for use in the hydroprocessing of lower grade, more refractory hydrocarbon feeds, capable of generating low aromatic products meeting new emission requirements. There is also a need for a better understanding of structure–performance relationships for these catalysts to design next generation of highly active self-supported catalysts for use in hydroprocessing.

SUMMARY

[009] In one aspect, the ~~invention~~ disclosure relates to a self-supported mixed metal sulfide (MMS) catalyst consisting essentially of nickel sulfide and tungsten sulfide, wherein the catalyst contains Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis. In one embodiment, the catalyst further comprises a metal promoter selected from Mo, Nb, Ti, and mixtures thereof, wherein the metal promoter is present in an amount of less 1% (mole).

[010] In a second aspect, the ~~invention~~ disclosure relates to a MMS catalyst consisting essentially of molybdenum sulfide and tungsten sulfide, wherein the catalyst contains at least 0.1 mol% of Mo and at least 0.1 mol% of W, on a transition metal basis. In one embodiment, the catalyst is characterized as having an HDS reaction rate constant of at least 10% higher than that of a catalyst comprising molybdenum sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on same metal molar basis in hydrotreating a Heavy Coker Gas Oil as a feedstock at identical process conditions as indicated in Table E.

[011] In a third aspect, the ~~invention~~ disclosure relates to a MMS catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized by an HDN reaction rate constant of at least 100 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics, and an HDS reaction rate constant of at least 550 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics in hydrotreating of a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and at given process conditions as indicated in Table E. In one embodiment, the catalyst is characterized by an HDN reaction rate constant of at least 4 hr^{-1} assuming first order kinetics, and an HDS reaction rate constant of at least 5 hr^{-1} assuming first order kinetics in hydrotreating of a Heavy Vacuum Gas Oil as a feedstock with properties indicated in Table B and at the steady state process conditions as indicated in Table F. In another embodiment, the catalyst is characterized by an HYD reaction rate constant and an HYL reaction rate constant of at least 10% higher than the rate constants of a catalyst comprising nickel sulfide and molybdenum sulfide, or a catalyst comprising nickel sulfide and tungsten sulfide, when compared on same metal molar basis in hydrotreating a diphenylether as a feedstock at identical process conditions as indicated in Table C.

[012] In a fourth aspect, the ~~invention~~ disclosure relates to a MMS catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, and wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.25), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15). In one embodiment, the catalyst is characterized having a molar ratio of metal components Ni:Mo:W in a range of: $0.33 <= Ni/(W+Mo) \leq 2.57$; $0.00 \leq Mo/(Ni+W) \leq 0.33$; and $0.18 \leq W/(Ni+Mo) \leq 3.00$.

[013] In a fifth aspect, the ~~invention~~ disclosure relates to a MMS catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase. In one embodiment, the molybdenum tungsten sulfide phase comprises at least a layer, wherein the at least a layer contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

[014] In a sixth aspect, the ~~invention~~ disclosure relates to a MMS catalyst comprising molybdenum (Mo) sulfide, tungsten (W) sulfide, and nickel (Ni) sulfide, wherein the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g. In one embodiment, the catalyst has a BET surface area of at least 30 m^2/g.

[014a] In one embodiment, there is provided a self-supported mixed metal sulfide (MMS) catalyst:

(a) consisting essentially of nickel sulfide and tungsten sulfide, wherein the catalyst contains Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis; or

(b) consisting essentially of molybdenum sulfide and tungsten sulfide, wherein the catalyst contains at least 0.1 mol% of Mo and at least 0.1 mol% of W, on a transition metal basis; or

(c). comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having an HDN reaction rate constant of at least 100 g feed hr-1 g catalyst -1 assuming first order kinetics, and an HDS reaction rate constant of at least 550 g feed hr-1 g catalyst -1 assuming first order kinetics in hydrotreating of a Heavy Coker Gas

Oil as a feedstock with properties indicated in Table A and under process conditions as indicated in Table E; or

(d) comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, and wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.25), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15); or

(e) comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase; or

(f) comprising molybdenum (Mo) sulfide, tungsten (W) sulfide, and nickel (Ni) sulfide, wherein the catalyst has a BET surface area of at least 20 m2/g and a pore volume of at least 0.05 cm3/g.

[015] In a seventh aspect, the ~~invention~~ disclosure relates to a method for making a MMS catalyst, the method comprising mixing a sufficient amount of a nickel (Ni) metal precursor, a sufficient amount of a molybdenum (Mo) metal precursor, and a sufficient amount of a tungsten (W) metal precursor to produce a catalyst precursor having a molar ratio Ni:Mo:W in relative proportions defined by a region of a ternary phase diagram showing transition metal elemental composition in terms of nickel, molybdenum, and tungsten mol-%, wherein the region is defined by five points ABCDE and wherein the five points are: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.55, Mo=0.00, W=0.45), C (Ni=0.48, Mo=0.14, W=0.38), D (Ni=0.48, Mo=0.20, W=0.33), E (Ni=0.62, Mo=0.14, W=0.24); and sulfiding the catalyst precursor under conditions sufficient to convert the catalyst precursor into a sulfide catalyst.

CLAIMS

1. A self-supported mixed metal sulfide (MMS) catalyst consisting essentially of nickel sulfide and tungsten sulfide, wherein the catalyst contains Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis.

2. The self-supported MMS catalyst of claim 1, wherein the catalyst further comprises a metal promoter selected from Mo, Nb, Ti, and mixtures thereof, wherein the metal promoter is present in an amount of less 1% (mole).

3. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is characterized as having an HDN reaction constant of at least 100 g feed·hr^{-1}·g $catalyst^{-1}$ in hydrotreating a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under the process conditions as indicated in Table E, assuming first order kinetics.

4. The self-supported MMS catalyst of claim 4, wherein the catalyst is characterized as having an HDN reaction constant of at least 110 g feed·hr^{-1}·g $catalyst^{-1}$ in hydrotreating a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under the process conditions as indicated in Table E, assuming first order kinetics.

5. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is characterized as having a HDN reaction rate constant of at least 4 hr^{-1} on catalyst weight hourly space velocity basis in hydrotreating a Heavy Vacuum Gas Oil as a feedstock with properties indicated in Table B and under steady state process conditions as indicated in Table F, assuming first order kinetics.

6. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is characterized as having an HYD reaction rate constant of at least 15% higher than that of a catalyst comprising nickel sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on same metal molar basis in hydrotreating of benzene as a feedstock at identical process conditions as indicated in Table D.

7. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is characterized as having NiS_x nanoparticles dispersed onto the tungsten sulfide phase.

8. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is characterized as having a multi-phased structure comprising a tungsten sulfide phase and an active nickel phase.

9. The self-supported MMS catalyst of claim 8, wherein the multi-phased structure further comprises a nickel sulphide phase.

10. The self-supported MMS catalyst of claim 9, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

11. The self-supported MMS catalyst of claim 9, wherein the nickel sulfide serves as support for the tungsten sulfide phase.

12. The self-supported MMS catalyst of claim 8, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into the tungsten sulfide phase.

13. The self-supported MMS catalyst of claim 8, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel decorating the edges of the tungsten sulfide phase.

14. The self-supported MMS catalyst of claim 8, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the tungsten sulfide phase or decorating the tungsten sulfide phase.

15. The self-supported MMS catalyst of any of claims 1 - 2, wherein the catalyst is prepared by sulfiding a nickel metal precursor and a tungsten metal precursor in an amount sufficient for the catalyst to contain Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis.

16. The self-supported MMS catalyst of claim 15, wherein the nickel metal precursor is selected from inorganic metal sulfides of nickel, sulfur-containing inorganic compounds of nickel, sulfur-containing organic compounds of nickel, nickel carbonate, nickel

hydroxide, nickel phosphate, nickel phosphite, nickel formate, nickel fumarate, nickel molybdate, nickel tungstate, nickel oxide, nickel alloys, cyclopentadienyl nickel, nickel naphthenate, and mixtures thereof.

17. The self-supported MMS catalyst of claim 15, wherein the tungsten metal precursor is selected from alkali metal tungstates, ammonium metallates of tungsten, inorganic tungsten compounds, tungsten naphthenate, pentacyclodienyl tungsten dihydride, tungsten oxide, W--P heteropolyanion compounds, W--Si heteropolyanion compounds, sulfur-containing inorganic compounds of tungsten, sulfur-containing organic compounds of tungsten, and mixtures thereof.

18. The self-supported MMS catalyst of claim 17, wherein the catalyst is prepared by sulfiding a molybdenum metal precursor and a tungsten metal precursor in an amount sufficient for the catalyst to contain Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis and under a H_2-containing gas pressure with at least a sulfiding agent at a temperature ranging from 25°C to 500°C from 10 minutes to 15 days.

19. A self-supported mixed metal sulfide (MMS) catalyst consisting essentially of molybdenum sulfide and tungsten sulfide, wherein the catalyst contains at least 0.1 mol% of Mo and at least 0.1 mol% of W, on a transition metal basis.

20. The self-supported MMS catalyst of claim 19, wherein the catalyst is characterized as having an HDS reaction rate constant of at least 10% higher than that of a catalyst comprising molybdenum sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on same metal molar basis in hydrotreating a Heavy Coker Gas Oil as a feedstock at identical process conditions as indicated in Table E.

21. The self-supported MMS catalyst of claim 20, wherein the HDS reaction rate constant is at least 15% higher than that of a catalyst comprising molybdenum sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on the same metal molar basis in hydrotreating of a Heavy Coker Gas Oil as a feedstock at identical process conditions as indicated in Table E.

22. The self-supported MMS catalyst of any of claims 19 - 20, wherein the catalyst is characterized as having a hydrogenolysis (HYL) reaction rate constant of at least 10% higher than a catalyst comprising molybdenum sulfide alone or a catalyst comprising tungsten sulfide catalyst alone, when compared on same metal molar basis in hydrotreating a diphenylether at identical process conditions as indicated in Table C.

23. The self-supported MMS catalyst of claim 22, wherein the HYL reaction rate constant is at least 15% higher than that of a catalyst comprising molybdenum sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on the same metal molar basis in hydrotreating of a diphenylether as a feedstock at identical process conditions as indicated in Table C.

24. The self-supported MMS catalyst of any of claims 19 - 20, wherein the catalyst is characterized as having a molybdenum tungsten sulfide phase comprising at least a layer containing at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

25. The self-supported MMS catalyst of claim 24, wherein the molybdenum sulfide and tungsten sulfide phase comprises 1 to 6 layers.

26. The self-supported MMS catalyst of claim 24, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as individual atoms forming an intralayer atomic mixture.

27. The self-supported MMS catalyst of claim 24, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as tungsten domains.

28. The self-supported MMS catalyst of claim 24, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as individual atoms forming an intralayer atomic mixture.

29. The self-supported MMS catalyst of claim 24, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as molybdenum domains

30. The self-supported MMS catalyst of claim 24, wherein the catalyst is characterized as having a molybdenum sulfide and tungsten sulfide phase comprising at least two layers, and wherein the at least two layers comprise inter-layer mixtures of tungsten sulfide and molybdenum sulfide.

31. The self-supported MMS catalyst of claim 24, wherein the at least a layer comprises mixtures of individual domains of tungsten sulfide and molybdenum sulfide.

32. The self-supported catalyst of any of claims 19 - 20, wherein the catalyst is prepared by sulfiding a molybdenum metal precursor and a tungsten metal precursor in an amount sufficient for the catalyst to contain at least 0.1 mol% of Mo and 0.1 mol% of W.

33. The self-supported MMS catalyst of claim 32, wherein the molybdenum metal precursor is selected from molybdenum metal, alkali metal molybdates, ammonium metallates of molybdenum, molybdenum sulphate, molybdenum phosphate, molybdenum silicate, molybdenum borate, molybdenum naphthenate, pentacyclodienyl molybdate, cyclopentadienyl Mo tricarbonyl dimer, ammonium salts of phosphomolybdic acids, phosphomolybdic acid, molybdenum oxide, Mo--P heteropolyanion compounds, Mo--Si heteropolyanion compounds, inorganic metal sulfides of molybdenum, sulfur-containing inorganic compounds of molybdenum, sulfur-containing organic compounds of molybdenum, and mixtures thereof.

34. The self-supported MMS catalyst of claim 32, wherein the tungsten metal precursor is selected from alkali metal tungstates, ammonium metallates of tungsten, inorganic tungsten compounds, tungsten naphthenate, pentacyclodienyl tungsten dihydride, tungsten oxide, W--P heteropolyanion compounds, W--Si heteropolyanion compounds, sulfur-containing inorganic compounds of tungsten, sulfur-containing organic compounds of tungsten, and mixtures thereof.

35. The self-supported MMS catalyst of claim 32, wherein the catalyst is prepared by sulfiding a molybdenum metal precursor and a tungsten metal precursor under a H_2-containing gas pressure with at least a sulfiding agent at a temperature ranging from 25°C to 500°C from 10 minutes to 15 days.

36. The self-supported MMS catalyst of any of claims 19 - 20, wherein the molybdenum sulfide is MoS_{2+e} and the tungsten sulfide is WS_{2+e}, and wherein e has a value between 0 and 1.

37. A self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having an HDN reaction rate constant of at least 100 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics, and an HDS reaction rate constant of at least 550 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics in hydrotreating of a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under process conditions as indicated in Table E.

38. The self-supported MMS catalyst of claim 37, wherein the catalyst is characterized as having an HDN reaction rate constant of at least 4 hr^{-1} assuming first order kinetics, and an HDS reaction rate constant of at least 5 hr^{-1}, assuming first order kinetics in hydrotreating of a Heavy Vacuum Gas Oil as a feedstock with properties indicated in Table B and under process conditions as indicated in Table F.

39. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst is characterized as having an HYD reaction rate constant and an HYL reaction rate constant of at least 10% higher than the rate constants of a catalyst comprising nickel sulfide and molybdenum sulfide, or a catalyst comprising nickel sulfide and tungsten sulfide, when compared on same metal molar basis in hydrotreating a diphenylether as a feedstock under process conditions as indicated in Table C.

40. The self-supported MMS catalyst of claim 39, wherein the HYD reaction rate constant and the HYL reaction rate constant each is at least 15% higher than the respective rate constant of a catalyst comprising nickel sulfide and molybdenum sulfide, or a catalyst comprising nickel sulfide and tungsten sulfide, when compared on the same metal molar basis

in hydrotreating of a diphenylether as a feedstock under process conditions as indicated in Table D.

41. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase.

42. The self-supported MMS catalyst of claim 41, wherein the molybdenum tungsten sulfide phase comprises at least a layer which contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

43. The self-supported MMS catalyst of claim 42, wherein the molybdenum tungsten sulfide phase comprises 1 to 6 layers.

44. The self-supported MMS catalyst of claim 42, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as individual atoms forming an intralayer atomic mixture.

45. The self-supported MMS catalyst of claim 42, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as tungsten domains.

46. The self-supported MMS catalyst of claim 42, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as individual atoms forming an intralayer atomic mixture.

47. The self-supported MMS catalyst of claim 42, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as molybdenum domains

48. The self-supported MMS catalyst of claim 42, wherein the surface of the molybdenum tungsten sulfide phase exhibits at least a 20% higher molybdenum-to-tungsten ratio than the bulk of the molybdenum tungsten sulfide phase.

49. The self-supported MMS catalyst of claim 42, wherein the at least a layer comprises mixtures of individual domains of tungsten sulfide and molybdenum sulfide.

50. The self-supported MMS catalyst of claim 41, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into the molybdenum tungsten sulfide phase.

51. The self-supported MMS catalyst of claim 41, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel decorating the edges of the molybdenum tungsten sulfide phase.

52. The self-supported MMS catalyst of claim 41, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the molybdenum tungsten sulfide phase or decorating the molybdenum tungsten sulfide phase.

53. The self-supported MMS catalyst of claim 41, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

54. The self-supported MMS catalyst of claim 52, wherein the molybdenum tungsten sulfide phase envelopes the slabs of Ni_9S_8 and Ni_3S_2 layers.

55. The self-supported MMS catalyst of claim 41, wherein the nickel sulfide phase serves as support for the molybdenum tungsten sulfide phase.

56. The self-supported MMS catalyst of claim 41, wherein the nickel sulfide phase stabilizes dispersion of the active nickel phase onto the molybdenum tungsten sulfide phase.

57. The self-supported MMS catalyst of claim 41, wherein the catalyst is characterized by an X-ray diffraction pattern showing peaks corresponding to MoS_2 phase and WS_2 phase.

58. The self-supported MMS catalyst of claim 41, wherein the catalyst is characterized by an X-ray diffraction pattern showing peaks corresponding to Ni_3S_2 phase.

59. The self-supported MMS catalyst of claim 41, wherein the catalyst is characterized by TEM image showing lattice fringes on nickel sulfide crystals of 4.60±0.5 Å and 2.87±0.5 Å.

60. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g.

61. The self-supported MMS catalyst of claim 60, wherein the catalyst has a BET surface area of at least 40 m^2/g and a pore volume of at least 0.05 cm^3/g.

62. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst after hydrotreating a Heavy Coker Gas Oil for at least 0.5 hrs, has a surface area reduction of less than 80%.

63. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.4 as characterized by XPS.

64. The self-supported MMS catalyst of claim 63, wherein the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.5 as characterized by XPS.

65. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

66. The self-supported MMS catalyst of claim 65, wherein the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.4 as characterized by XPS.

67. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst comprises molybdenum sulfide, nickel sulfide, and tungsten sulfide with molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15).

68. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst comprises molybdenum sulfide, nickel sulfide, and tungsten sulfide with molar ratios of metal components Ni:Mo:W in a region defined by six points ABCDEF of a ternary phase diagram, and wherein the six points ABCDEF are defined as: A (Ni=0.67,Mo=0.00,W=0.33), B (Ni=0.67, Mo=0.10, W=0.23), C (Ni=0.60, Mo=0.15, W=0.25), D (Ni=0.52, Mo=0.15, W=0.33), E (Ni=0.52, Mo=0.06, W=0.42), F (Ni=0.58, Mo=0.0, W=0.42).

69. The self-supported MMS catalyst of any of claims 37 - 38, wherein the catalyst comprises molybdenum sulfide, nickel sulfide, and tungsten sulfide with molar ratios of metal components Ni:Mo:W in a region defined by four points ABCD of a ternary phase diagram, and wherein the four points ABCD are defined as: A(Ni=0.67,Mo=0.00,W=0.33), B(Ni=0.58, Mo=0.0, W=0.42), C(Ni=0.52, Mo=0.15, W=0.33), D(Ni=0.60, Mo=0.15, W=0.25).

70. A self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, and wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.25), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15).

71. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized as having a molar ratio of metal components Ni:Mo:W in a range of:

$0.33 \leq Ni/(W+Mo) \leq 2.57$;

$0.00 \leq Mo/(Ni+W) \leq 0.33$; and

$0.18 \leq W/(Ni+Mo) \leq 3.00$.

72. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by six points ABCDEF of a ternary phase diagram, and wherein the six points ABCDEF are defined as: : A (Ni=0.67,Mo=0.00,W=0.33), B (Ni=0.67, Mo=0.10, W=0.23), C (Ni=0.60, Mo=0.15, W=0.25), D (Ni=0.52, Mo=0.15, W=0.33), E (Ni=0.52, Mo=0.06, W=0.42), F (Ni=0.58, Mo=0.0, W=0.42).

73. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized as having a molar ratio of metal components Ni:Mo:W in a range of:

$1.08 <= Ni/(Mo+W) <= 2.03$

$0 <= Mo/(Ni+W) <= 0.18$; and

$0.33 <= W/(Mo+Ni)) <= 0.72$.

74. The self-supported MMS catalyst of claim 70, wherein the catalyst comprises molybdenum sulfide, nickel sulfide, and tungsten sulfide with molar ratios of metal components Ni:Mo:W in a region defined by four points ABCD of a ternary phase diagram, and wherein the four points ABCD are defined as: A(Ni=0.67,Mo=0.00,W=0.33), B(Ni=0.58, Mo=0.0, W=0.42), C(Ni=0.52, Mo=0.15, W=0.33), D(Ni=0.60, Mo=0.15, W=0.25).

75. The self-supported MMS catalyst of claim 70, wherein the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g.

76. The self-supported MMS catalyst of claim 75, wherein the catalyst has a BET surface area of at least 40 m^2/g and a pore volume of at least 0.05 cm^3/g.

77. The self-supported MMS catalyst of claim 70, wherein the catalyst after hydrotreating a Heavy Coker Gas Oil for at least 0.5 hrs, has a surface area of at least 20% of original surface area before hydrotreating.

78. The self-supported MMS catalyst of claim 70, wherein the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.4 as characterized by XPS.

79. The self-supported MMS catalyst of claim 78, wherein the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.5 as characterized by XPS.

80. The self-supported MMS catalyst of claim 70, wherein the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

81. The self-supported MMS catalyst of claim 80, wherein the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.4 as characterized by XPS.

82. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized by an HDN reaction rate constant of at least 100 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics, and an HDS reaction rate constant of at least 550 g feed hr^{-1} g catalyst $^{-1}$ assuming first order kinetics in hydrotreating of a Heavy Coker Gas Oil as a feedstock with properties defined in Table A and under process conditions as defined in Table E.

83. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized by an HDN reaction rate constant of at least 4 hr^{-1} assuming first order kinetics, and an HDS reaction rate constant of at least 5 hr^{-1} assuming first order kinetics in hydrotreating of a Heavy Vacuum Gas Oil as a feedstock with properties defined by Table B and under process conditions as defined by Table F.

84. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized as having a combined HYD and HYL reaction rate constant of at least 10% higher than that of a catalyst comprising nickel sulfide and molybdenum sulfide, or a catalyst comprising nickel sulfide and tungsten sulfide, when compared on the same metal molar basis in hydrotreating of a diphenylether as a feedstock under process conditions as indicated in Table C.

85. The self-supported MMS catalyst of claim 84, wherein the combined HYD and HYL reaction rate constant is at least 15% higher than that of a catalyst comprising nickel

sulfide and molybdenum sulfide, or a catalyst comprising nickel sulfide and tungsten sulfide, when compared on the same metal molar basis in hydrotreating of a diphenylether as a feedstock under process conditions as indicated in Table D.

86. The self-supported MMS catalyst of claim 70, wherein the molybdenum sulfide is MoS_{2+e} and the tungsten sulfide is WS_{2+e}, and wherein e has a value between 0 and 1.

87. The self-supported MMS catalyst of claim 70, wherein the catalyst has a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase.

88. The self-supported MMS catalyst of claim 87, wherein the molybdenum tungsten sulfide phase comprises at least a layer, and wherein the at least a layer contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

89. The self-supported MMS catalyst of claim 88, wherein the molybdenum tungsten sulfide phase comprises 1 to 6 layers.

90. The self-supported MMS catalyst of claim 88, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as individual atoms forming an intralayer atomic mixture.

91. The self-supported MMS catalyst of claim 88, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as tungsten domains.

92. The self-supported MMS catalyst of claim 88, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as individual atoms forming an intralayer atomic mixture.

93. The self-supported MMS catalyst of claim 88, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as molybdenum domains

94. The self-supported MMS catalyst of claim 88, wherein the molybdenum tungsten sulfide phase comprises inter-layer mixtures of tungsten sulfide and molybdenum sulfide.

95. The self-supported MMS catalyst of claim 88, wherein the at least a layer comprises mixtures of individual domains of tungsten sulfide and molybdenum sulfide.

96. The self-supported MMS catalyst of claim 87, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into the molybdenum tungsten sulfide phase.

97. The self-supported MMS catalyst of claim 87, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the molybdenum tungsten sulfide phase or decorating the molybdenum tungsten sulfide phase.

98. The self-supported MMS catalyst of claim 87, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

99. The self-supported MMS catalyst of claim 87, wherein the nickel sulfide phase serves as support for the molybdenum tungsten sulfide phase.

100. The self-supported MMS catalyst of claim 95, wherein the molybdenum tungsten sulfide phase envelopes the slabs of Ni_9S_8 and Ni_3S_2 layers.

101. The self-supported MMS catalyst of claim 87, wherein the nickel sulfide phase stabilizes dispersion of the active nickel phase onto the molybdenum tungsten sulfide phase.

102. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized by an X-ray diffraction pattern showing any of: peaks corresponding to MoS_2 phase and WS_2 phase and peaks corresponding to Ni_3S_2 phase.

103. The self-supported MMS catalyst of claim 70, wherein the catalyst is characterized by TEM image showing lattice fringes on nickel sulfide of 4.60±0.5 Å and 2.87±0.5 Å.

104. A self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase.

105. The self-supported MMS catalyst of claim 104, wherein the molybdenum tungsten sulfide phase comprising at least a layer, wherein the at least a layer contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

106. The self-supported MMS catalyst of claim 105, wherein the molybdenum tungsten sulfide phase comprises 1 to 6 layers.

107. The self-supported MMS catalyst of claim 105, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as individual atoms forming an intralayer atomic mixture.

108. The self-supported MMS catalyst of claim 105, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as tungsten domains.

109. The self-supported MMS catalyst of claim 105, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as individual atoms forming an intralayer atomic mixture.

110. The self-supported MMS catalyst of claim 105, wherein the at least a layer comprises any of: molybdenum isomorphously substituted into tungsten sulfide as

molybdenum domains; inter-layer mixtures of tungsten sulfide and molybdenum sulfide; and mixtures of individual domains of tungsten sulfide and molybdenum sulfide.

111. The self-supported MMS catalyst of claim 104, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into the molybdenum tungsten sulfide phase.

112. The self-supported MMS catalyst of claim 104, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the molybdenum tungsten sulfide phase or decorating the molybdenum tungsten sulfide phase.

113. The self-supported MMS catalyst of claim 104, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

114. The self-supported MMS catalyst of claim 104, wherein the nickel sulfide phase serves as support for the molybdenum tungsten sulfide phase.

115. The self-supported MMS catalyst of claim 113, wherein the molybdenum tungsten sulfide phase envelopes the slabs of Ni_9S_8 and Ni_3S_2 layers.

116. The self-supported MMS catalyst of claim 104, wherein the nickel sulfide phase stabilizes dispersion of the active nickel phase onto the molybdenum tungsten sulfide phase.

117. The self-supported MMS catalyst of claim 104, wherein the catalyst is further characterized by an X-ray diffraction pattern showing peaks corresponding to MoS_2 phase and WS_2 phase.

118. The self-supported MMS catalyst of claim 104, wherein the catalyst is further characterized by an X-ray diffraction pattern showing peaks corresponding to Ni_3S_2 phase.

119. The self-supported MMS catalyst of claim 104, wherein the catalyst is further characterized by TEM image showing lattice fringes on nickel sulfide of 4.60±0.5 Å and 2.87±0.5 Å.

120. The self-supported MMS catalyst of claim 104, wherein the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g.

121. The self-supported MMS catalyst of claim 120, wherein the catalyst has a BET surface area of at least 40 m^2/g and a pore volume of at least 0.05 cm^3/g.

122. The self-supported MMS catalyst of claim 104, wherein the catalyst after hydrotreating a Heavy Coker Gas Oil for at least 0.5 hrs. has a surface area reduction of less than 80%.

123. The self-supported MMS catalyst of claim 104, wherein the catalyst is further characterized by a Ni surface concentration / Ni bulk concentration ratio of greater than 0.4 as characterized by XPS.

124. The self-supported MMS catalyst of claim 123, wherein the catalyst is further characterized by a Ni surface concentration / Ni bulk concentration ratio of greater than 0.5 as characterized by XPS.

125. The self-supported MMS catalyst of claim 104, wherein the catalyst is further characterized by a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

126. The self-supported MMS catalyst of claim 125, wherein the catalyst is further characterized by a W surface concentration / W bulk concentration ratio of greater than 0.4 as characterized by XPS.

127. The self-supported MMS catalyst of claim 104, wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as:

A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15).

128. The self-supported MMS catalyst of claim 127, wherein the catalyst is characterized by having a molar ratio of metal components Ni:Mo:W in a range of: $0.33 \leq Ni/(Mo+W) \leq 2.57$, a range of Mo/(Ni+W) molar ratios of $0.00 \leq Mo/(Ni+W) \leq 0.33$, and a range of W/(Ni+Mo) molar ratios of $0.18 \leq W/(Ni+Mo) \leq 3.00$.

129. The self-supported MMS catalyst of claim 127, wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by six points ABCDEF of a ternary phase diagram, and wherein the six points ABCDEF are defined as: : A (Ni=0.67,Mo=0.00,W=0.33), B (Ni=0.67, Mo=0.10, W=0.23), C (Ni=0.60, Mo=0.15, W=0.25), D (Ni=0.52, Mo=0.15, W=0.33), E (Ni=0.52, Mo=0.06, W=0.42), F (Ni=0.58, Mo=0.0, W=0.42).

130. The self-supported MMS catalyst of claim 127, wherein the catalyst is characterized as having a molar ratio of metal components Ni:Mo:W in a range of:

1.08<=Ni/(Mo+W)<=2.03

0<= Mo/(Ni+W)<=0.18; and

0.33<=W/(Mo+Ni))<=0.72.

131. The self-supported MMS catalyst of claim 127, wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by four points ABCD of a ternary phase diagram, and wherein the four points ABCD are defined as: A(Ni=0.67,Mo=0.00,W=0.33), B(Ni=0.58, Mo=0.0, W=0.42), C(Ni=0.52, Mo=0.15, W=0.33), D(Ni=0.60, Mo=0.15, W=0.25).

132. A self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum (Mo) sulfide, tungsten (W) sulfide, and nickel (Ni) sulfide, wherein the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g.

133. The self-supported MMS catalyst of claim 132, wherein the catalyst has a BET surface area of at least 30 m^2/g.

134. The self-supported MMS catalyst of claim 133, wherein the catalyst has a BET surface area of at least 40 m^2/g.

135. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized as having a surface area reduction of less than 80% after hydrotreating a Heavy Coker Gas Oil for at least 0.5 hrs.

136. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized by a Ni surface concentration / Ni bulk concentration ratio of greater than 0.4 as characterized by XPS.

137. The self-supported MMS catalyst of claim 136, wherein the catalyst is characterized by a Ni surface concentration / Ni bulk concentration ratio of greater than 0.5 as characterized by XPS.

138. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized by a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

139. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized by a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

140. The self-supported MMS catalyst of claim 139, wherein the catalyst is characterized by a W surface concentration / W bulk concentration ratio of greater than 0.4 as characterized by XPS.

141. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.55, Mo=0.00, W=0.45), C (Ni=0.48, Mo=0.14, W=0.38), D (Ni=0.48, Mo=0.20, W=0.33), E (Ni=0.62, Mo=0.14, W=0.24).

142. The self-supported MMS catalyst of claim 141, wherein the catalyst is characterized as having a molar ratio of metal components Ni:Mo:W in a range of:

$0.33 \leq Ni/(Mo+W) \leq 2.57$, a range of $Mo/(Ni+W)$ molar ratios of $0.00 \leq Mo/(Ni+W) \leq 0.33$, and a range of $W/(Ni+Mo)$ molar ratios of $0.18 \leq W/(Ni+Mo) \leq 3.00$..

143. The self-supported MMS catalyst of claim 141, wherein the catalyst is characterized as having a molar ratio of metal components Ni:Mo:W in a region defined by five points *ABCDE* of a ternary phase diagram, and wherein the five points *ABCDE* are defined as: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.55, Mo=0.00, W=0.45), C (Ni=0.48, Mo=0.14, W=0.38), D (Ni=0.48, Mo=0.20, W=0.33), E (Ni=0.62, Mo=0.14, W=0.24).

144. The self-supported MMS catalyst of claim 141, wherein the catalyst is characterized having a molar ratio of metal components Ni:Mo:W in a range of:

$1.24 \leq Ni/W \leq 2.68$;

$1.67 \leq W/Mo \leq \infty$; and

$0.91 \leq Ni/(W+Mo) \leq 2.57$.

145. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase.

146. The self-supported MMS catalyst of claim 145, wherein the molybdenum tungsten sulfide phase comprises at least a layer, wherein the at least a layer contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

147. The self-supported MMS catalyst of claim 146, wherein the molybdenum tungsten sulfide phase comprises 1 to 6 layers.

148. The self-supported MMS catalyst of claim 146, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as individual atoms forming an intralayer atomic mixture.

149. The self-supported MMS catalyst of claim 146, wherein the at least a layer comprises tungsten isomorphously substituted into molybdenum sulfide as tungsten domains.

150. The self-supported MMS catalyst of claim 146, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as individual atoms forming an intralayer atomic mixture.

151. The self-supported MMS catalyst of claim 146, wherein the at least a layer comprises molybdenum isomorphously substituted into tungsten sulfide as molybdenum domains

152. The self-supported MMS catalyst of claim 146, wherein the molybdenum tungsten sulfide phase comprises inter-layer mixtures of tungsten sulfide and molybdenum sulfide.

153. The self-supported MMS catalyst of claim 146, wherein the at least a layer comprises mixtures of individual domains of tungsten sulfide and molybdenum sulfide.

154. The self-supported MMS catalyst of claim 145, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into edge of the molybdenum tungsten sulfide phase.

155. The self-supported MMS catalyst of claim 145, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the molybdenum tungsten sulfide phase or decorating edge of the molybdenum tungsten sulfide phase.

156. The self-supported MMS catalyst of claim 145, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

157. The self-supported MMS catalyst of claim 145, wherein the nickel sulfide phase serves as support for the molybdenum tungsten sulfide phase.

158. The self-supported MMS catalyst of claim 156, wherein the molybdenum tungsten sulfide phase envelopes the slabs of Ni_9S_8 and Ni_3S_2 layers.

159. The self-supported MMS catalyst of claim 145, wherein the nickel sulfide phase stabilizes dispersion of the active nickel phase onto the molybdenum tungsten sulfide phase.

160. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized by an X-ray diffraction pattern showing peaks corresponding to MoS_2 phase and WS_2 phase.

161. The self-supported MMS catalyst of claim 132, wherein the catalyst is characterized by an X-ray diffraction pattern showing peaks corresponding to Ni_3S_2 phase.

162. The self-supported MMS catalyst of claim 145, wherein the catalyst is characterized by TEM image showing lattice fringes on the nickel sulfide phase of 4.60±0.5 Å and 2.87±0.5 Å.

163. A process for making a self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, the process comprising:

mixing a sufficient amount of a nickel (Ni) metal precursor, a sufficient amount of a molybdenum (Mo) metal precursor, and a sufficient amount of a tungsten (W) metal precursor to produce a catalyst precursor having a molar ratio of metal components Ni:Mo:W in relative proportions defined by a region of a ternary phase diagram showing transition metal elemental composition in terms of nickel, molybdenum, and tungsten mol-%, wherein the region is defined by five points ABCDE and wherein the five points are: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.55, Mo=0.00, W=0.45), C (Ni=0.48, Mo=0.14, W=0.38), D (Ni=0.48, Mo=0.20, W=0.33), E (Ni=0.62, Mo=0.14, W=0.24); and

sulfiding the catalyst precursor under conditions sufficient to convert the catalyst precursor into a sulfide catalyst.

164. The process of claim 163, wherein the amounts of a Ni precursor, an Mo metal precursor, and a W metal precursor are sufficient for the molar ratio Ni:Mo:W in relative proportions defined by a region defined by six points ABCDEF of the ternary phase diagram, and wherein the six points ABCDEF are defined as: A (Ni=0.67,Mo=0.00,W=0.33), B (Ni=0.67, Mo=0.10, W=0.23), C (Ni=0.60, Mo=0.15, W=0.25), D (Ni=0.52, Mo=0.15, W=0.33), E (Ni=0.52, Mo=0.06, W=0.42), F (Ni=0.58, Mo=0.0, W=0.42).

165. The process of claim 163, wherein the amounts of a Ni metal precursor, a Mo metal precursor, and a W metal precursor are sufficient for the catalyst precursor to have a molar ratio of metal components Ni:Mo:W in a range of: $0.33 \leq Ni/(Mo+W) \leq 2.57$, a range of Mo/(Ni+W) molar ratios of $0.00 \leq Mo/(Ni+W) \leq 0.33$, and a range of W/(Ni+Mo) molar ratios of $0.18 \leq W/(Ni+Mo) \leq 3.00$.

166. The process of claim 163, wherein the amounts of a Ni metal precursor, a Mo metal precursor, and a W metal precursor are sufficient for the catalyst to have a molar ratio of metal components Ni:Mo:W in a range of:

1.08<=Ni/(Mo+W)<=2.03;

0<= Mo/(Ni+W)<=0.18; and

0.33<=W/(Mo+Ni))<=0.72.

167. The process of claim 163, wherein the amounts of a Ni precursor, an Mo metal precursor, and a W metal precursor are sufficient for the molar ratio Ni:Mo:W in relative proportions defined by a region defined four points ABCD of the ternary diagram, and wherein the four points ABCD are defined as: A(Ni=0.67,Mo=0.00,W=0.33), B(Ni=0.58, Mo=0.0, W=0.42), C(Ni=0.52, Mo=0.15, W=0.33), D(Ni=0.60, Mo=0.15, W=0.25).

168. The process of claim 163, further comprising:

calcining the catalyst precursor to a temperature of at least 300°C prior to sulfiding the catalyst precursor.

169. The process of claim 163, further comprising:

heating the catalyst precursor to a temperature of at least 150°C prior to sulfiding the catalyst precursor.

170. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst has a BET surface area of at least 20 m^2/g and a pore volume of at least 0.05 cm^3/g.

171. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst has a BET surface area of at least 40 m^2/g and a pore volume of at least 0.05 cm^3/g.

172. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.4 as characterized by XPS.

173. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst has a Ni surface concentration / Ni bulk concentration ratio of greater than 0.5 as characterized by XPS.

174. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.3 as characterized by XPS.

175. The process of claim 174, wherein after sulfiding, the catalyst has a W surface concentration / W bulk concentration ratio of greater than 0.4 as characterized by XPS.

176. The process of any of claims 163 - 167, wherein after sulfiding, the catalyst shows a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase.

177. The process of claim 176, wherein the molybdenum tungsten sulfide phase comprises at least a layer and wherein the at least a layer contains at least one of: a) molybdenum sulfide and tungsten sulfide; b) tungsten isomorphously substituted into molybdenum sulfide as individual atoms or as tungsten sulfide domains; c) molybdenum

isomorphously substituted into tungsten sulfide as individual atoms or as molybdenum sulfide domains; and d) mixtures thereof.

178. The process of claim 176, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into edge of the molybdenum tungsten sulfide phase.

179. The process of claim 176, wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the molybdenum tungsten sulfide phase or decorating edge of the molybdenum tungsten sulfide phase.

180. The process of claim 176, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

181. The process of any of claims 163 - 167, wherein the molybdenum metal precursor is selected from molybdenum metal, alkali metal molybdates, ammonium metallates of molybdenum, molybdenum sulphate, molybdenum phosphate, molybdenum silicate, molybdenum borate, molybdenum naphthenate, pentacyclodienyl molybdate, cyclopentadienyl Mo tricarbonyl dimer, ammonium salts of phosphomolybdic acids, phosphomolybdic acid, molybdenum oxide, Mo--P heteropolyanion compounds, Mo--Si heteropolyanion compounds, inorganic metal sulfides of molybdenum, sulfur-containing inorganic compounds of molybdenum, sulfur-containing organic compounds of molybdenum, and mixtures thereof.

182. The process of any of claims 163 - 167, wherein the tungsten metal precursor is selected from alkali metal tungstates, ammonium metallates of tungsten, inorganic tungsten compounds, tungsten naphthenate, pentacyclodienyl tungsten dihydride, tungsten oxide, W--P heteropolyanion compounds, W--Si heteropolyanion compounds, sulfur-containing inorganic compounds of tungsten, sulfur-containing organic compounds of tungsten, and mixtures thereof.

183. The process of any of claims 163 - 167, wherein the nickel metal precursor is selected from inorganic metal sulfides of nickel, sulfur-containing inorganic compounds of nickel, sulfur-containing organic compounds of nickel, nickel carbonate, nickel hydroxide,

nickel phosphate, nickel phosphite, nickel formate, nickel fumarate, nickel molybdate, nickel tungstate, nickel oxide, nickel alloys, cyclopentadienyl nickel, nickel naphthenate, and mixtures thereof.

CLAIMS

1. A self-supported mixed metal sulfide (MMS) catalyst:

(a) consisting essentially of nickel sulfide and tungsten sulfide, wherein the catalyst contains Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis; or

(b) consisting essentially of molybdenum sulfide and tungsten sulfide, wherein the catalyst contains at least 0.1 mol% of Mo and at least 0.1 mol% of W, on a transition metal basis; or

(c). comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having an HDN reaction rate constant of at least 100 g feed hr-1 g catalyst -1 assuming first order kinetics, and an HDS reaction rate constant of at least 550 g feed hr-1 g catalyst -1 assuming first order kinetics in hydrotreating of a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under process conditions as indicated in Table E; or

(d) comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, and wherein the catalyst is characterized as having molar ratios of metal components Ni:Mo:W in a region defined by five points ABCDE of a ternary phase diagram, and wherein the five points ABCDE are defined as: A (Ni=0.72, Mo=0.00, W=0.25), B (Ni=0.25, Mo=0.00, W=0.75), C (Ni=0.25, Mo=0.25, W=0.50), D (Ni=0.60, Mo=0.25, W=0.15), E (Ni=0.72, Mo=0.13, W=0.15); or

(e) comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, wherein the catalyst is characterized as having a multi-phased structure comprising five phases: a molybdenum sulfide phase, a tungsten sulfide phase, a molybdenum tungsten sulfide phase, an active nickel phase, and a nickel sulfide phase; or

(f) comprising molybdenum (Mo) sulfide, tungsten (W) sulfide, and nickel (Ni) sulfide, wherein the catalyst has a BET surface area of at least 20 m2/g and a pore volume of at least 0.05 cm3/g.

2. The self-supported MMS catalyst of claim 1, consisting essentially of nickel sulfide and tungsten sulfide, wherein the catalyst contains Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis.

3. The self-supported MMS catalyst of claim 2, wherein the catalyst further comprises a metal promoter selected from Mo, Nb, Ti, and mixtures thereof, wherein the

metal promoter is present in an amount of less 1% (mole).

4. The self-supported MMS catalyst of any of claims 2 - 3, wherein the catalyst is characterized as having:

an HDN reaction constant of at least 100 g feed·hr^{-1}·g $catalyst^{-1}$ in hydrotreating a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under the process conditions as indicated in Table E, assuming first order kinetics; or

an HDN reaction constant of at least 110 g feed·hr^{-1}·g $catalyst^{-1}$ in hydrotreating a Heavy Coker Gas Oil as a feedstock with properties indicated in Table A and under the process conditions as indicated in Table E, assuming first order kinetics; or

a HDN reaction rate constant of at least 4 hr^{-1} on catalyst weight hourly space velocity basis in hydrotreating a Heavy Vacuum Gas Oil as a feedstock with properties indicated in Table B and under steady state process conditions as indicated in Table F, assuming first order kinetics.

5. The self-supported MMS catalyst of any of claims 2 - 3, wherein the catalyst is characterized as having an HYD reaction rate constant of at least 15% higher than that of a catalyst comprising nickel sulfide alone or a catalyst comprising tungsten sulfide alone, when compared on same metal molar basis in hydrotreating of benzene as a feedstock at identical process conditions as indicated in Table D.

6. The self-supported MMS catalyst of any of claims 2 - 3, wherein the catalyst is characterized as having NiS_x nanoparticles dispersed onto the tungsten sulfide phase.

7. The self-supported MMS catalyst of any of claims 2 - 3, wherein the catalyst is characterized as having a multi-phased structure comprising a tungsten sulfide phase and an active nickel phase.

8. The self-supported MMS catalyst of claim 7, wherein the multi-phased structure further comprises a nickel sulphide phase.

9. The self-supported MMS catalyst of claim 8, wherein the nickel sulfide phase comprises slabs of Ni_9S_8 and Ni_3S_2 layers.

10. The self-supported MMS catalyst of claim 8, wherein the nickel sulfide serves as support for the tungsten sulfide phase.

11. The self-supported MMS catalyst of claim 7, wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel substituted into the tungsten sulfide phase, or wherein the active nickel phase comprises at least one of atomic nickel and reduced nickel decorating the edges of the tungsten sulfide phase, or wherein the active nickel phase comprises NiS_x nanoparticles dispersed onto the tungsten sulfide phase or decorating the tungsten sulfide phase.

12. The self-supported MMS catalyst of any of claims 2 - 3, wherein the catalyst is prepared by sulfiding a nickel metal precursor and a tungsten metal precursor in an amount sufficient for the catalyst to contain Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis.

13. The self-supported MMS catalyst of claim 12, wherein the nickel metal precursor is selected from inorganic metal sulfides of nickel, sulfur-containing inorganic compounds of nickel, sulfur-containing organic compounds of nickel, nickel carbonate, nickel hydroxide, nickel phosphate, nickel phosphite, nickel formate, nickel fumarate, nickel molybdate, nickel tungstate, nickel oxide, nickel alloys, cyclopentadienyl nickel, nickel naphthenate, and mixtures thereof.

14. The self-supported MMS catalyst of claim 12, wherein the tungsten metal precursor is selected from alkali metal tungstates, ammonium metallates of tungsten, inorganic tungsten compounds, tungsten naphthenate, pentacyclodienyl tungsten dihydride, tungsten oxide, W--P heteropolyanion compounds, W--Si heteropolyanion compounds, sulfur-containing inorganic compounds of tungsten, sulfur-containing organic compounds of tungsten, and mixtures thereof.

15. The self-supported MMS catalyst of claim 14, wherein the catalyst is prepared by sulfiding a molybdenum metal precursor and a tungsten metal precursor in an amount sufficient for the catalyst to contain Ni:W in a mole ratio of 1:3 to 4:1, on a transition metal basis and under a H_2-containing gas pressure with at least a sulfiding agent at a temperature

ranging from 25°C to 500°C from 10 minutes to 15 days.

16. A process for making a self-supported mixed metal sulfide (MMS) catalyst comprising molybdenum sulfide, nickel sulfide, and tungsten sulfide, the process comprising:

mixing a sufficient amount of a nickel (Ni) metal precursor, a sufficient amount of a molybdenum (Mo) metal precursor, and a sufficient amount of a tungsten (W) metal precursor to produce a catalyst precursor having a molar ratio of metal components Ni:Mo:W in relative proportions defined by a region of a ternary phase diagram showing transition metal elemental composition in terms of nickel, molybdenum, and tungsten mol-%, wherein the region is defined by five points ABCDE and wherein the five points are: A (Ni=0.72, Mo=0.00, W=0.28), B (Ni=0.55, Mo=0.00, W=0.45), C (Ni=0.48, Mo=0.14, W=0.38), D (Ni=0.48, Mo=0.20, W=0.33), E (Ni=0.62, Mo=0.14, W=0.24); and

sulfiding the catalyst precursor under conditions sufficient to convert the catalyst precursor into a sulfide catalyst.