CLAIMS

What is claimed is:

1. In combination:

a cathode for direct electrochemical reduction of a feedstock comprising one ~~of~~ or more of carbon dioxide, carbon monoxide and carbohydrates containing aldehyde or ketone functional groups with active alpha-hydrogens to oxyhydrocarbon products, the cathode comprising a conductive support substrate, a co-catalyst other than a nickel phosphide and an electrocatalyst coating, the electrocatalyst coating comprising nanoparticles of Ni_xP_y, wherein x and y represent integers such that the compounds are selected from the group consisting of Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP_2, and NiP_3; or the electrocatalyst coating comprising nano-particles of Ni_xP_y is selected from the group consisting of Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP_2, and NiP_3, further alloyed with Fe_2P, wherein the alloy has a Ni-P:Fe_2P ratio between about 99:1 and 1:99 wt%;

wherein the conductive support substrate comprises hydrophobic regions and hydrophilic regions to aid in adsorption of the feedstock from gas or aqueous phase to achieve separation from water molecules, wherein at least some of the electrocatalyst nanoparticles are in the hydrophobic regions of the conductive support substrate and catalytically interact with the feedstock by electrical reduction to produce oxyhydrocarbon products; and

wherein the co-catalyst is positioned to act together with the electrocatalyst by incorporation into the hydrophilic or hydrophobic regions or the by dissolution in the electrolyte or by direct anchoring/incorporation into the catalyst surface.

2. The combination of claim 1,

wherein the co-catalyst comprises an acid selected from a Lewis acid or a Bronsted-Lowry acid~~.~~, optionally

~~3. The combination of claim 2,~~ wherein the acid is selected from the group consisting of Zn^{+2}, Fe^{+2}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Al^{+3}, AlO^{+}, Si^{4+}, SiO^{2+}, H_3BO_3, $B(OH)_2(OR)$, $B(OH)(OR)_2$, and mixtures of two or more thereof, wherein R = alkyl, aryl, arylalkyl, heteroaryl, and heteroarylalkyl, where the heteroatoms of heteroaryl and heterarylalkyl are selected from nitrogen, oxygen and sulfur.

~~4~~3. The combination of claim 1, wherein the co-catalyst comprises a base selected from a Lewis base or a Bronsted-Lowry base~~.~~, optionally

~~5. The combination of claim 4,~~ wherein the base is selected from the group consisting of NH_3, carbamide, urea, hydrazine, primary amines, secondary amines, tertiary amines, pyridines, and mixtures of two or more thereof.

~~6~~34. The combination of claim 1, wherein the co-catalyst comprises an ionomer or a conducting polymer.

~~7~~45. The combination of claim 1, wherein the co-catalyst comprises a ~~soluble~~ salt of Cu, Ag, Au, Zn, mixtures of two or more thereof, or oxides thereof.

~~8~~56. The combination of claim 1, wherein the cathode is in contact with an electrolyte solution comprising the co-catalyst or the co-catalyst is an ionic liquid electrolyte that possesses HCO_3^- or CO_3^{2-} or H^+ transport functionality and is in contact with the cathode~~.~~,

~~9. The combination of claim 8,~~

optionally wherein the cathode is in contact with the electrolyte solution comprising the co-catalyst and the conductive support further comprises the same co-catalyst.

~~10~~67. The combination of claim 1, wherein the co-catalyst is an ionic liquid that possesses HCO_3^- or CO_3^{2-} or H^+ transport functionality.

~~11~~78. The combination of claim 1, wherein the conductive support substrate further incorporates a material to be reduced, whereby the electrocatalyst coating catalytically interacts with the material to be reduced incorporated into the conductive support substrate~~.~~, optionally

~~12. The combination of claim 11,~~ wherein the material to be reduced comprises carbon dioxide, carbon monoxide, or a mixture thereof.

~~13~~89. The combination of claim 1 wherein the conductive support substrate is an ionomer or a conducting polymer.

~~14~~910. The combination of claim 1 wherein the feedstock comprises a plurality of hydrocarbon molecules containing either aldehyde or ketone functional groups or reactive alpha-hydrogens.

~~15~~10~~11~~. A method for generating oxyhydrocarbon products from water, carbon dioxide and/or carbon monoxide via an electrolysis reaction, the method comprising:

(a) placing the cathode of the combination of claim 1 in an electrolyte together with an anode;

(b) placing the anode and cathode in conductive contact with an external source of electric current;

(c) providing a source of carbon dioxide and/or carbon monoxide to the cathode; and

(d) applying the electric current to drive an electrolysis reaction at the cathode, whereby oxyhydrocarbon products are generated selectively from the carbon dioxide and/or carbon monoxide~~.~~;

optionally wherein the source of carbon dioxide and/or carbon monoxide is a flowing source.

~~16~~11~~12~~. The method of claim ~~15~~11, wherein the electrocatalyst and co-catalyst are selected to generate a product selected from the group consisting of 2,3-furandiol, 2-formylfuran-3-ol, ethylene glycol, 1,3-propanediol, 1,2-propanediol, stereo-isomers thereof, and combinations thereof.

~~17. The method of claim 15, wherein the source of carbon dioxide and/or carbon monoxide is a flowing source.~~

~~18~~12~~.~~ ~~A method for reduction of carbon dioxide to oxyhydrocarbon products, the method comprising:~~

~~(a) placing a cathode in an aqueous electrolyte together with an anode and a co-catalyst comprising an acid or a base or a charged ionic species, wherein the cathode comprises a conductive support substrate, and an electrocatalyst coating comprising nanoparticles of Ni_xP_y wherein x and y represent integers such that the compounds are selected from the group consisting of Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP_2, and NiP_3, wherein the co-catalyst can be on the conductive support, in the electrolyte, or both;~~

~~(b) placing the anode and cathode in conductive contact with an external source of electric current;~~

~~(c) providing a flowing source of carbon dioxide to the cathode; and~~

~~(d) applying the electric current to drive an electrolysis reaction that generates electrons at the anode that are delivered to the cathode, whereby an oxyhydrocarbon product is generated from the carbon dioxide, electrons and water, and the electrocatalyst and co-catalyst are selected so~~

~~that the oxyhydrocarbon product that is generated is selected from the group consisting of carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof.~~

~~19~~13. A method for reducing carbon dioxide to oxyhydrocarbon products, the method comprising:

(a) placing a cathode in an electrolyte together with an anode and a co-catalyst, wherein the cathode comprises a conductive support substrate and an electrocatalyst coating, the electrocatalyst coating comprising nanoparticles of Ni_xP_y wherein x and y represent integers such that the compounds are selected from the group consisting of Ni_3P, Ni_5P_2, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP_2, and NiP_3, wherein the co-catalyst can be on the conductive support, in the electrolyte, or both;

wherein the co-catalyst binds to an aldehyde, ketone or alcoholic functional group of a reaction intermediate, thereby activating it for further reaction with the electrocatalyst;

(b) placing the anode and cathode in conductive contact with an external source of electric current;

(c) providing a flowing source of carbon dioxide to the cathode; and

(d) applying the electric current to drive an electrolysis reaction that generates electrons at the anode that are delivered to the cathode, whereby an oxyhydrocarbon product is generated from the carbon dioxide, and the electrocatalyst and co-catalyst are selected so that the oxyhydrocarbon product that is generated is selected from the group consisting of carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof.

~~20~~14. The method of claim ~~19~~13 or the combination of claim 1, wherein the co-catalyst comprises a metal selected from the group consisting of Cu, Ag, Au, Zn, and intermetallic compounds thereof~~.~~, optionally

~~21. The method of claim 20,~~ wherein the co-catalytic metal or intermetallic compounds are in the form of nanoparticles.

~~22~~15. The combination of claim 1, wherein the co-catalyst binds to a reaction intermediate on the electrocatalyst surface or in solution and 1) influences the intermediate's binding orientation, and/or 2) activates the intermediate for subsequent reaction with surface-bound hydrides or other CO_2/CO reaction intermediates, and/or 3) influences the intermediate's binding strength to become stronger or weaker, and/or 4) facilitates the formation of new reaction intermediates on the surface.

~~23. The combination of claim 1, wherein the co-catalyst comprises a metal selected from the group consisting of Cu, Ag, Au, Zn, and intermetallic compounds thereof.~~

~~24. The combination of claim 23, wherein the co-catalytic metal or intermetallic compounds are in the form of nanoparticles.~~