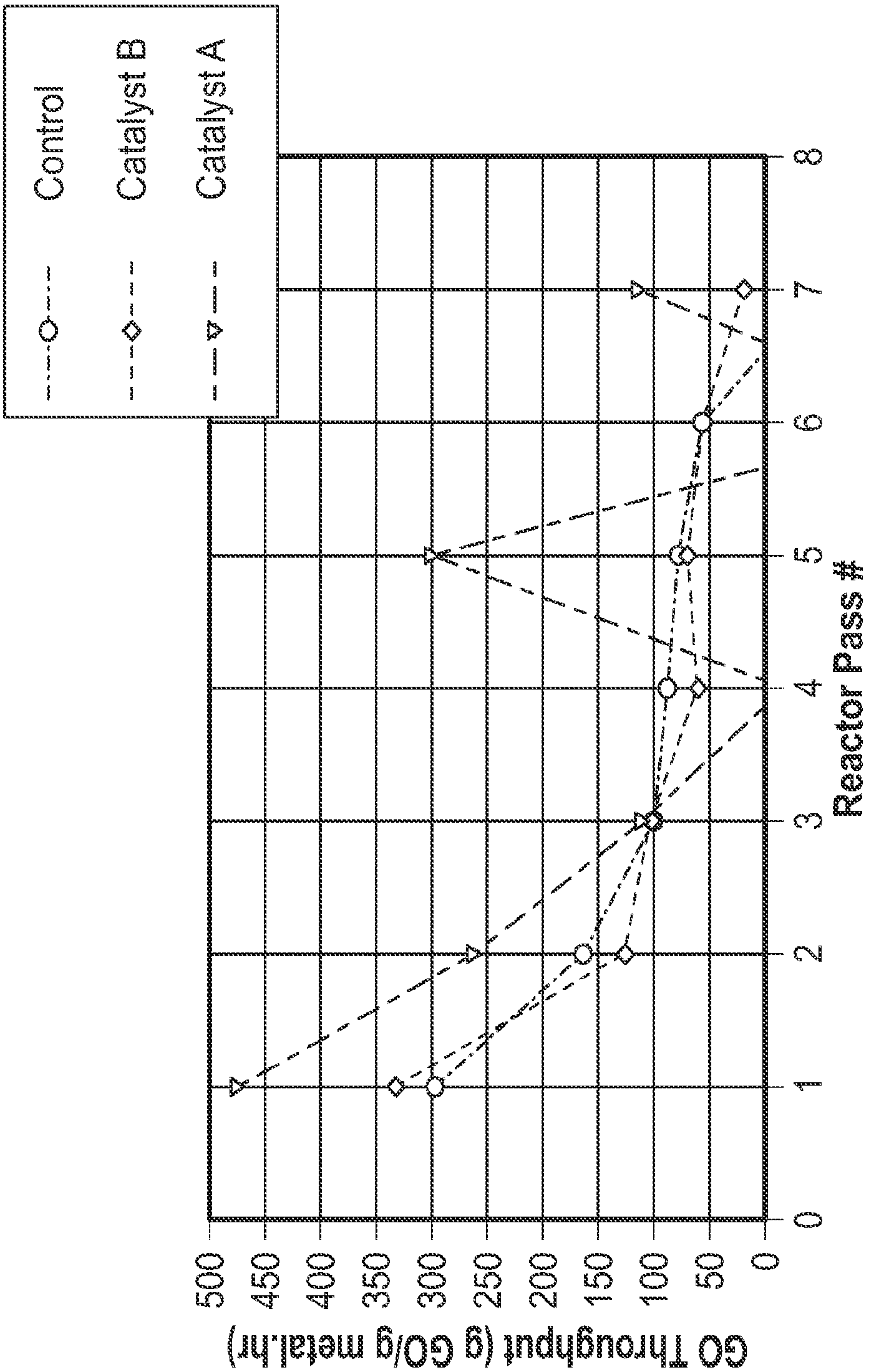
Control
Catalyst B
Catalyst A
GO Throughput (g GO/g metal.hr)
500
450
400
350
300
250
200
150
100
50
0
Reactor Pass #
0
1
2
3
4
5
6
7
8

FIG. 3

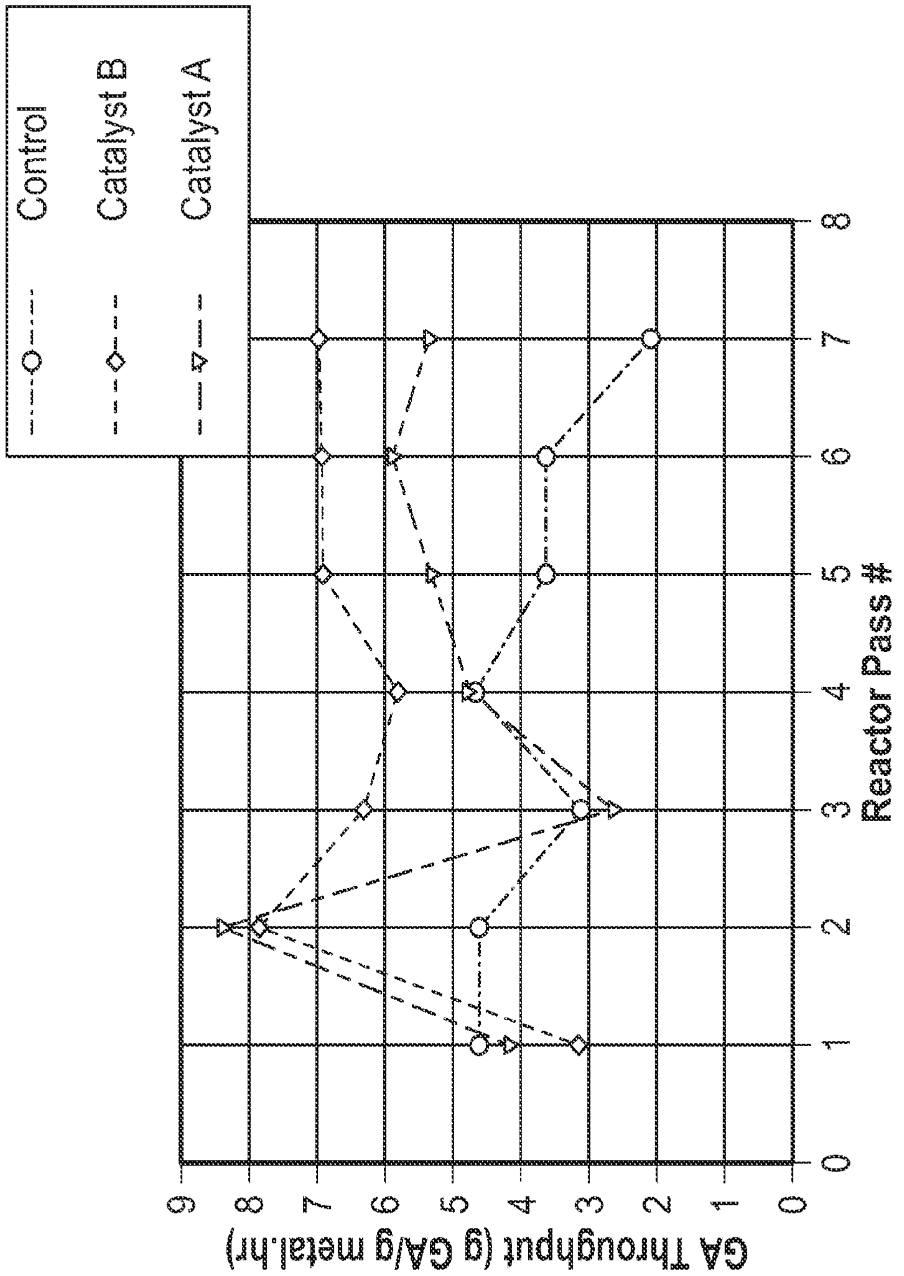
Control
Catalyst B
Catalyst A
GA Throughput (g GA/g metal.hr)
0
1
2
3
4
5
6
7
8
9
Reactor Pass #
0
1
2
3
4
5
6
7
8

FIG. 4

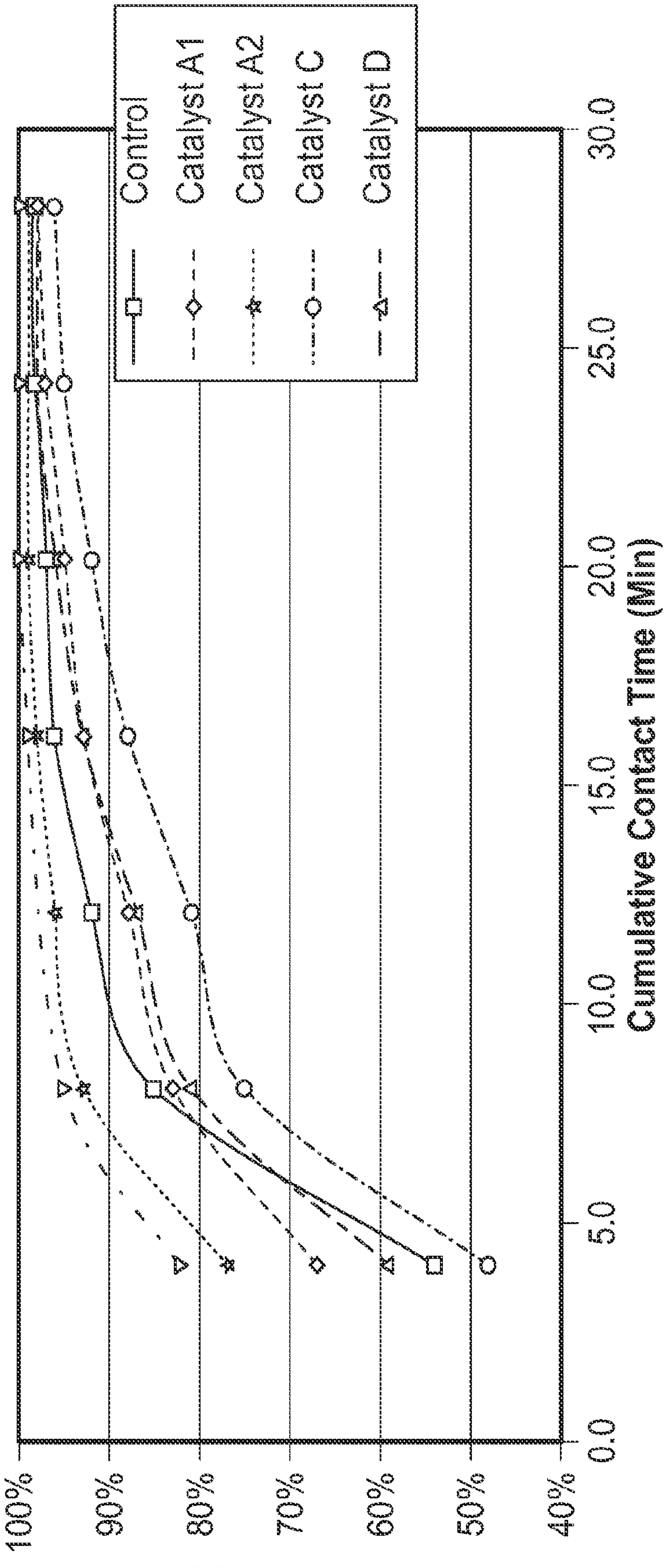
GDA Conversion
100%
90%
80%
70%
60%
50%
40%
Cumulative Contact Time (Min)
0.0
5.0
10.0
15.0
20.0
25.0
30.0
Control
Catalyst A1
Catalyst A2
Catalyst C
Catalyst D

FIG. 5

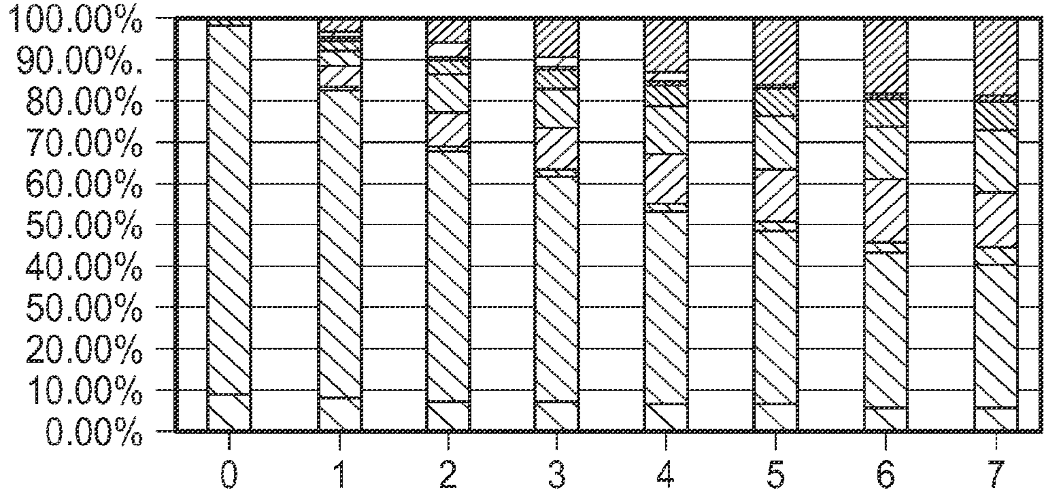
100.00%
90.00%.
80.00%
70.00%
60.00%
50.00%
40.00%
50.00%
20.00%
10.00%
0.00%
0
1
2
3
4
5
6
7
▨ Cumulative C mol % loss
▨ Cumulative non-CO2 C mol % loss
▨ Cumulative C yield of Carboxylic Acid
▨ Cumulative C yield of Carboxylic Acid B
▨ Cumulative C yield of Carboxylic Acid C
▨ Cumulative C yield of Carboxylic Acid D
▨ Cumulative C yield of 5-keto
▨ Cumulative C yield of 2-keto
▨ Cumulative C yield of GA
▨ Cumulative C yield of gulu
▨ Cumulative C yield of GO
▨ Cumulative C yield of GDA
▨ Cumulative C yield of dex

FIG. 6A

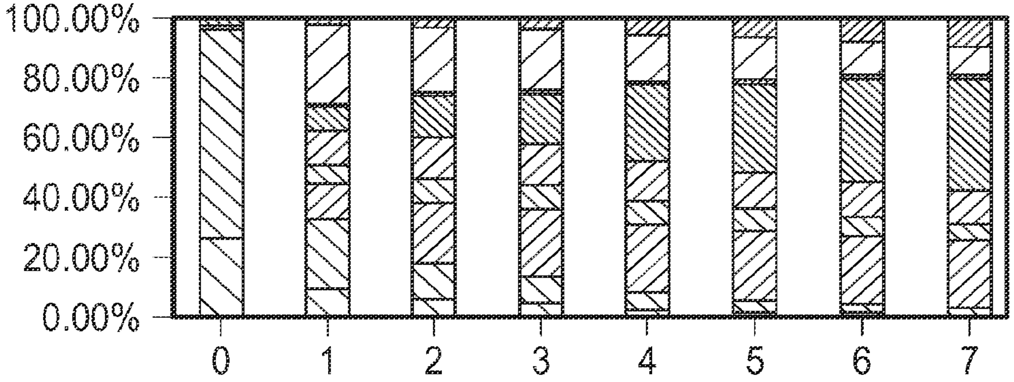
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
0
1
2
3
4
5
6
7

FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/052689

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***B01J 23/38*** (2024.01); ***B01J 23/42*** (2024.01); ***B01J 20/32*** (2024.01); *B01J 23/40* (2024.01)

CPC: ***B01J 23/38; B01J 23/42; B01J 20/3204;*** *B01J 23/40*

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010/077343 A1 (Celanese International Corporation) 07 August 2010 (07.08.2010) page 10, lines 15-20; page 30, lines 20-31; page 36, lines 15-28	1-14
Y	WO 2023/004432 A2 (Solugen, Inc.) 26 January 2023 (26.01.2023) para [0088], [0092]	1-14
L	Zhang et al. "Mixed noble metal-oxo clusters: platinum(IV)-gold(III) oxoanion [PtIV2AuIII3 O6((CH3)2AsO2)6]-" Chem. Commun., April 2023, 59, 5918-5921. page 5919, column 1, para 2	2-4
Y	Sanchez et al. "Pt catalysts supported on ion exchange resins for selective glycerol oxidation. Effect of Au incorporation" Catal. Today, 17 June 2017, 296, 35-42 page 2, column 2, para 1	12-14

☐ 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

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search **03 December 2024 (03.12.2024)**	Date of mailing of the international search report **06 February 2025 (06.02.2025)**
Name and mailing address of the ISA/US **COMMISSIONER FOR PATENTS** **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA** Facsimile No. **571-273-8300**	Authorized officer **KARI RODRIQUEZ** Telephone No. **PCT Help Desk: 571-272-4300**

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-14, directed to a method comprising: contacting a support material with a platinum salt and alkali aurate to form a metallated support; heat treating the metallated support to form a heat-treated metallated support; and reducing the heat treated metallated support to form a selective oxidation catalyst.

Group II: Claims 15-20 directed to a method, comprising: contacting a polyol with a catalyst comprising an alkali metal aurate and platinum salt on a support under conditions suitable for the formation of an oxidized product.

The inventions listed as above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires heat treating the metallated support to form a heat-treated metallated support; and reducing the heat treated metallated support to form a selective oxidation catalyst, not required by group II.

Group II requires contacting a polyol with a catalyst comprising under conditions suitable for the formation of an oxidized product; not required by group I.

Common Technical Features:

Groups I-II share the technical feature of a method comprising: contacting a support material with a platinum salt and alkali aurate to form a metallated support. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being obvious over WO 2010/077343 A1 to Celanese International Corporation (hereinafter "Celanese") in view of WO 2023/004432 A2 to Solugen, Inc. (hereinafter “Solugen”). Celanese teaches a method (page 30, lines 20-23,...The following Examples A-V describe the procedures used for the preparation of various catalysts employed...) comprising: contacting a support material with a platinum salt and alkali aurate to form a metallated support (page 30, lines 25-31,...Powdered and meshed high purity low surface area silica (94 g) of uniform particle size distribution of about 0.2 mm was dried at 120 °C in an oven under nitrogen atmosphere overnight and then cooled to room temperature. To this is added a solution of platinum nitrate (Chempur) (1.64 g) in distilled water (16 ml)...). Celanese further teaches contacting a support material with an alkali aurate to form a metallated support (page 36, lines 15-20,...The silica supports are impregnated with an aqueous solution containing sodium palladium tetrachlorate and sodium tetracholroaurate in sufficient amounts…), but does not specifically teach contacting a support material with a platinum salt and alkali aurate to form a metallated support. However, Solugen teaches in presenting catalysts for the oxidation of sugars contacting a support material with a platinum and gold species to form a selective oxidation catalyst (para [0088],... the metal catalyst comprises a metal oxidation catalyst. In such aspects, the metal oxidation catalyst is a supported transition-metal oxidation catalyst, alternatively a nanoparticle supported transition-metal oxidation catalyst. Hereinafter, these are collectively designated as the "TMC."...; para (para [0092],...The platinum and gold-containing compounds that function as a TMC may be produced by any suitable methodology. For example, the platinum and gold-containing TMCs may be produced using deposition procedures such as incipient wetness, ion-exchange, and deposition-precipitation..., it is understood the TMC can contain both platinum and gold and is an oxidation catalyst and can be made by any suitable methodology, such as those described by Celanese). Therefore, it would have been obvious to one skilled in the art to combine these references and contact a support material with both a platinum salt and an alkali aurate by routine experimentation.

As the shared technical features were known in the art, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-14**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.