

COPPER EXTRUDATE CATALYST AND APPLICATIONS FOR HYDROGENATION AND HYDROGENOLYSIS

CROSS-REFERENCE TO RELATED APPLICATIONS

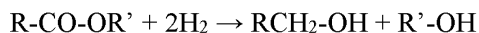
[0001] The present application claims the benefit of and priority to U.S. Patent Application No. 62/827,498, filed on April 1, 2019, the contents of which are incorporated herein by reference in their entirety.

FIELD

[0002] The present technology relates to catalysts that are useful as hydrogenolysis catalysts, and more particularly, to catalysts that are useful for hydrogenolysis of fatty acid ester compounds to form fatty alcohols. The present technology also relates to a method of preparing such catalysts and to the use of such catalysts in hydrogenolysis.

BACKGROUND

[0003] Hydrogenolysis is a chemical reaction used for conversion of esters to alcohols, illustrated generally by the following reaction:



Copper is a known catalyst for hydrogenolysis reaction. There is a continuing need to provide catalysts that maximize desired hydrogenolysis products while eliminating by-product formation and leaching of contaminants from the catalyst into the product (*e.g.*, silica). It is also desirable to provide hydrogenolysis catalysts, methods for their manufacture and methods of use, which exhibit higher catalyst activity, have longer service life, and operate at lower temperatures than existing catalysts.

SUMMARY

[0004] In one aspect, the present technology provides a hydrogenolysis catalyst that includes a catalytic component that includes copper oxide, manganese oxide, and aluminum oxide, and a binder that includes a zirconium component, where the catalyst includes at least

about 30.0 wt% copper oxide, and the catalyst is substantially free of silicon or an oxide thereof.

[0005] In one aspect, the present technology provides methods of making the catalyst for hydrogenolysis described herein is provided. The method includes mixing a catalytic component with a binder system and water to obtain a material mixture; forming the material mixture to obtain a formed material mixture; calcining the formed material mixture at a temperature, and for a time, sufficient to cure form the calcined hydrogenolysis catalyst; wherein: the catalytic component includes copper oxide, manganese oxide, and aluminum oxide; the binder system includes a zirconium component; the calcined hydrogenolysis catalyst comprises at least 30 wt% copper oxide; and the calcined hydrogenolysis catalyst is substantially free of silicon or an oxide thereof.

[0006] In another aspect, the present technology provides a catalyst for hydrogenolysis as prepared by the method described herein in any embodiment.

[0007] In an aspect, the present technology provides methods of conducting hydrogenolysis of fatty acid esters are provided, where the methods include hydrogenolysis of a fatty acid ester by contacting the fatty acid ester with a hydrogenolysis catalyst as described herein in any embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 illustrates a graph showing the %conversion to fatty alcohol of a wax ester feed using exemplary catalyst 5 and comparative reference catalyst containing silica according to the procedure in Example 2.

[0009] FIG. 2 illustrates a graph showing the cumulative intrusion (“pore volume,” cm^3/g) as a function of pore diameter ($\text{\AA}$) for exemplary catalysts 1A.

[0010] FIG. 3 illustrates a graph showing the incremental pore volume as a function of pore diameter ($\text{\AA}$) for exemplary catalyst 1A.

[0011] FIG. 4 illustrates a graph showing the X-ray powder diffraction spectra for exemplary catalyst 5.

DETAILED DESCRIPTION

[0012] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and may be practiced with any other embodiment(s).

[0013] As used herein, “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, “about” will mean up to plus or minus 10% of the particular term.

[0014] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein may be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, “such as”) provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential.

[0015] In general, “substituted” refers to an alkyl, alkenyl, cycloalkyl, or aryl group, as defined below (*e.g.*, an alkyl group) in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to a carbon(s) or hydrogen(s) atom

are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group will be substituted with one or more substituents, unless otherwise specified. In some embodiments, a substituted group is substituted with 1, 2, 3, 4, 5, or 6 substituents. Examples of substituent groups include: halogens (*i.e.*, F, Cl, Br, and I); hydroxyls; alkoxy, alkenoxy, alkynoxy, aryloxy, aralkyloxy, heterocycloxy, and heterocyclylalkoxy groups; carbonyls (oxo); carboxyls; esters; urethanes; oximes; hydroxylamines; alkoxyamines; aralkoxyamines; thiols; sulfides; sulfoxides; sulfones; sulfonyls; sulfonamides; amines; N-oxides; hydrazines; hydrazides; hydrazones; azides; amides; ureas; amidines; guanidines; enamines; imides; isocyanates; isothiocyanates; cyanates; thiocyanates; imines; nitro groups; nitriles (*i.e.*, CN); and the like.

[0016] As used herein, “alkyl” groups include straight chain and branched alkyl groups having from 1 to about 20 carbon atoms, and typically from 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. As employed herein, “alkyl groups” include cycloalkyl groups as defined below. Alkyl groups may be substituted or unsubstituted. Examples of straight chain alkyl groups include methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, sec-butyl, t-butyl, neopentyl, and isopentyl groups. Representative substituted alkyl groups may be substituted one or more times with, for example, amino, thio, hydroxy, cyano, alkoxy, and/or halo groups such as F, Cl, Br, and I groups. As used herein the term haloalkyl is an alkyl group having one or more halo groups. In some embodiments, haloalkyl refers to a per-haloalkyl group.

[0017] Alkenyl groups are straight chain, branched or cyclic alkyl groups having 2 to about 20 carbon atoms, and further including at least one double bond. In some embodiments alkenyl groups have from 2 to 12 carbons, or, typically, from 2 to 8 carbon atoms. Alkenyl groups may be substituted or unsubstituted. Alkenyl groups include, for instance, vinyl, propenyl, 2-butenyl, 3-butenyl, isobutenyl, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl groups among others. Alkenyl groups may be substituted similarly to alkyl groups. Divalent alkenyl groups, *i.e.*, alkenyl groups with two points of attachment, include, but are not limited to, CH-CH=CH₂, C=CH₂, or C=CHCH₃.

[0018] Reference to an “alkali metal component” means a material used to deliver an alkali metal, for example metal oxides, hydroxides, or carbonates, which may be in powder form or in an aqueous solution.

[0019] Reference to “binder” or “binder system” means a material suitable for binding components together to form a catalyst in a shape. Generally, the binder component is extrudable and used to form extruded catalysts and/or the binder component is able to form tableted catalysts. Thus, the binder or binder system, may include zirconium oxide, alumina, and mixtures thereof.

[0020] All references to pore diameters and pore volumes in the specification and claims of this application are based upon measurements utilizing mercury porosimetry. A typical method is described by R. Anderson, *Experimental Methods in Catalytic Research*, Academic Press, New York, 1968. The pore volumes are determined utilizing the catalysts in their oxide forms. That is, the pore diameters and pore volumes reported herein are obtained for the catalyst after calcination, but prior to any reduction of the oxide. Those skilled in the art often refer to the catalyst containing the metal oxides as the “oxide” or “oxide precursor” form of the catalyst.

[0021] The catalysts of the present technology are based upon a calcined co-precipitated mixture of copper oxide-alumina oxide and manganese oxide and zirconium acetate solution. Formation of the catalysts includes mixing and extruding of the precursor materials, followed by drying and calcination. Other additives may be included in the mixtures to form the catalysts.

[0022] The copper extrudate catalysts described herein exhibit improved catalytic hydrogenolysis activity over and equivalent selectivity for fatty alcohol processes than current commercially available catalysts that include commonly used binders (*e.g.*, calcium silicate, sodium silicate, silica sol, clay, *etc.*). These commonly used binders contain silica that may be leached out under reaction conditions, especially for fatty alcohol that impact product quality by the silica purity. The catalysts of the present technology as described herein, include zirconium based binder system (*e.g.*, ZrO_2 or $\text{ZrO}_2\text{-Al}_2\text{O}_3$) and do not contain

silica that could be leached to alcohol product in fatty alcohol production processes. Surprisingly, the inventors discovered the hydrogenolysis catalysts of the present technology exhibit strong mechanical strength, high activity for hydrogenation/hydrogenolysis reactions for fatty alcohol production, and improved selectivity across a broader operation temperature range compared to current commercial catalysts.

[0023] Provided are hydrogenolysis catalysts that are useful for the production of fatty alcohols from fatty acid esters. Methods of making and using the same are also provided. These catalysts are formed from a catalytic component and a binder, which are processed together, for example, by extrusion or by tableting, to form the catalyst. The catalytic component includes a copper oxide, manganese oxide, and aluminum oxide. The binder includes a zirconium component (*e.g.*, ZrO_2 or $\text{ZrO}_2\text{-Al}_2\text{O}_3$).

Catalyst Composition

[0024] In one aspect, a hydrogenolysis catalyst that includes a catalytic component that includes copper oxide, manganese oxide, and aluminum oxide, and a binder that includes a zirconium component, where the catalyst includes at least about 30.0 wt% copper oxide, and the catalyst is substantially free of silicon or an oxide thereof.

[0025] In any embodiment herein, the hydrogenolysis catalyst may be substantially free of silicon or an oxide thereof. In addition, the hydrogenolysis catalysts may be free of silicon or an oxide thereof in order to reduce exposure to such material. As used herein, the hydrogenolysis catalyst may be free of such materials if their presence is in an amount that does not materially affect the physical, chemical and catalytic characteristics of the catalysts when compared to those which are completely free of such materials. Preferably, if present, such materials will be present in trace amounts, but in amounts not greater than about 1.5% by weight, more preferably not greater than 0.5% weight. For example, the phrase “substantially free of silicon or oxides thereof” refers to less than about 1.5 wt%, less than about 1 wt%, less than about 0.5 wt%, less than about 0.1 wt%, less than about 0.01 wt%, or 0 wt% based on the total weight of the hydrogenolysis catalyst. In any embodiment herein, the hydrogenolysis catalyst may be free of silicon or an oxide thereof.

[0026] In any embodiment herein, the hydrogenolysis catalyst may include at least 30 wt% of copper oxide. For example, in any embodiment herein, the copper oxide may be present in an amount from about 35 wt% to about 75 wt% by weight of the hydrogenolysis catalyst. Suitable amounts of the copper oxide may include, but are not limited to, from about 35 wt% to about 75 wt%, about 40 wt% to about 65 wt%, about 45 wt% to about 55 wt%, or any range including and/or in between any two of the preceding values. For example, the amount of the copper oxide may include, but is not limited to, about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, or any range including and/or in between any two of the preceding values.

[0027] In any embodiment herein, the hydrogenolysis catalyst includes manganese oxide in an amount from about 0 wt% to about 10 wt% by weight of the hydrogenolysis catalyst. Suitable amounts of the manganese oxide include, but are not limited to, from about 0 wt% to about 10 wt%, about 3 wt% to about 10 wt%, about 5 wt% to about 10 wt%, about 6 wt% to about 9 wt%, or any range including and/or in between any two of the preceding values. For example, the manganese oxide may be present in an amount of about 1 wt%, about 2 wt%, about 3 wt%, about 4 wt%, about 5 wt%, about 6 wt%, about 7 wt%, about 8 wt%, about 9 wt%, about 10 wt%, or any range including and/or in between any two of the preceding values.

[0028] In any embodiment herein, the hydrogenolysis catalyst includes aluminum oxide in an amount from about 15 wt% to about 40 wt% by weight of the hydrogenolysis catalyst. Suitable amounts of the aluminum oxide may include, but are not limited to, from about 15 wt% to about 40 wt%, about 20 wt% to about 35 wt%, about 25 wt% to about 35 wt%, or any range including and/or in between any two of the preceding values. For example, the aluminum oxide may be present in an amount of about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, about 40 wt%, or any range including and/or in between any two of the preceding values.

[0029] The hydrogenolysis catalyst may include a binder, where the binder includes a zirconium component. In any embodiment herein, the zirconium component may be present

in the reduced metal or oxide forms or as a precursor to such forms and in one or more oxidation states as discussed above. For example, the zirconium component is present in the form of zirconium oxide (*e.g.*, ZrO_2). In any embodiment herein, the zirconium component is present in an amount from about 4 wt% to about 15 wt% by weight of the hydrogenolysis catalyst. Suitable amounts of the zirconium component include, but are not limited to, from about 4 wt% to about 15 wt%, about 5 wt% to about 12 wt%, about 5 wt% to about 8 wt%, or any range including and/or in between any two of the preceding values. For example, the zirconium component may be present in an amount of about 4 wt%, about 5 wt%, about 6 wt%, about 7 wt%, about 8 wt%, about 9 wt%, about 10 wt%, about 11 wt%, about 12 wt%, about 13 wt%, about 14 wt%, about 15 wt%, or any range including and/or in between any two of the preceding values.

[0030] In any embodiment herein, the binder may further include alumina. For example, the binder may be present as a zirconium oxide – aluminum oxide ($\text{ZrO}_2\text{-Al}_2\text{O}_3$) binder system.

[0031] In any embodiment herein, the hydrogenolysis catalyst may include from about 45% to about 55% of copper oxide, about 5 wt% to about 12 wt% manganese oxide, about 20 wt% to about 35 wt% aluminum oxide, and about 5 wt% to about 12 wt% zirconium oxide.

[0032] The hydrogenolysis catalyst as described herein in any embodiment may further include an alkali metal component. In any embodiment herein, the alkali metal is selected from the group consisting of sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and combinations thereof. These metals may be present in the reduced metal or oxide forms or as precursors to such forms and in one or more oxidation states as discussed above. For example, the alkali metal component may include sodium in the form of disodium oxide. In any embodiment herein, the alkali metal may be present in an amount from about 0 wt% to about 1 wt% by weight of the hydrogenolysis catalyst. For example, the alkali metal component may be present in an amount of about 0.01 wt%, 0.05 wt%, about 0.1 wt%, about 0.2 wt%, about 0.3 wt%, about 0.4 wt%, about 0.5 wt%, about 0.6 wt%, about 0.7 wt%, about

0.8 wt%, about 0.9 wt%, about 1 wt%, or any range including and/or in between any two of the preceding values.

[0033] The hydrogenolysis catalysts may be provided as tablets or extrudates. One way to process the blend of all of the ingredients is to extrude it through a shaping orifice to form an extruded catalyst body, or extrudate. Other catalyst bodies may be shaped into spheres or any other convenient formation. Another way is to tablet the catalysts. For example, the hydrogenolysis catalyst may be extruded or tableted in sizes including, but not limited to, 1/8" by 1/8", 3/16" by 3/16", 1/4" by 1/4", 3/16" by 1/4", 1/4" by 1/16", or 1/8" by 1/16".

[0034] In any embodiment herein, the hydrogenolysis catalyst may be provided in tableted or extruded form, and may exhibit a crush strength in an amount from about 1.0 lbs/mm to about 6.0 lbs/mm. For example, the hydrogenolysis catalyst may exhibit a side crush strength of about 1.0 lbs/mm, about 1.5 lbs/mm, about 2.0 lbs/mm, about 2.5 lbs/mm, about 3.0 lbs/mm, about 3.5 lbs/mm, about 4.0 lbs/mm, about 4.5 lbs/mm, about 5.0 lbs/mm, about 5.5 lbs/mm, about 6.0 lbs/mm, or any range including and/or in between any two of the preceding values. In some embodiments, the catalyst may exhibit a side crush strength from about 3.5 lbs/mm to about 5.0 lbs/mm. In any embodiment, the hydrogenolysis catalyst after use in one or more catalytic process (*i.e.*, spent catalyst) may exhibit a crush strength as described herein.

[0035] In any embodiment herein, the hydrogenolysis catalyst may be calcined. In any embodiment herein, the catalyst is a calcined and extruded catalyst.

[0036] Specifically, these hydrogenolysis catalysts contain a significant amount of mesoporosity. Reference to "mesoporosity" or "mesopore" means those pores having a pore diameter in the range of about 50 to about 1000 Angstroms (Å). For example, the hydrogenolysis catalysts may have a pore diameter from about 50 Å to about 1000 Å, about 75 Å to about 1000 Å, about 100 Å to about 900 Å, about 150 Å to about 850 Å, about 300 Å to about 800 Å, or any range including and/or in between any two of the preceding values.

[0037] In any embodiment herein, the hydrogenolysis catalyst may have a pore volume that is greater than or equal to $0.2 \text{ cm}^3/\text{g}$. For example, the hydrogenolysis catalyst may have a pore volume of about $0.2 \text{ cm}^3/\text{g}$, about $0.25 \text{ cm}^3/\text{g}$, about $0.3 \text{ cm}^3/\text{g}$, about $0.35 \text{ cm}^3/\text{g}$, about $0.4 \text{ cm}^3/\text{g}$, about $0.45 \text{ cm}^3/\text{g}$, about $0.5 \text{ cm}^3/\text{g}$, about $0.55 \text{ cm}^3/\text{g}$, about $0.6 \text{ cm}^3/\text{g}$, about $0.65 \text{ cm}^3/\text{g}$, about $0.7 \text{ cm}^3/\text{g}$, about $0.75 \text{ cm}^3/\text{g}$, about $0.8 \text{ cm}^3/\text{g}$, or any range including and/or in between any two of the preceding values.

[0038] In any embodiment herein, the hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 to about 1.5 g/cm^3 . For example, the hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 , about 0.9 g/cm^3 , about 1.0 g/cm^3 , about 1.2 g/cm^3 , about 1.3 g/cm^3 , about 1.4 g/cm^3 , about 1.5 g/cm^3 , or any range including and/or in between any two of the preceding values. In any embodiment herein, the hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 to about 1.5 g/cm^3 , about 0.8 g/cm^3 to about 1 g/cm^3 , about 0.8 g/cm^3 to about 0.95 g/cm^3 , or any range including and/or in between any two of the preceding values. In any embodiment herein, the hydrogenolysis catalyst may be in tablet form and have a packed bulk density of about 1.0 g/cm^3 , about 1.1 g/cm^3 , about 1.2 g/cm^3 , about 1.3 g/cm^3 , about 1.4 g/cm^3 , about 1.5 g/cm^3 , or any range including and/or in between any two of the preceding values.

[0039] In any embodiment herein, the hydrogenolysis catalyst may have a Brunauer-Emmett-Teller ("BET") surface area of about $15 \text{ m}^2/\text{g}$ to about $70 \text{ m}^2/\text{g}$. For example, the hydrogenation catalyst has a BET surface area of about $15 \text{ m}^2/\text{g}$, about $20 \text{ m}^2/\text{g}$, about $25 \text{ m}^2/\text{g}$, about $30 \text{ m}^2/\text{g}$, about $35 \text{ m}^2/\text{g}$, about $40 \text{ m}^2/\text{g}$, about $45 \text{ m}^2/\text{g}$, about $50 \text{ m}^2/\text{g}$, about $55 \text{ m}^2/\text{g}$, about $60 \text{ m}^2/\text{g}$, about $65 \text{ m}^2/\text{g}$, about $70 \text{ m}^2/\text{g}$, or any range including and/or in between any two of the preceding values. In any embodiment herein, the hydrogenation catalyst has a BET surface area of about $15 \text{ m}^2/\text{g}$ to about $70 \text{ m}^2/\text{g}$, about $25 \text{ m}^2/\text{g}$ to about $65 \text{ m}^2/\text{g}$, about $45 \text{ m}^2/\text{g}$ to about $60 \text{ m}^2/\text{g}$, about $50 \text{ m}^2/\text{g}$ to about $60 \text{ m}^2/\text{g}$, or any range including and/or in between any two of the preceding values.

[0040] In any embodiment herein, the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2θ peaks at 31.1° , 36.0° , 36.8° , 38.8° , 44.6° , 48.8° , 61.7° , 64.9° , 68.1° . In any embodiment herein, the hydrogenolysis

catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2 θ peaks at 18.9°, 31.1°, 32.5°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 53.6°, 58.3°, 59.1°, 61.7°, 64.9°, 66.8°, 68.1°, 72.2°, 75.1°, and 77.0°.

[0041] In any embodiment herein, the hydrogenolysis catalyst has a copper oxide crystallite size of about 60 Å to about 250 Å. For example, the calcined hydrogenolysis catalyst may have a copper oxide crystallite size of about 60 Å, about 65 Å, about 70 Å, about 75 Å, about 80 Å, about 85 Å, about 90 Å, about 95 Å, about 100 Å, about 105 Å, about 110 Å, about 120 Å, about 125 Å, about 130 Å, about 135 Å, about 140 Å, about 145 Å, about 150 Å, about 155 Å, about 160 Å, about 165 Å, about 170 Å, about 175 Å, about 180 Å, about 185 Å, about 190 Å, about 195 Å, about 200 Å, about 205 Å, about 210 Å, about 215 Å, about 220 Å, about 225 Å, about 230 Å, about 235 Å, about 240 Å, about 245 Å, about 250 Å, or any range including and/or in between any two of the preceding values. In any embodiment, the calcined hydrogenation catalyst may have a copper oxide crystallite size of about 200 Å to about 220 Å.

[0042] Method of Making

[0043] In one aspect, methods of making the catalyst for hydrogenolysis described herein is provided. The method includes mixing a catalytic component with a binder system and water to obtain a material mixture; forming the material mixture to obtain a formed material mixture; calcining the formed material mixture at a temperature, and for a time, sufficient to cure form the calcined hydrogenolysis catalyst; wherein: the catalytic component includes copper oxide, manganese oxide, and aluminum oxide; the binder system includes a zirconium component; the calcined hydrogenolysis catalyst comprises at least 30 wt% copper oxide; and the calcined hydrogenolysis catalyst is substantially free of silicon or an oxide thereof.

[0044] In any embodiment herein, the calcined hydrogenolysis catalyst is free of silicon or an oxide thereof.

[0045] In any embodiment herein, the catalytic component includes a mixture of copper oxide, manganese oxide, and aluminum oxide provided in a the form of a pre-calcined

powder. The pre-calcined powder may be calcined at a temperature from about 300°C to about 750°C. Suitable calcination temperatures may include, but are not limited to, about 300°C, about 350°C, about 400°C, about 450°C, about 500°C, about 550°C, about 600°C, about 650°C, about 700°C, about 750°C, or any range including and/or in between any two of the preceding values.

[0046] In any embodiment herein, the zirconium component may include zirconium acetate. In any embodiment herein, the binder may further include alumina.

[0047] In any embodiment herein, the method may further including mixing one or more extrusion aids in to the material mixture. Suitable extrusion aids may include, but are not limited to, a polymeric polysaccharide, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, or a mixture of two or more thereof. For example, the extrusion aid may be selected from a commercially available extrusion aid, including but not limited to, Zusoplast, Methocel, Walocel, or a mixture thereof.

[0048] The method includes calcining the material mixture at a temperature, and for a time, sufficient to cure form a calcined hydrogenolysis catalyst. In any embodiment herein, the calcining may occur at a temperature from about 200°C to about 1000°C. For example, the calcining may occur at a temperature of about 200°C, about 250°C, about 300°C, about 350°C, about 400°C, about 450°C, about 500°C, about 550°C, about 600°C, about 650°C, about 700°C, about 750°C, about 800°C, about 850°C, about 900°C, about 950°C, about 1000°C, or any range including and/or in between any two of the preceding values. In any embodiment herein, the calcining temperature may be from about 400°C to about 650°C, from about 400°C to about 550°C, or from about 450°C to about 500°C. In any embodiment herein, the calcination may occur over a period from about 0.5 h to about 4 h. In any embodiment, the calcination may occur over a period of about 0.5 h, about 1 h, about 1.5 h, about 2 h, about 2.5 h, about 3 h, about 3.5 h, about 4 h, or any range including and/or in between any two of the preceding values.

[0049] In any embodiment herein, forming the material mixture may be by extrusion, tableting, or spherization. In any embodiment herein, the forming may be extruding or

tableting the material mixture to obtain the formed material mixture. For example, the formed material mixture may be extruded or tableted in sizes including, but not limited to, 1/8" by 1/8", 3/16" by 3/16", 1/4" by 1/4", 3/16" by 1/4", 1/4" by 1/16", or 1/8" by 1/16". In any embodiment herein, the forming may include spherization of the material mixture to obtain the formed material mixture.

[0050] In any embodiment herein, the hydrogenolysis catalyst provided in tableted or extruded form, may exhibit a crush strength in an amount from about 1.0 lbs/mm to about 6.0 lbs/mm. For example, the catalyst may exhibit a side crush strength of about 1.0 lbs/mm, about 1.5 lbs/mm, about 2.0 lbs/mm, about 2.5 lbs/mm, about 3.0 lbs/mm, about 3.5 lbs/mm, about 4.0 lbs/mm, about 4.5 lbs/mm, about 5.0 lbs/mm, about 5.5 lbs/mm, about 6.0 lbs/mm, or any range including and/or in between any two of the preceding values. In some embodiments, the catalyst may exhibit a side crush strength from about 3.5 lbs/mm to about 5.0 lbs/mm.

[0051] The method may further include removing at least some of the water from the wet material mixture prior to calcining. For example, the removing may include drying the wet material mixture. In any embodiment herein, the removing may be conducted at a temperature including, but not limited to, from about 40°C to about 150°C. For example, the removing may occur at a temperature of about 40°C, about 50°C, about 60 °C, about 70°C, about 80°C, about 90°C, about 100°C, about 110°C, about 120°C, about 130°C, about 140°C, about 150°C, or any range including and/or in between any two of the preceding values.

[0052] In any embodiment herein, the calcined hydrogenolysis catalyst may include at least 30 wt% of copper oxide. For example, in any embodiment herein, the copper oxide may be present in an amount from about 35 wt% to about 75 wt% by weight of the calcined hydrogenolysis catalyst. Suitable amounts of the copper oxide may include, but are not limited to, from about 35 wt% to about 75 wt%, about 40 wt% to about 65 wt%, about 45 wt% to about 55 wt%, or any range including and/or in between any two of the preceding values. For example, the amount of the copper oxide may include, but is not limited to, about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65

wt%, about 70 wt%, about 75 wt%, or any range including and/or in between any two of the preceding values.

[0053] In any embodiment herein, the calcined hydrogenolysis catalyst includes manganese oxide in an amount from about 0 wt% to about 10 wt% by weight of the calcined hydrogenolysis catalyst. Suitable amounts of the manganese oxide include, but are not limited to, from about 0 wt% to about 10 wt%, about 3 wt% to about 10 wt%, about 5 wt% to about 10 wt%, about 6 wt% to about 9 wt%, or any range including and/or in between any two of the preceding values. For example, the manganese oxide may be present in an amount of about 1 wt%, about 2 wt%, about 3 wt%, about 4 wt%, about 5 wt%, about 6 wt%, about 7 wt%, about 8 wt%, about 9 wt%, about 10 wt%, or any range including and/or in between any two of the preceding values.

[0054] In any embodiment herein, the calcined hydrogenolysis catalyst includes aluminum oxide in an amount from about 15 wt% to about 40 wt% by weight of the calcined hydrogenolysis catalyst. Suitable amounts of the aluminum oxide may include, but are not limited to, from about 15 wt% to about 40 wt%, about 20 wt% to about 35 wt%, about 25 wt% to about 35 wt%, or any range including and/or in between any two of the preceding values. For example, the aluminum oxide may be present in an amount of about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, about 40 wt%, or any range including and/or in between any two of the preceding values.

[0055] In any embodiment herein, the zirconium component is present in the calcined hydrogenolysis catalyst in an amount from about 4 wt% to about 15 wt% by weight of the calcined hydrogenolysis catalyst. Suitable amounts of the zirconium component include, but are not limited to, from about 4 wt% to about 15 wt%, about 5 wt% to about 12 wt%, about 5 wt% to about 8 wt%, or any range including and/or in between any two of the preceding values. For example, the zirconium component may be present in an amount of about 4 wt%, about 5 wt%, about 6 wt%, about 7 wt%, about 8 wt%, about 9 wt%, about 10 wt%, about 11 wt%, about 12 wt%, about 13 wt%, about 14 wt%, about 15 wt%, or any range including and/or in between any two of the preceding values.

[0056] In any embodiment herein, the binder may further include alumina. For example, the binder may be present as a zirconium oxide – aluminum oxide ($\text{ZrO}_2\text{-Al}_2\text{O}_3$) binder system.

[0057] In any embodiment herein, the calcined hydrogenolysis catalyst may include from about 45% to about 55% of copper oxide, about 5 wt% to about 12 wt% manganese oxide, about 20 wt% to about 35 wt% aluminum oxide, and about 5 wt% to about 12 wt% zirconium oxide.

[0058] The calcined hydrogenolysis catalysts may have a pore diameter in the range of about 150 to about 1000 Angstroms ($\text{\AA}$). For example, the calcined hydrogenolysis catalysts may have a pore diameter from about 150 $\text{\AA}$ to about 1500 $\text{\AA}$, about 200 $\text{\AA}$ to about 1000 $\text{\AA}$, about 225 $\text{\AA}$ to about 800 $\text{\AA}$, about 250 $\text{\AA}$ to about 700 $\text{\AA}$, about 300 $\text{\AA}$ to about 600 $\text{\AA}$, or any range including and/or in between any two of the preceding values.

[0059] In any embodiment herein, the calcined hydrogenolysis catalyst may have a pore volume that is greater than or equal to 0.2 cm^3/g . For example, the calcined hydrogenolysis catalyst may have a pore volume of about 0.2 cm^3/g , about 0.25 cm^3/g , about 0.3 cm^3/g , about 0.35 cm^3/g , about 0.4 cm^3/g , about 0.45 cm^3/g , about 0.5 cm^3/g , about 0.55 cm^3/g , about 0.6 cm^3/g , about 0.65 cm^3/g , about 0.7 cm^3/g , about 0.75 cm^3/g , about 0.8 cm^3/g , or any range including and/or in between any two of the preceding values.

[0060] In any embodiment herein, the calcined hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 to about 1.5 g/cm^3 . For example, the calcined hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 , about 0.9 g/cm^3 , about 1.0 g/cm^3 , about 1.1 g/cm^3 , about 1.2 g/cm^3 , about 1.3 g/cm^3 , about 1.4 g/cm^3 , about 1.5 g/cm^3 , or any range including and/or in between any two of the preceding values. In any embodiment herein, the calcined hydrogenolysis catalyst may have a packed bulk density of about 0.8 g/cm^3 to about 1.5 g/cm^3 , about 0.8 g/cm to about 1 g/cm^3 , about 0.8 g/cm^3 to about 0.95 g/cm^3 , or any range including and/or in between any two of the preceding values. In any embodiment herein, the calcined hydrogenolysis catalyst may be in tablet form and have a packed bulk density of about 1.0 g/cm^3 , about 1.1 g/cm^3 , about 1.2 g/cm^3 , about 1.3 g/cm^3 ,

about 1.4 g/cm³, about 1.5 g/cm³, or any range including and/or in between any two of the preceding values.

[0061] In any embodiment herein, the calcined hydrogenolysis catalyst may have a BET surface area of about 15 m²/g to about 70 m²/g. For example, the calcined hydrogenation catalyst has a BET surface area of about 15 m²/g, about 20 m²/g, about 25 m²/g, about 30 m²/g, about 35 m²/g, about 40 m²/g, about 45 m²/g, about 50 m²/g, about 55 m²/g, about 60 m²/g, about 65 m²/g, about 70 m²/g, or any range including and/or in between any two of the preceding values. In any embodiment herein, the calcined hydrogenation catalyst has a BET surface area of about 15 m²/g to about 70 m²/g, about 25 m²/g to about 65 m²/g, about 45 m²/g to about 60 m²/g, about 50 m²/g to about 60 m²/g, or any range including and/or in between any two of the preceding values.

[0062] In any embodiment herein, the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2θ peaks at 31.1°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 61.7°, 64.9°, 68.1°. In any embodiment herein, the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2θ peaks at 18.9°, 31.1°, 32.5°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 53.6°, 58.3°, 59.1°, 61.7°, 64.9°, 66.8°, 68.1°, 72.2°, 75.1°, and 77.0°.

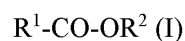
[0063] In any embodiment herein, the calcined hydrogenolysis catalyst has a copper oxide crystallite size of about 60 Å to about 250 Å. For example, the calcined hydrogenolysis catalyst may have a copper oxide crystallite size of about 60 Å, about 65 Å, about 70 Å, about 75 Å, about 80 Å, about 85 Å, about 90 Å, about 95 Å, about 100 Å, about 105 Å, about 110 Å, about 120 Å, about 125 Å, about 130 Å, about 135 Å, about 140 Å, about 145 Å, about 150 Å, about 155 Å, about 160 Å, about 165 Å, about 170 Å, about 175 Å, about 180 Å, about 185 Å, about 190 Å, about 195 Å, about 200 Å, about 205 Å, about 210 Å, about 215 Å, about 220 Å, about 225 Å, about 230 Å, about 235 Å, about 240 Å, about 245 Å, about 250 Å, or any range including and/or in between any two of the preceding values. In any embodiment, the calcined hydrogenolysis catalyst may have a copper oxide crystallite size of about 200 Å to about 220 Å.

[0064] In another aspect, the present technology provides a catalyst for hydrogenolysis as prepared by the method described herein in any embodiment.

[0065] **Methods of Use**

[0066] In an aspect, methods of conducting hydrogenolysis of fatty acid esters are provided, where the methods include hydrogenolysis of a fatty acid ester by contacting the fatty acid ester with a hydrogenolysis catalyst as described herein in any embodiment.

[0067] In any embodiment herein, the fatty acid ester may be a compound of Formula I:



wherein R^1 and R^2 are each independently a branched or unbranched C_1 to C_{24} alkyl or a branched or unbranched C_2 to C_{24} alkenyl.

[0068] In any embodiment herein, R^1 and R^2 may each independently be a C_{10} to C_{14} branched or unbranched alkyl or a C_{10} to C_{14} branched or unbranched alkenyl. In any embodiment herein, R^1 and R^2 may each independently be a C_{12} to C_{14} branched or unbranched alkyl. In some embodiments herein, when R^1 is a C_{10} to C_{18} branched or unbranched alkyl or a C_{10} to C_{18} branched or unbranched alkenyl, R^2 may be a C_1 to C_6 alkyl. For example, R^2 may be a C_1 to C_4 alkyl. In any embodiment herein, R^2 may be a methyl.

[0069] In any embodiment herein, R^1 and R^2 together may be represented by a C_1 to C_{24} alkyl or C_1 to C_{24} alkenyl such that the compound represented by Formula (I) forms a wax ester having a total of 12 to 36 carbon atoms.

[0070] The hydrogenolysis catalysts of the present technology exhibits improved activity and selectivity for fatty alcohol formation at lower temperatures compared to current commercially available catalyst, such as catalyst containing silicon or oxides thereof (FIG. 1). In any embodiment herein, the method may be conducted at a temperature of at least about 170°C . For example, the temperature may be from about 170°C to about 250°C , about 170°C to about 220°C , or about 170°C to about 180°C . Suitable temperatures include, but are not

limited to, about 170°C, about 175°C, about 180°C, about 185°C, about 190°C, about 195°C, about 200°C, about 205°C, about 210°C, about 215°C, about 220°C, about 225°C, about 230°C, about 235°C, about 240°C, about 245°C, about 250°C, or any range including and/or in between any two of the preceding values.

[0071] The present invention, thus generally described, will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting of the present invention.

EXAMPLES

[0072] **Example 1-5:** A series of copper catalysts having varying levels of copper oxide, manganese oxide, aluminum oxide, and zirconium oxide were prepared as follows. Calcined copper manganese aluminum powder, zirconium acetate, alumina, organic binder (*i.e.*, Zusoplast), and water were mixed and kneaded. The mixture was then extruded with an extruder and dried. The extrudates were then calcined at 250° to 1000°C. As shown in FIG. 2, the exemplary catalyst 1A exhibited pore volumes of about 0.1-0.35 cm³/g at pore diameters ranging from 100-1000 Å. FIG. 3 shows exemplary catalyst 1A exhibited a mesoporosity between 50 to 1000 Å. The catalysts had the properties outlined in Table 1, where “3F” means 3-fluted or tri-lobe.

[0073] Catalysts 1E, 3A, 4A, 5, and a reference catalyst containing copper on silica were characterized by temperature-programmed-reduction and Cu metal dispersion. The results are summarized in the table below.

Catalyst	Temperature-Programed Reduction (TPR) Peak Temperature, °C	Dispersion, %
1E	140	2.4
3A	132	2.4
4A	132	2.3
5	136	2.6
Ref. Catalyst	155	1.8

Temperature-programmed-reduction peak temperatures is an indication of easiness of catalyst reduction by hydrogen. Lower peak temperature catalysts will be reduced easier under the same reduction conditions. As shown in the table above, Catalysts 1E, 3A, 4A, and 5

exhibited lower peak temperatures than the reference catalyst. Also, Catalysts 1E, 3A, 4A, and 5 exhibited higher copper metal dispersion than the reference catalyst. Copper metal dispersion is the ratio of surface copper metal to the total copper metal. Higher copper dispersion means smaller copper metal crystallite size that generally will have higher catalytic activity. These will be further demonstrated in Examples 6 and 7 for the hydrogenolysis activities of esters.

[0074] *XRD Analysis:* A PANalytical MPD X'Pert Pro diffraction system was used to collect data for exemplary catalysts 5. Cu K α radiation was used in the analysis with generator settings of 45kV and 40mA. The optical path consisted of a 1° divergence slit, 2° anti-scatter slit, the sample, and an X'Celerator position sensitive detector. Each catalyst sample was first prepared by backpacking the sample into round mount. The data collection from the round mount covered a range from 10° to 90° 2 θ using a step scan with a step size of 0.017° 2 θ and a scan speed of 0.036° 2 θ per second. The X'Pert Pro HighScore program was used for phase identification analysis.

[0075] As shown below, monoclinic and/or cubic copper oxide (CuO/Cu₂O) were the predominant phases for exemplary catalyst 5.

Phase Determination

Ex.	Phase Match Candidate	Semi-quantitative (wt%)	[†] ICDD Ref.
5	monoclinic copper oxide (CuO)	47	4-008-2756
	cubic copper aluminum oxide (CuAl ₂ O ₄)	40	4-011-8980
	cubic copper manganese oxide (Cu ₃ Mn ₃ O ₈)	7	4-007-6753
	cubic zirconium oxide (ZrO ₂)	6	4-013-3441

*Reduced catalyst.

[†]International Centre for Diffraction Data (ICDD)

[0076] The full listing of 2 θ peaks in FIG. 4 is 18.9°, 31.1°, 32.5°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 53.6°, 58.3°, 59.1°, 61.7°, 64.9°, 66.8°, 68.1°, 72.2°, 75.1°, and 77.0°.

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Table 1. Catalysts 1-5

Example	% CuO	% Al ₂ O ₃	% MnO	% ZrO ₂	% Na ₂ O	Size (3F)	Packed bulk density (g/cc)	Crush strength, lbs/mm	Calcination Temp. (°C)
1A	51.7	29.5	8.8	7.3	0.4	1/16"	1.0	--	500
1B	51.7	29.5	8.8	7.3	0.4	1/16"	--	--	400
1C	51.7	29.5	8.8	7.3	0.4	1/16"	1.0	--	500
*1D	51.7	29.5	8.8	7.3	0.4	1/16"	1.0	--	500
1E	51.7	29.5	8.8	7.3	0.4	1/16"	1.0	--	500
*1F	51.7	29.5	8.8	7.3	0.4	1/16"	1.0	--	500
3A	52.2	29.9	8.8	8.3	0.4	1/16"	1.0	3.5	500
*3B	52.2	29.9	8.8	8.3	0.4	1/16"	1.0	3.5	500
3C	52.2	29.9	8.8	8.3	0.4	1/16"	1.0	3.5	500
*3D	52.2	29.9	8.8	8.3	0.4	1/16"	1.0	3.5	500
4A	51.2	29.7	8.6	8.1	0.4	1/16"	--	4.0	500
4B	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
*4C	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
4D	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
*4E	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
4F	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
*4G	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
4H	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
*4I	51.2	29.7	8.6	8.1	0.4	1/16"	1.1	4.0	500
5	52.0	30.4	8.9	7.2	0.4	1/16"	1.0	--	500

*Reduced catalyst

[0077] **EXAMPLE 6:** Fatty Acid Wax Ester Hydrogenolysis Testing in a liquid phase process. For liquid phase wax ester hydrogenolysis catalyst testing, 100 cc of catalyst extrudates as described in Example 1 was loaded into a 1.25" ID stainless steel fixed-bed down flow reactor. An equal volume of inert 14 X 28 mesh α -alumina granules was loaded with the catalyst and served as interstitial packing. The reactor was also equipped with a 3/16" thermowell that housed six thermocouples, one at the inlet and five spaced equally throughout the catalyst bed which was approximately 8" in length. The reactor and heated via furnace jacketed around the reactor tube.

[0078] Once loaded, the reactor was purged with 2 standard liter per minute (slpm) N_2 for approximately 1 hour to remove air and subsequently heated to 190 °C under flowing N_2 . The catalyst was activated by introducing H_2 in a stepwise fashion at atmospheric pressure. Once the reduction was complete, the temperature was ramped down to 170°C in 100 standard liter per hour (slph) hydrogen. The temperature was stabilized at 170°C, and the reactor was pressurized from atmospheric pressure to 1015 psig.

[0079] The commercial wax ester feed (C_{12} - C_{14} wax ester) was then pumped into the reactor at a rate of 63 g/hr to give an overall LHSV of about 0.73 hr^{-1} . The hydrogen:wax ester molar ratio was 50.

FEED Composition, C_{12} C_{14} wax ester (WE)	
Compound	Amount, wt. %
10:10 WE	0.1
10:10 ether	0.0
11:12 WE	0.0
12:12 WE	53.3
12:12 ether	0.0
12:14 + 14:12 WE	36.9
14:14 WE	8.7
16:12 WE	0.0
C_{18} alcohol	1.0

Hydrogenolysis was carried out according to the following reaction scheme:



[0080] Product samples were collected every 24 hours on stream at temperatures of 170°C, 180°C, 190°C, 200°C, and/or 220°C, respectively. These samples were analyzed by an off-line Agilent 6890 GC equipped with Quadrex Carbowax 20 M column (75 m x 0.32 mm x 0.25 μ m) and flame ionization detector. C₁₂, C₁₄, C₁₆, and C₁₈ fatty alcohols are the desired product while hydrocarbons (*e.g.*, dodecane, hexadecane) are side products. No other products were detected in any appreciable quantity.

[0081] As shown in Table 2, the exemplary catalysts 1A, 1B, and 5 showed an overall improved %conversion of wax ester at temperatures ranging from 170°C to 220°C compared to the reference copper catalyst containing silica. The exemplary copper catalysts showed an average increase in %conversion of the wax ester compared to the reference copper catalyst of approximately 14% at 170°C, 24% at 180°C, and 13% at 190°C, respectively. As shown in FIG. 1, the exemplary catalyst 5 showed an increase in %conversion of the wax ester compared to the reference copper catalyst of 33% at 170°C, 28% at 180°C, 9% at 190°C, 8% at 200°C, and 0.4% at 220°C, respectively. As shown in Table 3, exemplary catalyst 5 also showed a lower %conversion to the hydrocarbon by-product at 200°C and 220°C, respectively. Accordingly, the exemplary catalyst of the present technology exhibits a higher % conversion at lower temperatures over the comparative commercial reference catalyst.

Table 2.

Examples	Conversion, %				
	170°C	180°C	190°C	200°C	220°C
*Ref.	47.9	54.7	71.3	82	90.9
1A	61		82.5		
1B	51.1	73.5	76.4		
5	63.7	69.8	77.8	88.3	91.3

*Reference copper and silica catalyst.

Table 3.

Example Catalysts	Hydrocarbon Make, %	
	200°C	220°C
*Ref.	0.06	0.23

5	0.03	0.17
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*Reference copper and silica catalyst.

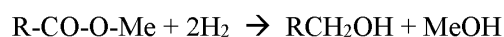
[0082] **EXAMPLE 7:** Fatty Acid Methyl Ester Hydrogenolysis Testing in a gas phase process. For gas phase methyl ester hydrogenolysis catalyst testing, 15 cc of catalyst (extrudates) was loaded into a 0.9" ID stainless steel fixed-bed down flow reactor. An equal volume of inert 28 X 48 mesh α -alumina granules was loaded with the catalyst and served as interstitial packing. The reactor was also equipped with a 3/16" thermowell that housed six thermocouples, one at the inlet and five spaced equally throughout the catalyst bed which was approximately 6" in length. The reactor and heated via furnace jacketed around the reactor tube.

[0083] Once loaded, the reactor was purged with 15 slph N₂ for approximately 1 hour to remove air and subsequently heated to 190 °C under flowing N₂. The catalyst was activated by introducing H₂ in a stepwise fashion at atmospheric pressure. Once the reduction was complete, the temperature was stabilized at 210°C, and the reactor was pressurized from atmospheric pressure to 435 psig.

[0084] After pressurization, with the temperature stable at 210°C, the hydrogen flow rate was adjusted to 800 slph. The commercial methyl feed (C₁₂-C₁₄ methyl ester) was then pumped into the reactor at a rate of 32.5 g/hr to give an overall LHSV of about 2.5 hr⁻¹. The hydrogen: methyl ester molar ratio was 250.

FEED Composition, C₁₂ C₁₄ methyl ester (ME)	
Compound	Amount, wt. %
C ₈ ME	0.0
C ₁₀ ME	0.3
C ₁₂ ME	73.7
C ₁₄ ME	25.3
C ₁₆ ME	0.6
C ₁₈ (18:0) ME	0.0
C ₁₈ (18:1) ME	0.0
C ₁₈ (18:2) ME	0.0
C ₂₄ wax ester	0.0

Hydrogenolysis was carried out according to the following reaction scheme:



[0085] Product samples were collected every 24 hours on stream at temperatures of 210°C and 230°C, respectively. These samples were analyzed by an off-line Agilent 6890 GC equipped with Quadrex Carbowax 20 M column (75 m x 0.32 mm x 0.25 µm) and flame ionization detector. C₁₂, C₁₄, C₁₆, and C₁₈ fatty alcohols are the desired product while hydrocarbons (*e.g.*, dodecane, tetradecane and hexadecane) are side products. No other products were detected in any appreciable quantity.

[0086] As shown in Table 4, exemplary catalyst 5 showed comparative gas phase hydrogenolysis %conversion of methyl ester to the fatty alcohol product at 210°C to 230°C compared to the reference copper catalyst containing silica. Similarly, exemplary catalyst 5 showed low %conversion of the methyl ester to the hydrocarbon by-product compared to the reference copper catalyst containing silica.

Catalyst	Temp., °C	Conversion, %	Hydrocarbon concentration, %
*Ref.	210	90.9	0.1
	230	96.4	0.46
5	210	91.2	0.27
	230	95.5	0.38

*Reference copper and silica catalyst.

[0087] As shown in the examples above, the catalysts of the present technology surprisingly show improved liquid phase hydrogenolysis %conversion of wax ester feeds to the fatty alcohol products and lower conversion to the hydrocarbon by-product over commercial copper catalysts containing silica. In addition, the catalysts of the present technology surprisingly show comparative gas phase hydrogenolysis %conversion of methyl ester feeds to the fatty alcohol product and low conversion to the hydrocarbon by-product comparable with commercial copper catalysts containing silica.

[0088] While certain embodiments have been illustrated and described, it should be understood that changes and modifications may be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

[0089] The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed

herein. Thus, for example, the terms “comprising,” “including,” “containing,” etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the claimed technology. Additionally, the phrase “consisting essentially of” will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase “consisting of” excludes any element not specified.

[0090] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations may be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, or compositions, which can of course vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0091] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0092] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range may be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein may be readily broken down into a lower third, middle

third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like, include the number recited and refer to ranges which may be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0093] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0094] Other embodiments are set forth in the following claims.

WHAT IS CLAIMED IS:

1. A hydrogenolysis catalyst comprising:
a catalytic component comprising copper oxide, manganese oxide, and aluminum oxide; and
a binder comprising a zirconium component,
wherein:
the catalyst comprises at least about 30.0 wt% copper oxide, and
the catalyst is substantially free of silicon or an oxide thereof.
2. The hydrogenolysis catalyst of claim 1, wherein the copper oxide is present in an amount from about 35 wt% to about 75 wt% by weight of the hydrogenolysis catalyst.
3. The hydrogenolysis catalyst of claim 1 or 2, wherein the copper oxide is present in an amount from about 45 wt% to about 55 wt%.
4. The hydrogenolysis catalyst of any one of claims 1-3, wherein the manganese oxide is present in an amount from about 0 wt% to about 10 wt% by weight of the hydrogenolysis catalyst.
5. The hydrogenolysis catalyst of any one of claims 1-4, wherein the manganese oxide is present in an amount from about 5 wt% to about 12 wt% by weight of the hydrogenolysis catalyst.
6. The hydrogenolysis catalyst of any one of claims 1-5, wherein the aluminum oxide is present in an amount from about 15 wt% to about 40 wt% by weight of the hydrogenolysis catalyst.
7. The hydrogenolysis catalyst of any one of claims 1-6, wherein the aluminum oxide is present in an amount from about 20 wt% to about 35 wt% by weight of the hydrogenolysis catalyst.
8. The hydrogenolysis catalyst of any one of claims 1-7, wherein zirconium component is zirconium oxide.

9. The hydrogenolysis catalyst of any one of claims 1-8, wherein the zirconium component is present in an amount from about 4 wt% to about 15 wt% by weight of the hydrogenolysis catalyst.
10. The hydrogenolysis catalyst of any one of claims 1-9, wherein the zirconium component is present in an amount from about 5 wt% to about 12 wt% by weight of the hydrogenolysis catalyst.
11. The hydrogenolysis catalyst of any one of claims 1-10, wherein the binder further comprises alumina.
12. The hydrogenolysis catalyst of any one of claims 1-11, wherein the hydrogenolysis catalyst further comprises an alkali metal component.
13. The hydrogenolysis catalyst of claim 12, wherein alkali metal component comprises sodium.
14. The hydrogenolysis catalyst of any one of claims 1-13, wherein the alkali metal is present in an amount from about 0 wt% to about 1 wt%.
15. The hydrogenolysis catalyst of any one of claims 1-14, wherein the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2 θ peaks at 31.1°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 61.7°, 64.9°, 68.1° is in an unreduced form and exhibits an X-ray powder diffraction profile with 2 θ peaks.
16. The hydrogenolysis catalyst of any one of claims 1-15, wherein the hydrogenolysis catalyst is a calcined and extruded hydrogenolysis catalyst.
17. The hydrogenolysis catalyst of any one of claims 1-16, wherein the hydrogenolysis catalyst exhibits a pore volume of greater than 0.25 cm³/g.
18. The hydrogenolysis catalyst of any one of claims 1-17, wherein the hydrogenolysis catalyst exhibits a packed bulk density of about 0.8 g/cm³ to about 1.5 g/cm³.

19. The hydrogenolysis catalyst of any one of claims 1-18, wherein the hydrogenolysis catalyst has a Brunauer-Emmett-Teller ("BET") surface area from about 15 m²/g to about 70 m²/g.
20. The hydrogenolysis catalyst of any one of claims 1-19, wherein the hydrogenolysis catalyst is in the form of a solid extrudate or tablet.
21. The hydrogenolysis catalyst of claim 15, wherein the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2θ peaks at 18.9°, 31.1°, 32.5°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 53.6°, 58.3°, 59.1°, 61.7°, 64.9°, 66.8°, 68.1°, 72.2°, 75.1°, and 77.0°.
22. A method of preparing a calcined hydrogenation catalyst, the method comprising:
 - mixing a catalytic component with a binder system and water to obtain a material mixture;
 - forming the material mixture to obtain a formed material mixture;
 - calcining the formed material mixture at a temperature, and for a time, sufficient to cure form the calcined hydrogenolysis catalyst;wherein:
 - the catalytic component comprises copper oxide, manganese oxide, and aluminum oxide;
 - the binder system comprises a zirconium component;
 - the calcined hydrogenolysis catalyst comprises at least 30 wt% copper oxide;
 - and
 - the calcined hydrogenolysis catalyst is substantially free of silicon or an oxide thereof.
23. The method of claim 22, wherein the catalytic component comprises pre-calcined powder comprising copper oxide, manganese oxide, and aluminum oxide.
24. The method of claim 23, wherein the pre-calcined powder was calcined at a temperature from about 400°C to about 800°C.

25. The method of any one of claims 22-24, wherein the zirconium component is zirconium acetate.
26. The method of any one of claims 22-25, wherein the binder system further comprises alumina.
27. The method of any one of claims 22-26, further comprising mixing an extrusion aid selected from polymeric polysaccharide, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, or a mixture of two or more thereof.
28. The method of any one of claims 22-27, further comprising removing at least some of the water from the wet material mixture prior to calcining.
29. The method of any one of claims 22-28, wherein the calcining is conducted at a temperature from about 200°C to about 1000°C.
30. The method of claim 29, wherein the temperature is from about 450°C to about 550°C.
31. A hydrogenolysis catalyst prepared by the method of any one of claims 22-30.
32. A method of conducting hydrogenolysis of a fatty acid ester, the method comprising contacting the fatty acid ester with a hydrogenolysis catalyst comprising:
a catalytic component comprising copper oxide, manganese oxide, and aluminum oxide; and
a binder comprising a zirconium component;
wherein:
the hydrogenolysis catalyst comprises at least 30% copper oxide; and
the hydrogenolysis catalyst is substantially free of silicon or an oxide thereof.
33. The method of claim 32, wherein the fatty acid ester is represented by Formula I:
$$R^1-CO-OR^2 \text{ (I)}$$

wherein

R^1 and R^2 are each independently a branched or unbranched C_1 to C_{24} alkyl or a branched or unbranched C_2 to C_{24} alkenyl.

34. The method of claim 33, wherein R^1 and R^2 are each independently a C_{10} to C_{14} branched or unbranched alkyl or a C_{10} to C_{14} branched or unbranched alkenyl.
35. The method of claim 33, wherein R^1 and R^2 are each independently a C_{12} to C_{14} branched or unbranched alkyl.
36. The method of claim 33, wherein when R^1 is a C_{10} to C_{18} branched or unbranched alkyl or a C_{10} to C_{18} branched or unbranched alkenyl, R^2 is a C_1 to C_6 alkyl.
37. The method of claim 36, wherein R^2 is methyl.
38. The method of any one of claims 33-37, wherein the copper oxide is present in an amount from about 35 wt% to about 75 wt% by weight of the hydrogenolysis catalyst.
39. The method of any one of claims 33-38, wherein the manganese oxide is present in an amount from about 1 wt% to about 20 wt% by weight of the hydrogenolysis catalyst.
40. The method of any one of claims 33-39, wherein the aluminum oxide is present in an amount from about 15 wt% to about 40 wt% by weight of the hydrogenolysis catalyst.
41. The method of any one of claims 33-40, wherein zirconium component is zirconium oxide.
42. The method of any one of claims 33-41, wherein the zirconium component is present in an amount from about 1 wt% to about 20 wt% by weight of the hydrogenolysis catalyst.
43. The method of any one of claims 33-42, wherein the binder further comprises alumina.
44. The method of any one of claims 33-43, wherein the hydrogenolysis catalyst further comprises an alkali metal component.

45. The method of claim 44, wherein alkali metal component comprises sodium.
46. The method of any one of claims 44 or 45, wherein the alkali metal is present in an amount from about 0 wt% to about 1 wt%.
47. The method of any one of claims 33-46, wherein the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2 θ peaks 31.1°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 61.7°, 64.9°, 68.1°.
48. The method of any one of claims 33-47, wherein the hydrogenolysis catalyst is a calcined and extruded hydrogenolysis catalyst.
49. The method of any one of claims 33-48, wherein the hydrogenolysis catalyst exhibits a pore volume of greater than 0.25 cm³/g.
50. The method of any one of claims 33-49, wherein the hydrogenolysis catalyst exhibits a packed bulk density of about 0.8 g/cm³ to about 1.5 g/cm³.
51. The method of any one of claims 33-50, wherein the hydrogenolysis catalyst has a Brunauer-Emmett-Teller ("BET") surface area from about 15 m²/g to about 70 m²/g.
52. The method of claim 47, wherein the hydrogenolysis catalyst is in an unreduced form and exhibits an X-ray powder diffraction profile with 2 θ peaks at 18.9°, 31.1°, 32.5°, 36.0°, 36.8°, 38.8°, 44.6°, 48.8°, 53.6°, 58.3°, 59.1°, 61.7°, 64.9°, 66.8°, 68.1°, 72.2°, 75.1°, and 77.0°.
53. The method of any one of claims 33-52, wherein the method is conducted at a temperature of at least about 170°C.
54. The method of claim 53, wherein the temperature is from about 170°C to about 220°C.
55. The hydrogenolysis catalyst of any one of claims 1-21, wherein the hydrogenolysis catalyst is free of silicon or an oxide thereof.

56. The method of any one of claims 22-30, wherein the calcined hydrogenolysis catalyst is free of silicon or an oxide.
57. The method of any one of claims 32-54, wherein the hydrogenolysis catalyst is free of silicon or an oxide.
58. The method of any one of claims 22-30, wherein forming the material mixture comprises extrusion, tableting, or spherization.