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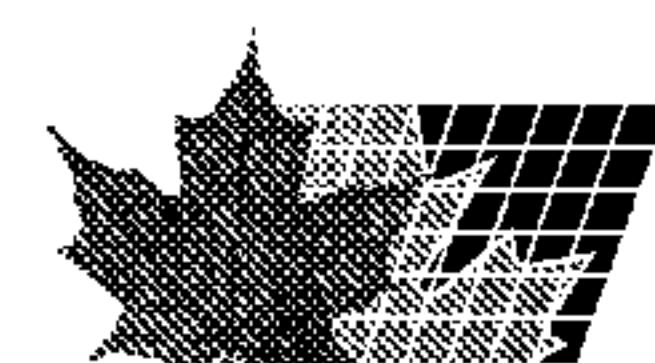
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(54) Title: HIGHLY ACTIVE SLURRY CATALYST COMPOSITION

(57) **Abrégé/Abstract:**

The instant invention is directed to the preparation of a catalyst composition suitable for the hydroconversion of heavy oils. The catalyst composition is prepared by a series of steps, involving mixing a group VIB metal oxide and aqueous ammonia to form an aqueous mixture, and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal. Subsequent steps involve mixing the slurry with a hydrocarbon oil and combining the resulting mixture with hydrogen gas and a second hydrocarbon oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.



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(54) **Title:** HIGHLY ACTIVE SLURRY CATALYST COMPOSITION

(57) **Abstract:** The instant invention is directed to the preparation of a catalyst composition suitable for the hydroconversion of heavy oils. The catalyst composition is prepared by a series of steps, involving mixing a group VIB metal oxide and aqueous ammonia to form an aqueous mixture, and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal. Subsequent steps involve mixing the slurry with a hydrocarbon oil and combining the resulting mixture with hydrogen gas and a second hydrocarbon oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.

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HIGHLY ACTIVE SLURRY CATALYST COMPOSITION

FIELD OF THE INVENTION

The present invention relates to the preparation of slurry catalyst compositions useful in the processing of heavy oils. These oils are characterized by low hydrogen to carbon ratios and high carbon residues, asphaltenes, nitrogen, sulfur and metal contents.

BACKGROUND OF THE INVENTION

Slurry catalyst compositions and means for their preparation are known in the refining arts. Some examples are discussed below.

U.S. Patent No. 4,710,486 discloses a process for the preparation of a dispersed Group VIB metal sulfide hydrocarbon oil hydroprocessing catalyst. Process steps include reacting aqueous ammonia and a Group VIB metal compound, such as molybdenum oxide or tungsten oxide, to form a water soluble oxygen-containing compound such as ammonium molybdate or tungstate.

U.S. Patent No. 4,970,190 discloses a process for the preparation of a dispersed Group VIB metal sulfide catalyst for use in hydrocarbon oil hydroprocessing. This catalyst is promoted with a Group VIII metal. Process steps include dissolving a Group VIB metal compound, such as molybdenum oxide or tungsten oxide, with ammonia to form a water soluble compound such as aqueous ammonium molybdate or ammonium tungstate.

U.S. Patent No. 5,164,075 and U.S. Patent No. 5,484,755 disclose processes for preparation of high activity slurry catalysts for hydroprocessing heavy heavy hydrocarbon oils produced from Group VIB metal compounds. An aqueous mixture of the metal compound is

1 sulfided with from greater than about 8 to about 14 standard cubic feet of
2 hydrogen sulfide per pound of Group VIB metal. These patents demonstrate
3 a process of forming a slurry catalyst precursor and adding it to a heavy feed
4 oil to form the active catalyst.

5

6 These patents do not demonstrate the criticality of the oil viscosity in the
7 formation of a highly active catalyst composition, nor the significance of using
8 two distinctly different oils in forming such catalyst composition. In the
9 inventions disclosed in these patents, the failure to form the oil and water
10 emulsion or the slurry phase results in an inactive catalyst or a catalyst having
11 low activity.

12

13 This invention discloses a new slurry catalyst composition that is highly active.
14 This activity results from preparation of the catalyst using a process
15 employing two hydrocarbon oils having appropriate viscosity ranges at 212°F.
16 The first heavier oil is preferably a vacuum gas oil (VGO) and the second is
17 preferably a light naphtha.

18

19

SUMMARY OF THE INVENTION

20

21 This invention is directed to a highly active catalyst composition which is
22 suitable for processing heavy hydrocarbon oils. The catalyst is prepared by
23 the following steps, resulting in a catalyst composition suitable for the
24 hydroconversion of heavy oils, which is prepared by:

25

26 (a) mixing a Group VI B metal oxide and aqueous ammonia to form a
27 Group VI metal compound aqueous mixture;

28

29 (b) sulfiding, in an initial reactor, the aqueous mixture of step (a) with a gas
30 comprising hydrogen sulfide to a dosage greater than 8 SCF of
31 hydrogen sulfide per pound of Group VI B metal to form a slurry;

- 1 (c) promoting the slurry with a Group VIII metal compound;
- 2 (d) mixing the slurry of step (c) with a first hydrocarbon oil having a
3 viscosity of at least 2 cSt (or 32.8 SSU) @ 212°F to form Mixture X;
- 4 (e) combining Mixture X with hydrogen gas and a second hydrocarbon oil
5 in a second reaction zone, the second hydrocarbon oil having a boiling
6 point in the range from 50°F to 300°F and having a lower viscosity than
7 the first hydrocarbon oil; thereby forming an active catalyst composition
8 admixed with a liquid hydrocarbon; and
- 9 (f) recovering the active catalyst composition.

10 According to another aspect, there is provided a catalyst composition
11 suitable for the hydroconversion of heavy oils, which is prepared by:

- 12 (a) mixing a Group VI B metal oxide and aqueous ammonia to form a
13 Group VI metal compound aqueous mixture;
- 14 (b) sulfiding, in a first reaction zone, the aqueous mixture of step (a) with a
15 gas comprising hydrogen sulfide to a dosage greater than 8 SCF of
16 hydrogen sulfide per pound of Group VIB metal to form a slurry;
- 17 (c) promoting the slurry with a Group VIII metal;
- 18 (d) mixing the slurry of step (c) with a first hydrocarbon oil having a viscosity
19 of at least 2 cSt @ 212°F to 15 cSt @ 212°F to form Mixture X;
- 20 (e) combining Mixture X with hydrogen gas and a second hydrocarbon oil
21 in a second reaction zone, the second hydrocarbon oil having a boiling
22 point in the range from 50°F to 300°F and having a lower viscosity that
23 the first hydrocarbon oil, thereby forming an active catalyst composition

1 admixed with a hydrocarbon; and

2 (f) recovering the active catalyst composition by separation from the second
3 hydrocarbon oil.

4 This new highly active slurry catalyst composition may be stored in an active
5 and concentrated state. The catalyst composition can be directly introduced
6 into any of the known heavy oil or residuum upgrading processes under the
7 existing conditions of that process. The catalyst can upgrade the very high
8 viscosity carbonaceous and/or highly paraffinic feedstocks with or without
9 dilution of the feedstock.

10 BRIEF DESCRIPTION OF THE DRAWING

11 The Figure illustrates the steps involved in the preparation of the catalyst
12 composition.

13 DETAILED DESCRIPTION OF THE INVENTION

14 This invention relates to a new highly active slurry catalyst composition
15 formed from the addition of a first hydrocarbon oil having a viscosity of at least
16 2 cSt (or 32.8 SSU) @ 212°F, and a second hydrocarbon oil having a boiling
17 point in the range from 50°F to 300°F. The preferred viscosity range for the

1 first hydrocarbon oil is from at least about 2 cSt (or 32.8 SSU) @ 212°F to
2 15 cSt (or 77.9 SSU) @ 212°F.

3

4 The Figure illustrates the steps involved in the process of this invention. The
5 active slurry catalyst composition is prepared by mixing line 5, containing an
6 oxide of Group VI B metal such as tungsten or molybdenum, and line 7,
7 containing aqueous ammonia, in a mixing zone 10. The temperature of the
8 mixing zone is generally in the range from about 80°F to about 200°F,
9 preferably from about 100°F to about 150°F, and most preferably from about
10 110°F to about 120°F. The pressure of the mixing zone 10 is generally from
11 about atmospheric pressure to about 100 psig, preferably from about 5 psig to
12 about 35 psig, and most preferably from about 10 psig to about 20 psig. The
13 Group VI B metal oxide is dissolved in water containing the ammonia. The
14 amount of ammonia added is based on the ratio of NH_3 to Group VI B oxide in
15 lbs/lbs and generally ranges from 0.1 lbs/lbs to about 1.0 lbs/lbs, preferably
16 from about 0.15 lbs/lbs to about 0.50 lbs/lbs, and most preferably from about
17 0.2 lbs/lbs to about 0.30 lbs/lbs. The dissolved metal oxide in aqueous
18 ammonia is moved via line 15 to the first reaction zone.

19

20 The amount of hydrogen sulfide (line 9) added to the reaction zone 20 is
21 based on the ratio of H_2S to Group VI B metal oxide in SCF/lbs and generally
22 ranges from 4.0 SCF/lbs to about 20 SCF/lbs, preferably from about
23 8.0 SCF/lbs to about 15 SCF/lbs, and most preferably from about 12 to
24 14 SCF/lbs. The reaction time in the first reaction zone ranges from about
25 1 hour to 10 hours, preferably from 3 hours to 8 hours, and most preferably
26 from about 4 hours to 6 hours. Conditions include a temperature in the range
27 from 80°F to 200°F, preferably in the range from 100°F to 180°F, and most
28 preferably in the range from 130°F to 160°F. Pressure is in the range from
29 100 to 3000 psig, preferably in the range from 200 to 1000 psig, and most
30 preferably from 300 to 500 psig. The resultant aqueous slurry is the catalyst
31 precursor.

1 The aqueous slurry is combined with a Group VIII metal compound such as Ni
2 or Co, as disclosed in U.S. Patent No. 5,484 755. As an enhancement of the
3 denitrogenation activity of the active slurry catalyst of the present invention, it
4 is preferred that a Group VIII metal compound be added to the slurry before
5 mixing the slurry with feed oil and a hydrogen containing gas at elevated
6 temperature and pressure. Such Group VIII metals are exemplified by nickel
7 and cobalt. It is preferred that the weight ratio of nickel or cobalt to
8 molybdenum range from about 1:100 to about 1:2. It is most preferred that
9 the weight ratio of nickel to molybdenum range from about 1:25 to 1:10, i.e.,
10 promoter/molybdenum of 4-10 weight percent. The Group VIII metal,
11 exemplified by nickel, is normally added in the form of the sulfate, and
12 preferably added to the slurry after sulfiding at a pH of about 10 or below and
13 preferably at a pH of about 8 or below. Group VIII metal nitrates, carbonates
14 or other compounds may also be used. In view of the high activity of the
15 slurry catalyst of the present invention, the further promotion by Group VIII
16 metal compounds is very advantageous.

17
18 The aqueous slurry is moved, via line 25, to mixing zone 30. Mixing zone 30
19 employs an inert atmosphere which can comprise nitrogen, refinery gas, or
20 any other gas having little or no oxygen. The aqueous slurry and a first
21 hydrocarbon oil (line 11), such as VGO, are mixed continuously in a high
22 shear mode to maintain a homogeneous slurry in mixer 30. High shear
23 mixing encompasses a range from 100 to 1600 RPM. Preferably the mixing
24 rate is greater than 500 RPM and most preferably greater than 1500 RPM.

25
26 The first hydrocarbon oil has a kinetic viscosity of at least 2 cSt (or 32.8 SSU)
27 @ 212°F. The kinetic viscosity can generally range from about 2 cSt (or
28 32.8 SSU) @ 212°F to about 15 cSt (77.9 SSU) @ 212°F, preferably from
29 about 4 cSt (39.5 SSU) @ 212°F to about 10 cSt (59.2 SSU) @ 212°F, and
30 most preferably from about 5 cSt (42.7 SSU) @ 212°F to about 8 cSt
31 (52.4 SSU) @ 212°F. The first hydrocarbon oil causes the initial

1 transformation of the catalyst precursor to an oil base from a water base. The
2 ratio of Group VI B metal oxide to oil is at least less than 1.0, preferably less
3 than 0.5, and more preferably less than 0.1. If the kinetic viscosity of the oil is
4 below about 2 cSt (or 32.8 SSU) @ 212°F or above about 15 cSt (77.9 SSU)
5 @ 212°F, the first transformation of the catalyst precursor will result in catalyst
6 particles agglomerating or otherwise not mixing.

7

8 The material from mixing zone 30 moves to reaction zone 40 via line 35. Prior
9 to entering reaction zone 40, the material may be combined with makeup oil
10 of the viscosity range of the first hydrocarbon oil. Hydrogen is also added to
11 the mixture before it enters reaction zone 40.

12

13 In reaction zone 40, a second, lighter hydrocarbon oil is added to the material
14 from mixing zone 30. The second oil, preferably a light naphtha, preferably
15 possesses a kinetic viscosity of less than 0.3 cSt at 212°F. One source of this
16 second oil may be recycle material from the high pressure separator 50 (line
17 45). High shear mixing is also employed in the reaction zone 40 in order to
18 maintain a homogenous slurry.

19

20 The second hydrocarbon oil has a boiling point generally in the range from
21 about 50°F to about 300°F, preferably from about 75°F to about 250°F, and
22 most preferably from about 100°F to about 150°F. The ratio of the volume of
23 the second oil to the first oil is greater than 1, preferably greater than 5, and
24 most preferably greater than 10. The temperature of the reaction zone 40
25 generally ranges from about 300°F to 700°F, preferably from about 350°F to
26 about 600°F, and most preferably from about 350°F to about 500°F. The
27 pressure of the reaction zone 40 generally ranges from about 1000 psig to
28 about 3500 psig, preferably from about 1500 psig to about 3000 psig, and
29 most preferably from about 2000 psig to about 3000 psig. The hydrogen flow
30 to the reaction zone 40 generally ranges from about 500 SCFB to about
31 10,000 SCFB, preferably from about 1000 SCFB to about 8000 SCFB, and

1 most preferably from about 3000 SCFB to about 6000 SCFB. The reaction
2 time in the reaction zone 40 ranges from about 11 minutes to 5 hours,
3 preferably from 30 minutes to 3 hours, and most preferably from about 1 hour
4 to 1.5 hours. The resultant slurry mixture is the active catalyst composition in
5 a mixture of the first hydrocarbon oil and the second hydrocarbon oil. The
6 slurry mixture is passed, through line 55, to high pressure separator 50. The
7 high pressure separator operates in a range from 300°F to 700°F. The
8 second hydrocarbon oil is removed overhead through line 45 and recirculated
9 back to the third reaction zone 40. The active catalyst composition is moved
10 through line 65 to storage tank 60. The active catalyst composition is
11 continuously mixed in storage tank 60 to maintain a homogenous slurry in a
12 hydrogen atmosphere with little or no oxygen. In this way, the catalyst activity
13 and stability are maintained.

14

15 The catalyst composition is useful for upgrading carbonaceous feedstocks
16 which include atmospheric gas oils, vacuum gas oils, deasphalted oils,
17 olefins, oils derived from tar sands or bitumen, oils derived from coal, heavy
18 crude oils, synthetic oils from Fischer-Tropsch processes, and oils derived
19 from recycled oil wastes and polymers. The catalyst composition is useful for
20 but not limited to hydrogenation upgrading processes such as thermal
21 hydrocracking, hydrotreating, hydrodesulphurization, hydrodenitrification, and
22 hydrodemetallization.

23

24

EXAMPLES

25

26

Example 1: for catalyst preparation (with light oil)

27

28 540 gram MoO_3 is mixed with 79 grams of NH_3 and 2381 grams of H_2O to
29 form a solution of total 3000 grams. The solution is then reacted with
30 10.71 SCF of H_2S by passing a gas mixture of 20% H_2S in H_2 into the solution
31 under strong mixing. The reactor temperature is 150°F and the total pressure

1 is 400 psig, and the reaction time is 4 hours. After reaction, 460 grams NiSO_4
2 solution which contains 36 grams of Ni is added to the above obtained slurry.
3 The obtained slurry mixture is then mixed with 3500 grams of vacuum gas oil
4 at 100°F. The viscosity of the VGO is 5 cSt @ 212°F. The resulting mixture
5 is then pumped into a *continuously flow stirred tanked reactor* (perfectly mixed
6 flow reactor) and mixed with heptane and H_2 , the ratio of heptane/VGO is 9:1
7 and H_2 gas rate is 5000 SCF/B. The reactor pressure is 2500 psig and
8 reactor temperature is 400°F, the total reaction time is 1 hour. The reaction
9 products go to a hot high pressure separator with temperature 500°F (HPS is
10 also at 2500 psig) to separate gas and liquid slurry. The obtained liquid slurry
11 contains the highly active catalyst component.

1 **WHAT IS CLAIMED IS:**

- 2 1. A catalyst composition suitable for the hydroconversion of heavy oils,
3 which is prepared by:
- 4 (a) mixing a Group VI B metal oxide and aqueous ammonia to form
5 a Group VI metal compound aqueous mixture;
- 6 (b) sulfiding, in a first reaction zone, the aqueous mixture of step (a)
7 with a gas comprising hydrogen sulfide to a dosage greater than
8 8 SCF of hydrogen sulfide per pound of Group VIB metal to form
9 a slurry;
- 10 (c) promoting the slurry with a Group VIII metal;
- 11 (d) mixing the slurry of step (c) with a first hydrocarbon oil having a
12 viscosity of at least 2 cSt @ 212°F to 15 cSt @ 212°F to form
13 Mixture X;
- 14 (e) combining Mixture X with hydrogen gas and a second
15 hydrocarbon oil in a second reaction zone, the second
16 hydrocarbon oil having a boiling point in the range from 50°F to
17 300°F and having a lower viscosity than the first hydrocarbon oil,
18 thereby forming an active catalyst composition admixed with a
19 hydrocarbon; and
- 20 (f) recovering the active catalyst composition by separation from
21 the second hydrocarbon oil.
- 22 2 The catalyst composition of claim 1, wherein conditions in the first
23 reaction zone comprise a temperature in the range from at least
24 about 80°F to about 200°F, and a pressure in the range from at least

- 1 about 100 psig to about 3000 psig.
- 2 3. The catalyst composition of claim 2, wherein conditions in the first
3 reaction zone comprise a temperature in the range from at least about
4 100°F to about 180°F, and a pressure in the range from at least about
5 200 psig to about 1000 psig.
- 6 4. The catalyst composition of claim 3, wherein conditions in the first
7 reaction zone comprise a temperature in the range from at least about
8 130°F to about 160°F, and a pressure in the range from at least about
9 300 psig to about 500 psig.
- 10 5. The catalyst composition of claim 1, wherein the first hydrocarbon oil
11 viscosity ranges from at least about 2 cSt @ 212°F to about 15 cSt @
12 212°F.
- 13 6. The catalyst composition of claim 1, wherein the Group VIII metal
14 compound of step (c) is selected from the group consisting of nickel
15 sulfates and cobalt sulfates.
- 16 7. The catalyst composition of claim 1, wherein mixing of components
17 occurs in high shear mode, in the range from 100 RPM to 1600 RPM.
- 18 8. The catalyst composition of claim 6, in which the weight ratio of nickel or
19 cobalt to the Group VI metal compound ranges from 1:100 to about 1:2.
- 20 9. The catalyst composition of claim 8, wherein the second hydrocarbon
21 oil boils in the range from at least 75°F to 250°F.
- 22 10. The catalyst composition of claim 1, wherein the ratio of the volume of
23 the second hydrocarbon oil to the first hydrocarbon oil is greater than 1.

- 1 11. The catalyst composition of claim 1, wherein the ratio of the volume of
2 the second hydrocarbon oil to the first hydrocarbon oil is greater than 5.
- 3 12. The catalyst composition of claim 1, wherein the ratio of the volume of
4 the second hydrocarbon oil to the first hydrocarbon oil is greater than
5 10.
- 6 13. The catalyst composition of claim 1, wherein the first hydrocarbon oil is
7 a vacuum gas oil.
- 8 14. The catalyst composition of claim 1, wherein the second hydrocarbon
9 oil possess a kinetic viscosity of less than 0.3 cSt at 212°F.
- 10 15. The catalyst composition of claim 1, wherein the second hydrocarbon
11 oil is a light naphtha.
- 12 16. The catalyst composition of claim 15, wherein the conditions of the
13 second reaction zone comprise a temperature in the range from at least
14 about 350°F to about 600°F, and a pressure in the range from at least
15 about 1000 psig to about 3500 psig.
- 16 17. The catalyst composition of claim 16, wherein the conditions of the
17 second reaction zone comprise a temperature in the range from at
18 least about 350°F to about 600°F, and the pressure in the range from
19 at least about 1500 psig to about 3000 psig.
- 20 18. The catalyst composition of claim 1, which is recovered by means of a
21 high pressure separator.
- 22 19. The catalyst composition of claim 1, which is stored in an active and
23 concentrated state.

Figure 1

