SUMMARY

[0009a] In an aspect, there is provided a NiW, NiMo or NiMoW bulk catalyst precursor composition comprising nickel oxide, and molybdenum oxide or tungsten oxide or mixtures thereof, and an organic component prepared from an organic additive, wherein the total amount of molybdenum oxide and tungsten oxide is at least 30 wt%, the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05, the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 10; and wherein the organic additive is selected from Acetic acid, Aspartic acid, Citric acid, Formic acid, Fumaric acid, Gluconic acid, Glutamic acid, Glyoxylic acid, Ketoglutaric acid, Maleic acid, Malic acid, Oxaloacetic acid, Propionic acid, Pyruvic acid, Succinic acid, Fructose, Glucose, Lactose, Saccharose, Sorbitol, Xylitol, Serine and mixtures thereof.

[0009b] In another aspect, there is provided a process for hydroprocessing of a hydrocarbon feedstock comprising sulphur and nitrogen containing organic compounds comprising the step of contacting the hydrocarbon feedstock with a NiW, NiMo or NiMoW oxidic bulk catalyst obtained from a bulk catalyst precursor composition as defined above, the catalyst comprising a minimum metal loading of 2.0 moles of molybdenum plus tungsten per liter reactor, wherein the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05, a molar ratio of carbon to molybdenum plus tungsten between 1.5 and 10.

[0009c] In another aspect, there is provided a process for the manufacture of a mixed metal oxide organic phase catalyst precursor as defined above, the process comprising:

a. forming a solution in protic liquid of one or more soluble metal compounds comprising nickel and molybdenum or tungsten or mixtures thereof and one or more organic compound, wherein the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05;
b. evaporating the protic liquid;
c. partially decomposing the metal-organic phase to form the mixed metal oxide organic phase catalyst precursor wherein the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 10;

   wherein the one or more organic compound is Acetic acid, Aspartic acid, Citric acid, Formic acid, Fumaric acid, Gluconic acid, Glutamic acid, Glyoxylic acid, Ketoglutaric acid, Maleic acid, Malic acid, Oxaloacetic acid, Propionic acid, Pyruvic acid, Succinic

acid, Fructose, Glucose, Lactose, Saccharose, Sorbitol, Xylitol, Serine and mixtures thereof.

[0009d] In another aspect, there is provided a process for the manufacture of an oxidic catalyst comprising shaping of the bulk catalyst precursor as defined above.

[0010] Accordingly, one embodiment of the current disclosure is a bulk catalyst precursor (i.e. no support material is added as such) comprising Ni and Mo and/or W and an organic component, wherein the molar ratio of C:(Mo+W) ranges from 1.5 to 10. The bulk catalyst precursor is prepared from a mixture of metal-precursors with an organic agent. The organic agent is partly decomposed to form a mixed metal-oxide/C phase which is in effect the bulk catalyst precursor. This bulk catalyst precursor (i) is effectively insoluble in water (ii) does not have any appreciable pore volume or surface area and (iii) does not contain a (nano)crystalline metal-oxide phase as characterized by XRD. A bulk catalyst is made from the bulk catalyst precursor. After conventional liquid phase sulfidation, the active sufidic bulk catalyst is formed which has a very high activity in different hydroprocessing applications. After sulfidation of the oxidic catalyst, it is possible that the sulfidic catalyst (i) shows surface area as measured via N_2 physisorption and hexane adsorption (ii) loses some of its C during sulfidation.

[0011] In one embodiment it is disclosed a bulk catalyst precursor composition comprising Nickel, Molybdenum and/or Tungsten, and an organic component, wherein the amount of molybdenum oxide plus tungsten oxide is at least 30 wt%, wherein the molar ratio of C:(Mo+W) ranges from 1.5 to 10. The ratio of Ni:(Mo+W) is at least 0.05.

[0012] In another embodiment, a bulk catalyst is provided that is obtained by shaping the bulk catalyst precursor by any method known in the art, such as extrusion, pelletizing, and/or beading. The bulk catalyst is characterized by a minimum metal loading of 2.0 moles of molybdenum plus tungsten per liter reactor, wherein the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05 and the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 10. The MoO_3+WO_3 loading of this bulk catalyst is higher than what is typically applied in supported hydroprocessing catalysts. In another embodiment, a sulfided catalyst is provided that is formed by sulfiding the above bulk catalyst composition.

[0013] In another embodiment, the method for preparing a bulk catalyst precursor is disclosed. The method includes combining at least one Ni compound and at least one Group VIB metal compound with at least one organic agent, thereby forming a solution. The solution is then evaporated and dried. The drying can be carried out by using commonly available

drying methods such as spray-drying, freeze drying, or plate drying, etc. The dried material is then subjected to a further heat treatment at about 300° C. to about 500° C. to form a bulk catalyst precursor, which can be shaped by any method known in the art to obtain a bulk catalyst. The bulk catalyst is then sulfided under sulfiding conditions to produce a sulfided catalyst.

[0014] In another embodiment, a method for hydroprocessing a hydrocarbon feedstock is provided. The method includes contacting said feedstock with a sulfided bulk catalyst, the sulfided bulk catalyst formed by sulfiding the bulk catalyst as described above.

[0015] In accordance with another embodiment of the disclosure there is provided a process for the hydroprocessing of a hydrocarbon feedstock wherein the feedstock is contacted under hydroprocessing conditions with the aforementioned bulk catalyst composition. The bulk catalyst composition according to this disclosure can be used in virtually all hydroprocessing processes to treat a plurality of feedstocks under wide-ranging reaction conditions, including but not limited to pre-treating a feedstock prior to it being hydrocracked, pre-treating a feedstock prior to it being catalytically cracked or treating a feedstock to generate a transportation fuel with a specific maximum sulphur concentration. Generally, these reaction conditions comprise a temperature in the range from about 200° to about 450°C, hydrogen pressures in the range from about 5 to about 300 Bar, liquid hourly space velocities (LHSV) in the range from about 0.1 to about 10 h^{-1} and H_2/oil ratios in the range from about 50 to about 2000 Nl/l. However, it is preferred to employ the catalyst of the present disclosure in the hydroprocessing of, and more particularly, the hydrodesulfurisation (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) of feedstocks comprising a diesel oil or a vacuum gas oil under conditions at least comprising liquid hourly space velocities (LHSV) in the range from about 0.1 to about 10 h^{-1} and H_2/oil ratios in the range from about 50 to about 2000 Nl/l. The bulk catalyst precursor composition has been found to show improved hydrodesulfurisation activity in applications ranging from 30 to 80 bar in treating a host of different Distillate feed streams. It is fully expected that the bulk catalyst precursor of the disclosure will have advantages in other hydroprocessing application such as the treatment of VGO fractions and in a broader pressure range as well.

CLAIMS

1. A NiW, NiMo or NiMoW bulk catalyst precursor composition comprising nickel oxide, and molybdenum oxide or tungsten oxide or mixtures thereof, and an organic component prepared from an organic additive, wherein the total amount of molybdenum oxide and tungsten oxide is at least 30 wt%, the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05, the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 10; and wherein the organic additive is selected from Acetic acid, Aspartic acid, Citric acid, Formic acid, Fumaric acid, Gluconic acid, Glutamic acid, Glyoxylic acid, Ketoglutaric acid, Maleic acid, Malic acid, Oxaloacetic acid, Propionic acid, Pyruvic acid, Succinic acid, Fructose, Glucose, Lactose, Saccharose, Sorbitol, Xylitol, Serine and mixtures thereof.

2. The bulk catalyst precursor of Claim 1 further comprising a BET-SA as measured by N_2 physisorption of < 40 m^2/g.

3. The bulk catalyst precursor of Claim 1 further comprising Ni-crystals detected by transmission electron microscopy technique (TEM).

4. The bulk catalyst precursor of Claim 1 further comprising a peak at 45 ° 2theta in a XRD pattern recorded using X-ray radiation with a wavelength of 1.54 Å.

5. The bulk catalyst precursor of Claim 1 characterized by the absence of any peaks with a Full Width at Half Maximum in radians (FWHM) of smaller than 2° 2 theta in the range of 10-40 ° 2theta in its XRD pattern recorded using X-ray radiation with a wavelength of 1.54 Å.

6. The bulk catalyst precursor of Claim 1 wherein the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 7.0

7. The bulk catalyst precursor of Claim 1 further comprising a molar ratio of nickel to molybdenum plus tungsten between 0.10 and 1.05.

8. The bulk catalyst precursor of Claim 6 wherein the molar ratio of nickel to molybdenum plus tungsten is between 0,20 and 0.75.

9. The bulk catalyst precursor of Claim 1 further comprising an amount of nickel oxide between 2 and 30 wt %.

10. The bulk catalyst precursor of Claim 1 wherein the total amount of molybdenum oxide plus tungsten oxide is between 40 and 80 wt %.

11. The bulk catalyst precursor of Claim 1 wherein the amount of carbon is between 10 and 30 wt %

12. A process for hydroprocessing of a hydrocarbon feedstock comprising sulphur and nitrogen containing organic compounds comprising the step of contacting the hydrocarbon feedstock with a NiW, NiMo or NiMoW oxidic bulk catalyst obtained from a bulk catalyst precursor composition according to any one of claims 1 to 11, the catalyst comprising a minimum metal loading of 2.0 moles of molybdenum plus tungsten per liter reactor, wherein the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05, a molar ratio of carbon to molybdenum plus tungsten between 1.5 and 10.

13. The process of Claim 12 wherein the catalyst further comprises a peak at 45 ° 2theta in the XRD pattern recorded using X-ray radiation with a wavelength of 1.54 Å.

14. The process of Claim 12 wherein the catalyst further comprises Ni-crystals detected by transmission electron microscopy technique (TEM).

15. The process according to Claim 12 wherein the catalyst comprises an inorganic binder comprising silica, silica-alumina, alumina, titania, titania-coated alumina, zirconia, bentonite, attapulgite, or mixtures thereof.

16. The process of Claim 12 wherein the metal loading of molybdenum plus tungsten per liter reactor is between 3.0 and 7.0.

17. The process of Claim 12 wherein the molar ratio of carbon to molybdenum plus tungsten between 1.5 and 7.0.

18. The process of Claim 12 wherein the molar ratio of nickel to molybdenum plus tungsten is between 0.10 and 1.05.

19. The process of Claim 12 wherein the molar ratio of nickel to molybdenum plus tungsten is between 0.20 and 0.75

20. A process for the manufacture of a mixed metal oxide organic phase catalyst precursor according to any one of claims 1 to 11, the process comprising:

a. forming a solution in protic liquid of one or more soluble metal compounds comprising nickel and molybdenum or tungsten or mixtures thereof and one or more organic compound, wherein the molar ratio of nickel to molybdenum plus tungsten is higher than 0.05;
b. evaporating the protic liquid;
c. partially decomposing the metal-organic phase to form the mixed metal oxide organic phase catalyst precursor wherein the molar ratio of carbon to molybdenum plus tungsten is between 1.5 and 10;
wherein the one or more organic compound is Acetic acid, Aspartic acid, Citric acid, Formic acid, Fumaric acid, Gluconic acid, Glutamic acid, Glyoxylic acid, Ketoglutaric acid, Maleic acid, Malic acid, Oxaloacetic acid, Propionic acid, Pyruvic acid, Succinic acid, Fructose, Glucose, Lactose, Saccharose, Sorbitol, Xylitol, Serine and mixtures thereof.

21. The process of Claim 20 wherein the one or more organic compound is an organic acid or a sugar.

22. A process for the manufacture of an oxidic catalyst comprising shaping of the bulk catalyst precursor of Claim 20.

23. The process of Claim 22 wherein the shaping of the bulk catalyst precursor comprises forming an extrudate with an inorganic binder and water and then drying the extrudates at a temperature of at least 120°C.

24. A process for the manufacture of a sulphidic catalyst comprising sulphiding the bulk catalyst of Claim 20.