CLAIMS

1. A supported catalyst comprising a carrier, phosphorus, at least one Group VI metal, at least one Group VIII metal, and a polymer, where

the molar ratio of phosphorus to Group VI metal is about 1:1.5 to less than about 1:12,

the molar ratio of the Group VI metal to the Group VIII metal is about 1:1 to about 5:1, and

the polymer has a carbon backbone and comprises functional groups having at least one heteroatom.

2. A catalyst as in Claim 1 wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina.

3. A catalyst as in Claim 1 wherein the molar ratio of phosphorus to Group VI metal is about 1:2.5 to less than about 1:12.

4. A catalyst as in Claim 1 wherein the functional groups of the polymer are carboxylic acid groups.

5. A catalyst as in Claim 1 wherein the polymer is polymaleic acid, polyfumaric acid, or polyacrylic acid.

6. A catalyst as in any of Claims 1-5 wherein said Group VI metal is molybdenum and/or tungsten, and/or wherein said Group VIII metal is nickel and/or cobalt.

7. A catalyst as in any of Claims 1-5 wherein the catalyst has a polymer loading of about 1.5 wt% or more, relative to the total weight of the other components in the catalyst.

8. A catalyst as in any of Claims 1-5 wherein the catalyst has an average particle size of about 0.5 mm to about 5 mm.

9. A catalyst as in any of Claims 1-5 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.

10. A method for hydrotreating, hydrodenitrogenation, and/or hydrodesulfurization, which method comprises contacting a hydrocarbon feed and a catalyst of any of Claims 1-9.

11. A process for forming a supported catalyst, which process comprises

I) bringing together a carrier, one or more monomer species, a polar solvent, at least one phosphorus compound, at least one Group VI metal compound, and at least one Group VIII metal compound, and optionally an initiator, in any of the following combinations:
   - a carrier, one or more monomer species, a polar solvent, and optionally an initiator,
   - a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VI metal compound, and at least one Group VIII metal compound, and optionally an initiator, or
   - a carrier and an impregnation solution, forming an impregnated carrier, followed by mixing the impregnated carrier with one or more monomer species and optionally an initiator,

   to form a monomer-containing mixture, where said monomer species is soluble in the polar solvent and has carbon-carbon unsaturation and at least one functional group comprising at least one heteroatom; and

II) polymerizing at least a portion of said monomer species in the monomer-containing mixture to form a polymerized product;

III) when I) does not include at least one phosphorus compound, at least one Group VI metal compound, and at least one Group VIII metal compound, either

- contacting an impregnation solution and the monomer-containing mixture during the polymerizing in II), or
- contacting the polymerized product and an impregnation solution;

to form a supported catalyst, where the molar ratio of phosphorus to Group VI metal is about 1:1.5 to less than about 1:12, where the molar ratio of the Group VI metal to the Group VIII metal is about 1:1 to about 5:1, and where said impregnation solution comprises a polar solvent, phosphorus, at least one Group VI metal, and at least one Group VIII metal.

12. A process as in Claim 11 further comprising removing excess solvent from the supported catalyst.

13. A process as in Claim 11 wherein a single impregnation step is carried out

a) in I) when bringing together a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VI metal compound, and at least one Group VIII metal compound;

b) in I), when bringing together a carrier and an impregnation solution; or

c) in III).

14. A process as in Claim 12 wherein the polymerizing is carried out during the removal of excess solvent.

15. A process as in Claim 11 further comprising sulfiding the catalyst.

16. A process as in Claim 11 wherein a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VI metal compound, and at least one Group VIII metal compound are brought together in I).

17. A process as in Claim 11 wherein the heteroatom of the functional group of the monomer species is nitrogen, oxygen, phosphorus, or sulfur.

18. A process as in Claim 11 wherein the functional group of the monomer species is a carboxylic acid group, an ester group, or an amido group.

19. A process as in Claim 11 wherein the monomer species is maleic acid, fumaric acid, acrylic acid, 2-carboxyethyl acrylate, or N-hydroxyethyl acrylamide.

20. A process as in Claim 11 wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina.

21. A process as in Claim 11 wherein the molar ratio of phosphorus to Group VI metal is about 1:2.5 to less than about 1:12.

22. A process as in Claim 16 wherein said polar solvent is water.

23. A process as in Claim 16 wherein said phosphorus compound is a water soluble acidic phosphorus compound.

24. A process as in Claim 16 wherein said Group VI metal compound is an oxide or an oxo-acid.

25. A process as in Claim 16 wherein said Group VIII metal compound is a carbonate, hydroxide, or hydroxy-carbonate.

26. A process as in any of Claims 22-25 wherein said Group VI metal compound is a molybdenum compound and/or a tungsten compound, and/or wherein said Group VIII compound is a nickel and/or cobalt compound.

27. A process as in any of Claims 11-26 wherein the carrier has been calcined and/or extruded prior to step I) of the process.

28. A process as in any of Claims 11-26 wherein the carrier has an average particle size of about 0.5 mm to about 5 mm, and wherein the supported catalyst has an average particle size of about 0.5 mm to about 5 mm.

29. A supported catalyst formed as in any of Claims 11-26.

30. A supported catalyst as in Claim 29 wherein said Group VI metal is molybdenum and/or tungsten, and/or wherein said Group VIII compound is nickel and/or cobalt.

31. A supported catalyst as in any of Claims 29-30 wherein the catalyst has an average particle size of about 0.5 mm to about 5 mm.

32. A supported catalyst as in any of Claims 29-30 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.

AMENDED CLAIMS
received by the International Bureau on 6 March 2014 (06.03.2014)

1. A supported catalyst comprising a carrier, phosphorus, at least one Group VIB metal, at least one Group VIII metal, and a polymer, where

the molar ratio of phosphorus to Group VIB metal is about 1:1.5 to less than about 1:12,

the molar ratio of the Group VIB metal to the Group VIII metal is about 1:1 to about 5:1, and

the polymer has a carbon backbone and comprises functional groups having at least one heteroatom.

2. A catalyst as in Claim 1 wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina.

3. A catalyst as in Claim 1 wherein the molar ratio of phosphorus to Group VIB metal is about 1:2.5 to less than about 1:12.

4. A catalyst as in Claim 1 wherein the functional groups of the polymer are carboxylic acid groups.

5. A catalyst as in Claim 1 wherein the polymer is polymaleic acid, polyfumaric acid, or polyacrylic acid.

6. A catalyst as in any of Claims 1-5 wherein said Group VIB metal is molybdenum and/or tungsten, and/or wherein said Group VIII metal is nickel and/or cobalt.

7. A catalyst as in any of Claims 1-5 wherein the catalyst has a polymer loading of about 1.5 wt% or more, relative to the total weight of the other components in the catalyst.

st as in any of Claims 1-5 wherein the catalyst has an size of about 0.5 mm to about 5 mm.

9. A catalyst as in any of Claims 1-5 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.

10. A method for hydrotreating, hydrodenitrogenation, and/or hydrodesulfurization, which method comprises contacting a hydrocarbon feed and a catalyst of any of Claims 1-9.

11. A process for forming a supported catalyst, which process comprises

I) bringing together components in any of the following combinations:

a-i) a carrier, one or more monomer species, a polar solvent, and optionally an initiator,

b-i) a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound, and optionally an initiator, or

c-i) a carrier and an impregnation solution, forming an impregnated carrier, followed by mixing the impregnated carrier with one or more monomer species and optionally an initiator,

to form a monomer-containing mixture, where said monomer species is soluble in the polar solvent and has carbon-carbon unsaturation and at least one functional group comprising at least one heteroatom; and

II) polymerizing at least a portion of said monomer species in the monomer-containing mixture to form a polymerized product;

III) when I) does not include at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound, either

a-iia) contacting an impregnation solution and the monomer-containing mixture during the polymerizing in II), or

a-iib) contacting the polymerized product and an impregnation solution;

to form a supported catalyst, where the molar ratio of phosphorus to Group VIB metal is about 1:1.5 to less than about 1:12, where the molar ratio of the Group VIB metal to the Group VIII metal is about 1:1 to about 5:1, and where said impregnation solution comprises a

orus, at least one Group VIB metal, and at least one G

where a polymer is formed during the polymerizing and the polymer has a carbon backbone and comprises functional groups having at least one heteroatom.

12. A process as in Claim 11 further comprising removing excess solvent from the supported catalyst.

13. A process as in Claim 11 wherein a single impregnation step is carried out

a) in I) when bringing together a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound;

b) in I), when bringing together a carrier and an impregnation solution; or

c) in III).

14. A process as in Claim 12 wherein the polymerizing is carried out during the removal of excess solvent.

15. A process as in Claim 11 further comprising sulfiding the catalyst.

16. A process as in Claim 11 wherein a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound are brought together in I).

17. A process as in Claim 11 wherein the heteroatom of the functional group of the monomer species is nitrogen, oxygen, phosphorus, or sulfur.

18. A process as in Claim 11 wherein the functional group of the monomer species is a carboxylic acid group, an ester group, or an amido group.

19. A process as in Claim 11 wherein the monomer species is maleic acid, fumaric acid, acrylic acid, 2-carboxyethyl acrylate, or N-hydroxyethyl acrylamide.

20. A process as in Claim 11 wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina.

21. A process as in Claim 11 wherein the molar ratio of phosphorus to Group VIB metal is about 1:2.5 to less than about 1:12.

22. A process as in Claim 16 wherein said polar solvent is water.

23. A process as in Claim 16 wherein said phosphorus compound is a water soluble acidic phosphorus compound.

24. A process as in Claim 16 wherein said Group VIB metal compound is an oxide or an oxo-acid.

25. A process as in Claim 16 wherein said Group VIII metal compound is a carbonate, hydroxide, or hydroxy-carbonate.

26. A process as in any of Claims 22-25 wherein said Group VIB metal compound is a molybdenum compound and/or a tungsten compound, and/or wherein said Group VIII compound is a nickel and/or cobalt compound.

27. A process as in any of Claims 11-26 wherein the carrier has been calcined and/or extruded prior to step I) of the process.

28. A process as in any of Claims 11-26 wherein the carrier has an average particle size of about 0.5 mm to about 5 mm, and wherein the supported catalyst has an average particle size of about 0.5 mm to about 5 mm.

29. A supported catalyst formed as in any of Claims 11-26.

30. A supported catalyst as in Claim 29 wherein said Group VIB metal is molybdenum and/or tungsten, and/or wherein said Group VIII compound is nickel and/or cobalt.

31. A supported catalyst as in any of Claims 29-30 wherein the catalyst has an average particle size of about 0.5 mm to about 5 mm.

32. A supported catalyst as in any of Claims 29-30 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.

CLAIMS

1. A supported catalyst comprising a carrier, phosphorus, at least one Group VIB metal, at least one Group VIII metal, and a polymer, where

the molar ratio of phosphorus to Group VIB metal is about 1:1.5 to less than about 1:12,

the molar ratio of the Group VIB metal to the Group VIII metal is about 1:1 to about 5:1, and

the polymer has a carbon backbone and comprises functional groups having at least one heteroatom.

2. A catalyst as in Claim 1 wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina, and/or wherein the functional groups of the polymer are carboxylic acid groups.

3. A catalyst as in Claim 1 wherein the molar ratio of phosphorus to Group VIB metal is about 1:2.5 to less than about 1:12.

4. A catalyst as in Claim 1 wherein the polymer is polymaleic acid, polyfumaric acid, or polyacrylic acid.

5. A catalyst as in any of Claims 1, 2, 3, or 4 wherein said Group VIB metal is molybdenum and/or tungsten, and/or wherein said Group VIII metal is nickel and/or cobalt.

6. A catalyst as in any of Claims 1, 2, 3, or 4 wherein the catalyst has a polymer loading of about 1.5 wt% or more, relative to the total weight of the other components in the catalyst.

7. A catalyst as in any of Claims 1, 2, 3, or 4 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.

8. A method for hydrotreating, hydrodenitrogenation, and/or hydrodesulfurization, which method comprises contacting a hydrocarbon feed and a catalyst of any of Claims 1, 2, 3, 4, 5, 6, or 7.

9. A process for forming a supported catalyst, which process comprises

I) bringing together components in any of the following combinations:

a-i) a carrier, one or more monomer species, a polar solvent, and optionally an initiator,

b-i) a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound, and optionally an initiator, or

c-i) a carrier and an impregnation solution, forming an impregnated carrier, followed by mixing the impregnated carrier with one or more monomer species and optionally an initiator,

to form a monomer-containing mixture, where said monomer species is soluble in the polar solvent and has carbon-carbon unsaturation and at least one functional group comprising at least one heteroatom; and

II) polymerizing at least a portion of said monomer species in the monomer-containing mixture to form a polymerized product;

III) when I) does not include at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound, either

a-iia) contacting an impregnation solution and the monomer-containing mixture during the polymerizing in II), or

a-iib) contacting the polymerized product and an impregnation solution; to form a supported catalyst, where the molar ratio of phosphorus to Group VIB metal is about 1:1.5 to less than about 1:12, where the molar ratio of the Group VIB metal to the Group VIII metal is about 1:1 to about 5:1, where said impregnation solution comprises a polar solvent, phosphorus, at least one Group VIB metal, and at least one Group VIII metal, where a polymer is formed during the polymerizing and the polymer has a carbon backbone and comprises functional groups having at least one heteroatom.

10. A process as in Claim 9 further comprising removing excess solvent from the supported catalyst and/or further comprising sulfiding the catalyst.

11. A process as in Claim 9 wherein a single impregnation step is carried out

a) in I) when bringing together a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound;

b) in I), when bringing together a carrier and an impregnation solution; or

c) in III).

12. A process as in Claim 10 wherein the polymerizing is carried out during the removal of excess solvent.

13. A process as in Claim 9 wherein a carrier, one or more monomer species, at least one phosphorus compound, at least one Group VIB metal compound, and at least one Group VIII metal compound are brought together in I).

14. A process as in Claim 9 wherein the heteroatom of the functional group of the monomer species is nitrogen, oxygen, phosphorus, or sulfur; wherein said carrier is silica, alumina, silica-alumina, alumina with silica-alumina dispersed therein, alumina-coated silica, or silica-coated alumina; and/or wherein the molar ratio of phosphorus to Group VIB metal is about 1:2.5 to less than about 1:12.

15. A process as in Claim 9 wherein the functional group of the monomer species is a carboxylic acid group, an ester group, or an amido group.

16. A process as in Claim 9 wherein the monomer species is maleic acid, fumaric acid, acrylic acid, 2-carboxyethyl acrylate, or N-hydroxyethyl acrylamide.

17. A process as in Claim 13 wherein said polar solvent is water; wherein said phosphorus compound is a water soluble acidic phosphorus compound; wherein said Group VIB metal compound is an oxide or an oxo-acid; and/or wherein said Group VIII metal compound is a carbonate, hydroxide, or hydroxy-carbonate.

18. A process as in Claim 17 wherein said Group VIB metal compound is a molybdenum compound and/or a tungsten compound, and/or wherein said Group VIII compound is a nickel and/or cobalt compound.

19. A process as in any of Claims 9-16, 17, or 18 wherein the carrier has been calcined and/or extruded prior to step I) of the process.

20. A supported catalyst formed as in any of Claims 9-16, 17, or 18.

21. A supported catalyst as in Claim 20 wherein said Group VIB metal is molybdenum and/or tungsten, and/or wherein said Group VIII compound is nickel and/or cobalt.

22. A supported catalyst as in any of Claims 20-21 wherein the catalyst has an average particle size of about 0.5 mm to about 5 mm.

23. A supported catalyst as in any of Claims 20-21 wherein the carrier is about 40 wt% to about 80 wt% of the catalyst, relative to the total weight of the carrier, hydrogenation metals, and phosphorus, where the hydrogenation metals and phosphorus are expressed as their oxides.