CLAIMS

1. A bulk catalyst precursor having the formula:

$$A_v[Ni(OH)_x(L)^p{}_y]_z[Mo_mW_{1-m}O_4][Ti(OH)_nO_{2-n/2}]_w$$

wherein:

(i) A is an alkali metal cation, a rare earth metal cation, an ammonium cation, an organic ammonium cation, phosphonium cation, or a combination thereof;

(ii) L is an organic compound-based component; and

(iii) $0 < y \leq 2/p$; $0 \leq x < 2$; $0 \leq v < 2$; $0 < z$; $0 < m < 1$; $0 < n < 4$; $0.1 < w/(z+1) < 10$;

wherein the bulk catalyst precursor defined by a region of a quaternary phase diagram defined by eight points *ABCDEFGH* and wherein the eight points, on a metal oxide basis (wt. %), are: *A* (Ni=52.5, Mo=3.5, W=14, Ti=30), *B* (Ni=38.5, Mo=17.5, W=14, Ti=30), *C* (Ni=21, Mo=17.5, W=31.5, Ti=30), *D* (Ni=35, Mo=3.5, W=31.5, Ti=30), *E* (Ni=60, Mo=4, W=16, Ti=20), *F* (Ni=44, Mo=20, W=16, Ti=20), *G* (Ni=24, Mo=20, W=36, Ti=20), and *H* (Ni=40, Mo=4, W=36, Ti=20). and

wherein the bulk catalyst precursor is prepared according to a first method comprising:

(a) combining in a reaction mixture:

(i) a Ni-containing precursor;

(ii) a Mo-containing precursor;

(iii) a W-containing precursor;

(iv) a Ti-containing precursor;

(v) an organic compound-based component; and

(vi) a protic liquid; and

(b) reacting the mixture under conditions sufficient to cause precipitation of the bulk catalyst precursor;

wherein the steps to prepare the bulk catalyst precursor are carried out at a temperature of no more than 200°C;

or

wherein the bulk catalyst precursor is prepared according to a second method comprising:

(a) combining in a reaction mixture:

(i) a Ni-containing precursor;

(ii) a Mo-containing precursor;

(iii) a W-containing precursor;

(iv) an organic compound-based component; and

(v) a protic liquid; and

(b) reacting the mixture under conditions sufficient to cause precipitation of an intermediate bulk catalyst precursor; and

(c) compositing the intermediate bulk catalyst precursor with a Ti-containing precursor to form the bulk catalyst precursor;x

wherein the steps to prepare the bulk catalyst precursor are carried out at a temperature of no more than 200°C.

2. The bulk catalyst precursor of claim 1, wherein the organic compound-based component is selected from the group of:

(i) an organic acid or salt thereof, a sugar, a sugar alcohol, or a combination thereof; or

(ii) glyoxylic acid, pyruvic acid, lactic acid, malonic acid, oxaloacetic acid, malic acid, fumaric acid, maleic acid, tartaric acid, gluconic acid, citric acid, oxamic acid, serine, aspartic acid, glutamic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, fructose, glucose, galactose, mannose, sucrose, lactose, maltose, erythritol, xylitol, mannitol, sorbitol, or a combination thereof.

3. The bulk catalyst precursor of claim 1, further comprising 1 to 15 wt. % of a binder.

4. The bulk catalyst precursor of claim 1, having one or more of the following properties: a BET specific surface area of from 50 to 250 m^2/g; a pore volume of from 0.02 to 0.80 cm^3/g; and particle density of 1.00 to 3.00 g/ cm^3.

5. A method for preparing the bulk catalyst precursor of claim 1, the method comprising:

(a) combining in a reaction mixture:

(i) a Ni-containing precursor;

(ii) a Mo-containing precursor;

(iii) a W-containing precursor;

(iv) a Ti-containing precursor;

(v) an organic compound-based component; and

(vi) a protic liquid; and

(b) reacting the mixture under conditions sufficient to cause precipitation of the bulk catalyst precursor;

wherein the steps to prepare the bulk catalyst precursor are carried out at a temperature of no more than 200°C.

6. The method of claim 5, wherein the reaction mixture is prepared by:

preparing a first mixture comprising a Ni-containing precursor, a protic liquid, and an organic compound-based component;

preparing a second mixture comprising a Mo-containing precursor, a W-containing precursor, and a protic liquid;

adding a Ti-containing precursor to the first mixture, the second mixture, or a combination thereof;

heating both the first and second mixtures to a temperature of from 60°C to 150°C;

combining the first and second mixtures together;

optionally, wherein the Ti-containing precursor is selected from TiO_2 nanoparticles, colloidal TiO_2, fumed TiO_2, titanium hydroxide, organotitanium compounds, titanium halides, organotitanium halides, water-soluble titanium salts, or a combination thereof.

7. A method for preparing the bulk catalyst precursor of claim 1, the method comprising:

(a) combining in a reaction mixture:

(i) a Ni-containing precursor;

(ii) a Mo-containing precursor;

(iii) a W-containing precursor;

(iv) an organic compound-based component; and

(v) a protic liquid; and

(b) reacting the mixture under conditions sufficient to cause precipitation of an intermediate bulk catalyst precursor; and

(c) compositing the intermediate bulk catalyst precursor with a Ti-containing precursor to form the bulk catalyst precursor;

wherein the steps to prepare the bulk catalyst precursor are carried out at a temperature of no more than 200°C.

8. The method of claim 7, wherein the reaction mixture is prepared by:

preparing a first mixture comprising a Ni-containing precursor, a protic liquid, and an organic compound-based component;

preparing a second mixture comprising a Mo-containing precursor, a W-containing precursor, and a protic liquid;

heating both the first and second mixtures to a temperature of from 60°C to 150°C; and

combining the first and second mixtures together.

9. The method of claim 7, wherein:

(i) the Ti-containing precursor is selected from TiO_2 nanoparticles, fumed TiO_2, or a combination thereof, or

(ii) the intermediate bulk catalyst precursor is a Ni–Mo–W bulk catalyst precursor.

10. The method of claim 5 or claim 7, wherein:

(i) the reacting is carried out at one or more temperatures either (a) in a range of 60°C to 100°C under atmospheric pressure or (b) above 100°C under autogenous pressure, or

(ii) the organic compound-based component is selected from an organic acid or salt thereof, a sugar, a sugar alcohol, or a combination thereof, optionally, wherein the organic compound-based component is selected from glyoxylic acid, pyruvic acid, lactic acid, malonic acid, oxaloacetic acid, malic acid, fumaric acid, maleic acid, tartaric acid, gluconic acid, citric acid, oxamic acid, serine, aspartic acid, glutamic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, fructose, glucose, galactose, mannose, sucrose, lactose, maltose, erythritol, xylitol, mannitol, sorbitol, or a combination thereof.

11. The method of claim 5 or claim 7, further comprising one or more of the following steps:

compositing the bulk catalyst precursor with 0.1 to 40 wt. % with a material selected from the group of binder materials, conventional hydroprocessing catalysts, cracking compounds, or mixtures thereof;

spray-drying, (flash) drying, milling, kneading, slurry-mixing, dry or wet mixing, or combinations thereof;

shaping,

drying and/or thermally treating at a temperature of no more than 200°C; or

sulfiding.