~~**WHAT IS CLAIMED IS:**~~**CLAIMS**

1. A hydrogenation catalyst comprising:

copper oxide;

an alkali metal; ~~and~~

an acid-stabilized silica; and

manganese oxide

wherein:

the hydrogenation catalyst has a Brunauer-Emmett-Teller ~~("BET")~~ surface area of greater than or equal to ~~about~~ 15 m^2/g, and

wherein the copper oxide is present in an amount from 70.0 wt.% to 80.0 wt.% by weight of the hydrogenation catalyst, and

wherein the acid-stabilized silica is formed from an acid-stabilized silica solution having a pH of less than 3.5, and

wherein the hydrogenation catalyst has less than 1.5 wt.% chromium or an oxide thereof, based on the total weight of the catalyst.~~.~~

2. The hydrogenation catalyst of claim 1, wherein the Brunauer-Emmett-Teller ~~BET~~ surface area is from ~~about~~ 15 m^2/g to ~~about~~ 70 m^2/g.

~~3. The hydrogenation catalyst of claim 1 or 2, wherein the BET surface area is from about 50 m^2/g to about 60 m^2/g.~~

~~4. The hydrogenation catalyst of any one of claims 1-3, wherein the copper oxide is present in an amount from about 50.0 wt% to about 85.0 wt% by weight of the hydrogenation catalyst.~~

~~5. The hydrogenation catalyst of any one of claims 1-4, wherein the copper oxide is present in an amount from about 65.0 wt% to about 80.0 wt% by weight of the hydrogenation catalyst.~~

~~6~~3. The hydrogenation catalyst of any one of claims 1-~~5~~2, wherein the copper oxide is present in an amount from about 70.0 wt% to about 75.0 wt% by weight of the hydrogenation catalyst.

~~7~~4. The hydrogenation catalyst of any one of claims 1-~~6~~3, wherein the alkali metal component comprises sodium.

~~8. The hydrogenation catalyst of any one of claims 1-7, wherein the alkali metal component comprises disodium oxide.~~

~~9~~5. The hydrogenation catalyst of any one of claims 1-~~8~~4, wherein the alkali metal component is present in an amount from 0.01 wt.% to ~~about~~ 8.0 wt.% by weight of the hydrogenation catalyst.

~~10. The hydrogenation catalyst of any one of claims 1-9, wherein the alkali metal component is present in an amount from about 3.0 wt% to about 5.0 wt% by weight of the hydrogenation catalyst.~~

~~11~~6. The hydrogenation catalyst of any one of claims 1-~~10~~ 5 further comprising from ~~about~~ 1.0 wt.% to ~~about~~ 18.0 wt.% of calcium oxide by weight of the hydrogenation catalyst.

~~12. The hydrogenation catalyst of any one of claims 1-11 further comprising a transition metal component selected from the group consisting of manganese, zinc, nickel, cobalt, and iron.~~

~~13. The hydrogenation catalyst of any one of claims 1-11 further comprising a transition metal component that is manganese oxide.~~

~~7~~14. The hydrogenation catalyst of according to claim 1~~any one of claims 12 or 13~~, wherein the manganese oxide ~~transition metal component~~ is present in an amount from 0.01 wt.% to ~~about~~ 5.0 wt.% by weight of the hydrogenation catalyst.

~~15. The hydrogenation catalyst of any one of claims 1-14, wherein the acid-stabilized silica is formed from an acid-stabilized silica solution having a pH of less than about 3.5.~~

~~16~~8. The hydrogenation catalyst of any one of claims 1-~~7~~15, wherein the acid-stabilized silica is present in an amount from ~~about~~ 5.0 wt.% to ~~about~~ 20.0 wt.% by weight of the hydrogenation catalyst.

~~17. The hydrogenation catalyst of any one of claims 1-16, wherein the acid-stabilized silica is present in an amount from about 10.0 wt% to about 18.0 wt% by weight of the hydrogenation catalyst.~~

~~18. The hydrogenation catalyst of any one of claims 1-17 further comprises from greater than 0 wt% to about 1.0 wt% crystalline silica by weight of the hydrogenation catalyst.~~

~~19. The hydrogenation catalyst of any one of claims 1-18 further comprising from about 0 wt% to about 10 wt% of a clay material.~~

~~20~~9. The hydrogenation catalyst of any one of claims 1-~~19~~8, wherein the hydrogenation catalyst is a calcined and extruded hydrogenation catalyst.

~~21~~10. The hydrogenation catalyst of any one of claims 1-~~20~~9, wherein the hydrogenation catalyst material exhibits a pore volume ≥ 0.25 cm^3/g.

~~22~~11. The hydrogenation catalyst of any one of claims 1-~~21~~10, wherein the hydrogenation catalyst exhibits a packed bulk density of ~~about~~ 0.8 g/cm^3 to ~~about~~ 1.5 g/cm^3.

~~23. The hydrogenation catalyst of any one of claims 1-22, wherein the hydrogenation catalyst is free of, or is substantially free of, chromium or an oxide thereof.~~

~~24. The hydrogenation catalyst of any one of claims 1-23, wherein the hydrogenation catalyst is in the form of a solid extrudate or tablet.~~

~~25~~12. A method of preparing a calcined hydrogenation catalyst, the method comprising:

mixing a copper oxide and a clay material to obtain a dry material mixture;

combining the dry material mixture with an aqueous acid-stabilized silica solution, an alkali metal hydroxide, manganese oxide ~~caustic material,~~ and water to obtain a wet material mixture; and

calcining the wet material mixture at a temperature, and for a time, sufficient to cure form a calcined hydrogenation catalyst;

wherein:

the calcined hydrogenation catalyst has a Brunauer-Emmett-Teller ~~("BET")~~ surface area of greater than or equal to ~~about~~ 15 m^2/g; and

wherein the copper oxide is present in an amount from 70.0 wt.% to 80.0 wt.% by weight of the calcined hydrogenation catalyst; and

wherein the hydrogenation catalyst has less than 1.5 wt.% chromium or an oxide thereof, based on the total weight of the calcined hydrogenation catalyst;

the acid-stabilized silica solution has a pH of less than about 3.5.

~~26. The method of claim 25, wherein the calcined hydrogenation catalyst has a BET surface area of about 15 m^2 to about 70 m^2/g.~~

~~27. The method of claim 25 or 26, wherein the calcined hydrogenation catalyst has a BET surface area of about 50 m^2/g to about 60 m^2/g.~~

~~28. The method of any one of claims 25-27 further comprising mixing an alkaline earth metal component into the dry material mixture.~~

~~29. The method of claim 28, wherein the alkaline earth metal component is calcium hydroxide.~~

~~30. The method of any one of claims 25-29, wherein the clay material comprises an alumino-silicate attapulgite clay.~~

~~31. The method of any one of claims 25-30 further comprising mixing a transition metal component selected from the group consisting of manganese, zinc, nickel, cobalt, and iron into the dry material mixture.~~

~~32. The method of claim 31, wherein the transition metal component comprises manganese oxide.~~

~~33. The method of any one of claim 25-32 further comprising mixing one or more binders, extrusion aids, or a combination of any two or more thereof into the dry material mixture.~~

~~34. The method of claim 33, wherein the one or more binders or extrusion aids are selected from a polymeric polysaccharide, hydroxypropyl methyl cellulose, hydroxylethyl methyl cellulose, or a mixture of two or more thereof.~~

~~35. The method of any one of claims 25-34, wherein the caustic material comprises an alkali metal hydroxide.~~

~~36. The method of claim 35, wherein the alkali metal hydroxide is sodium hydroxide.~~

~~37. The method of any one of claims 25-36 further comprising removing at least some of the water from the wet material mixture prior to calcining.~~

~~38. The method of claim 37, wherein the removing of the water is conducted at a temperature from about 40°C to about 150°C.~~

~~39. The method of claim 38, wherein the temperature is from about 50°C to about 60°C.~~

~~40. The method of any one of claims 25-39, wherein the method further comprises extruding the wet material mixture prior to calcining.~~

~~41. The method of any one of claims 25-40, wherein the calcining is conducted at a temperature from about 400°C to about 650°C.~~

~~42. The method of claim 41, wherein the temperature is from about 400°C to about 550°C.~~

~~43. The method of claim 42, wherein the temperature is from about 450°C to about 500°C.~~

~~44. A hydrogenation catalyst prepared by the method of any one of claims 25-43.~~

~~45~~13. A method of hydrogenating a ketone or aldehyde, the method comprising contacting the ketone or aldehyde with a hydrogenation catalyst according to any of the claims 1-11.~~comprising:~~

~~copper oxide;~~

~~an alkali metal component; and~~

~~an acid-stabilized silica;~~

~~wherein:~~

the hydrogenation catalyst has a Brunauer-Emmett-Teller ("BET") surface area of greater than or equal to about 15 m^2/g.

46. The method of claim 45, wherein the acid-stabilized silica is formed from an acid-stabilized silica solution having a pH of less than about 3.5

47. The method of claim 45 or 46, wherein the hydrogenation catalyst has a BET surface area of about 15 m^2/g to about 70 m^2/g.

48. The method of any one of claims 45-47, wherein the hydrogenation catalyst has a BET surface area of about 50 m^2/g to about 60 m^2/g.

49. The method of claim 48, wherein the hydrogenation catalyst is present in an amount from about 50.0 wt% to about 85.0 wt% by weight of the hydrogenation catalyst.

50. The method of any one of claims 45-49, wherein the alkali metal component comprises sodium.

51. The method of any one of claims 45-50, wherein the alkali metal component is present in an amount from 0 wt% to about 8.0 wt% by weight of the hydrogenation catalyst.

52. The method of any one of claims 45-51, wherein the hydrogenation catalyst further comprises about 1.0 wt% to about 18.0 wt% of calcium oxide by weight of the hydrogenation catalyst.

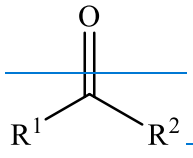
53. The method of any one of claims 46-52, wherein the hydrogenation catalyst further comprises a transition metal component selected from the group consisting of manganese, zinc, nickel, cobalt, and iron.

54. The method of claim 53, wherein the transition metal component is present in an amount from 0 wt% to about 5.0 wt% by weight of the catalyst.

55. The method of any one of claims 45-54, wherein the acid-stabilized silica is present in an amount from about 5.0 wt% to about 20.0 wt% by weight of the catalyst.

~~56. The method of any one of claims 45-55, wherein the inorganic matrix further comprises 0 wt% to about 1.0 wt% of a crystalline silica by weight of the catalyst.~~

~~57. The method of any one of claims 45-56, wherein the ketone is represented by Formula I:~~



~~(I);~~

~~wherein~~

~~R^1 is a substituted or unsubstituted C_1 to C_{18} alkyl, a substituted or unsubstituted C_3 to C_8 cycloalkyl, or a substituted or unsubstituted C_6 to C_{14} aryl; and~~

~~R^2 is a hydrogen or a substituted or unsubstituted C_1 to C_{18} alkyl.~~

~~58. The method of claim 57, wherein R^1 is a substituted or unsubstituted C_6 to C_{14} aryl.~~

~~59. The method of claim 57 or 58, wherein R^1 is a substituted or unsubstituted phenyl.~~

~~60. The method of 59, wherein R^1 is a phenyl optionally substituted with one or more of a halogen, amine, hydroxyl, or a C_1 to C_6 alkyl.~~

~~61. The method of claim 60, wherein R^2 is methyl.~~

~~62. The method of any one of claims 46-61, wherein the ketone is a phenyl alkyl ketone.~~

~~63. The method of claim 62, wherein the phenyl alkyl ketone is acetophenone.~~

~~64~~14. A method of synthesizing butanediol, the method comprising:

contacting a stream of dimethyl maleate with a hydrogenation catalyst according to any of the claims 1-11.~~comprising:~~

~~copper oxide;~~

~~an alkali metal component; and~~

~~an acid-stabilized silica;~~

~~wherein:~~

~~the hydrogenation catalyst has a Brunauer-Emmett-Teller ("BET") surface area of greater than or equal to about 15 m^2/g; and~~

the silica is formed from an acid-stabilized silica solution having a pH of less than about 3.5.

65. The method of claim 64, wherein the hydrogenation catalyst has a BET surface area of about 15 m^2/g to about 70 m^2/g.

66. The method of claim 64 or 65, wherein the hydrogenation catalyst has a BET surface area of about 50 m^2/g to about 60 m^2/g.

67. The method of any one of claims 64-66, wherein the copper oxide is present in an amount from about 50.0 wt% to about 85.0 wt% by weight of the hydrogenation catalyst.

68. The method of any one of claims 64-67, wherein the alkali metal component comprises sodium.

69. The method of any one of claims 64-68, wherein the alkali metal component is present in an amount from 0 wt% to about 8.0 wt% by weight of the hydrogenation catalyst.

70. The method of any one of claims 64-69, wherein the hydrogenation catalyst further comprises from about 1.0 wt% to about 18.0 wt% of calcium oxide by weight of the hydrogenation catalyst.

71. The method of any one of claims 64-70, wherein the hydrogenation catalyst further comprises a transition metal component selected from the group consisting of manganese, zinc, nickel, cobalt, and iron.

72. The method of claim 71, wherein the transition metal component is present in an amount from 0 wt% to about 5.0 wt% by weight of the catalyst.

73. The method of any one of claims 64-72, wherein the acid-stabilized silica is present in an amount from about 5.0 wt% to about 20.0 wt% by weight of the catalyst.

74. The method of any one of claims 64-73, wherein the hydrogenation catalyst further comprises 0 wt% to about 1.0 wt% crystalline silica by weight of the hydrogenation catalyst.

~~75. The hydrogenation catalyst of any one of claims 1-24, wherein the hydrogenation catalyst is in an unactivated form and exhibits an X-ray powder diffraction profile with 2θ peaks at 29.6°, 35.5°, 38.7°, and 58.9°.~~

~~76. The hydrogenation catalyst of claim 75, wherein the hydrogenation catalyst is in an unactivated form and exhibits an X-ray powder diffraction profile with 2θ peaks at 26.7°, 29.6°, 35.5°, 38.7°, 58.9°, 53.4°, 68.2°, 61.6°, 66.3°, 68.0°, 72.3°, 75.1°, and 82.9°.~~

~~77. The hydrogenation catalyst of any one of claims 1-24, 75, or 76, wherein the hydrogenation catalyst has a copper oxide crystallite size of about 60 Å to about 200 Å.~~

~~78. The hydrogenation catalyst of claim 77, wherein the hydrogenation catalyst has a copper oxide crystallite size of about 70 Å to about 165 Å.~~

~~79. The method of any one of claims 25-44, wherein the hydrogenation catalyst is in an unactivated form and exhibits an X-ray powder diffraction profile with 2θ peaks at 29.6°, 35.5°, 38.7°, and 58.9°.~~

~~80. The method catalyst of claim 79, wherein the hydrogenation catalyst is in an unactivated form and exhibits an X-ray powder diffraction profile with 2θ peaks at 26.7°, 29.6°, 35.5°, 38.7°, 58.9°, 53.4°, 68.2°, 61.6°, 66.3°, 68.0°, 72.3°, 75.1°, and 82.9°.~~

~~81. The method of any one of claims 25-44 or 80, wherein the hydrogenation catalyst has a copper oxide crystallite size of about 60 Å to about 200 Å.~~

~~82. The method of claim 81, wherein the catalyst has a copper oxide crystallite size of about 70 Å to about 165 Å.~~

~~83~~15. A method of hydrogenating an ester, the method comprising contacting the ester with a hydrogenation catalyst according to any of the claims 1-11.~~comprising:~~

~~copper oxide;~~

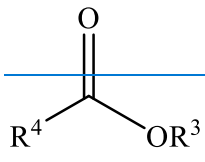
~~an alkali metal component; and~~

~~an acid-stabilized silica;~~

wherein:

the hydrogenation catalyst has a Brunauer-Emmett-Teller ("BET") surface area of greater than or equal to about 15 m^2/g.

84. The method of claim 83, wherein the ester is represented by Formula II:



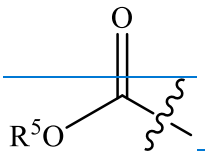
(II),

wherein

R^3 is a substituted or unsubstituted C_1 to C_{18} alkyl; and

R^4 is hydrogen, a C_1 to C_{18} alkyl, a C_2 to C_{18} alkenyl, a C_3 to C_8 cycloalkyl, or a C_6 to C_{14} aryl,

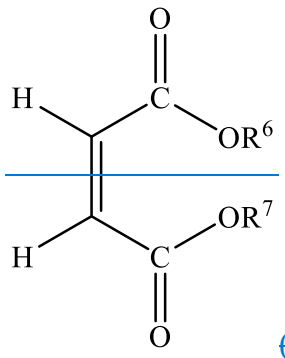
wherein the C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, C_3 to C_8 cycloalkyl, or C_6 to C_{14} aryl is optionally substituted with one or more of a halogen, amine, hydroxyl, a C_1 to C_6 alkyl, or an ester represented by Formula (III),



(III),

wherein R^5 is hydrogen, a substituted or unsubstituted C_1 to C_{18} alkyl, a substituted or unsubstituted C_2 to C_{18} alkenyl, a substituted or unsubstituted C_3 to C_8 cycloalkyl, or a substituted or unsubstituted C_6 to C_{14} aryl.

85. The method of claim 83 or 84, wherein the ester is represented by Formula (IV):



~~(IV),~~

~~wherein:~~

~~R^6 and R^7 are each independently a substituted or unsubstituted C_1 to C_{12} alkyl, a substituted or unsubstituted C_2 to C_{12} alkenyl, a substituted or unsubstituted C_3 to C_8 cycloalkyl, or a substituted or unsubstituted C_6 to C_{14} aryl; and~~

~~the ester of Formula (IV) has a *cis* configuration or a *trans* configuration.~~