Claims

1. A multi-metallic bulk catalyst precursor comprising:

(a) 1 to 60 wt. % of a Ni metal component, on a metal oxide basis;

(b) 1 to 40 wt. % of a Mo metal component, on a metal oxide basis;

(c) 5 to 80 wt. % of a W metal component, on a metal oxide basis;

(d) 0.01 to 20 wt. % of a Nb metal component, on a metal oxide basis;

(e) 2 to 45 wt. % of a Ti metal component, on a metal oxide basis; and

(f) 0 to 10 wt. % of a Cu metal component, on a metal oxide basis;

wherein the bulk catalyst precursor is of formula:

$$A_v[Ni_{1-a-b}Nb_aCu_b(OH)_x(L)^p_y]_z[Mo_mW_{1-m}O_4][Ti(OH)_nO_{2-n/2}]_w$$

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

2. The multi-metallic bulk catalyst precursor of claim 1, further comprising an organic compound.

3. The multi-metallic bulk catalyst precursor of claim 2, wherein the organic compound is selected from the group of an organic acid or salt thereof, a sugar, a sugar alcohol, or a combination thereof.

4. The multi-metallic bulk catalyst precursor of claim 2, wherein the organic compound is selected from the group of 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.

5. The multi-metallic bulk catalyst precursor of claim 2, wherein a molar ratio of Ni to the organic compound is in a range of 3:1 to 20:1.

6. The multi-metallic bulk catalyst precursor of claim 1, wherein a molar ratio of Nb/(Ni+Mo+W+Ti+Cu) is in a range of from 10:1 to 1:10.

7. The multi-metallic bulk catalyst precursor of claim 1, wherein a molar ratio of Ni/W is in a range of 10:1 to 1:10.

8. The multi-metallic bulk catalyst precursor of claim 1, wherein a molar ratio of W/Mo is in a range of 100:1 to 1:100.

9. The multi-metallic bulk catalyst precursor of claim 1, further comprising 1 to 15 wt. % of a binder.

10. The multi-metallic 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.

11. The multi-metallic bulk catalyst precursor of claim 1, wherein the Ni, Mo, W and Nb metal components make up at least 70 wt. % of the multi-metallic bulk catalyst precursor, calculated as oxides.

12. The multi-metallic bulk catalyst precursor of claim 1, wherein the Ni, Mo, W and Nb metal components make up at least 90 wt. % of the multi-metallic bulk catalyst precursor, calculated as oxides.

13. The multi-metallic bulk catalyst precursor of claim 1, wherein the Ti metal component is present in an amount ranging from 10 wt. % to 35 wt. %, on a metal oxide basis.

14. The multi-metallic bulk catalyst precursor of claim 1, wherein the Cu metal component is present in an amount ranging from 0.1 wt. % to 10 wt. %, on a metal oxide basis.

15. A sulfided multi-metallic bulk catalyst characterized in that it is a bulk catalyst precursor according to claim 1 that has been sulfided.

16. 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 Nb-containing precursor;

(v) a Ti-containing precursor and/or a Cu-containing precursor;

(vi) an organic compound; and

(vii) 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.

17. The method of claim 16, wherein the reaction mixture is prepared by:

preparing a first mixture comprising a Ni-containing precursor, a Nb-containing precursor, an optional Cu-containing precursor, a protic liquid, and, an organic compound;

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.

18. The method of claim 17, 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.

19. 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 Nb-containing precursor;

(v) optionally, a Cu-containing precursor;

(vi) an organic compound; and

(vii) 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.

20. The method of claim 19, wherein the reaction mixture is prepared by:

preparing a first mixture comprising a Ni-containing precursor, a Nb-containing precursor, an optional Cu-containing precursor, a protic liquid, and an organic compound;

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.

21. The method of claim 19, wherein the Ti-containing precursor is selected from TiO_2 nanoparticles, fumed TiO_2, or a combination thereof.

22. The method of claim 19, wherein the intermediate bulk catalyst precursor is a Ni–Mo–W–Nb or a Ni–Mo–W–Nb–Cu bulk catalyst precursor.

23. The method of claim 16 or claim 19, wherein 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.

24. The method of claim 16 or claim 19, wherein the organic compound is selected from an organic acid or salt thereof, a sugar, a sugar alcohol, or a combination thereof.

25. The method of claim 24, wherein the organic compound 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.

26. The method of claim 16 or claim 19, further comprising one or more of the following steps:

compositing the bulk catalyst precursor with 0 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.