

CLAIMS

1. A catalyst composition having improved activity and stability in the hydrodemetallation of heavy hydrocarbons, said catalyst composition comprising:

(a) a support which comprises precipitated, extruded and calcined alumina comprising spherical or substantially spherical shaped particles, said support exhibiting a crystalline structure having a first dimension as measured along a 120 XRD plane and a second dimension as measured along a 020 XRD plane, wherein the ratio of the second dimension to the first dimension is less than 1.0; and

(b) at least one catalytic agent selected from the group consisting of a metal of Group 6 of The Periodic Table, a metal of Group 9 of The Periodic Table, a metal of Group 10 of The Periodic Table, and combinations thereof and optionally phosphorous;

wherein the support has a total pore volume in the range of from about 0.8 cc/g to about 1.2 cc/g, with greater than 8% of the total pore volume having a diameter greater than 350Å, and 40% or greater of the total pore volume having a diameter in the range of about 200Å to about 500Å and at least 5% of the total pore volume having a diameter above 1500Å, wherein total pore volume and pore volume distribution values are determined by mercury penetration porosimetry.

2. The catalyst of claim 1 wherein said at least one catalytic agent is selected from the group consisting of cobalt, nickel, molybdenum, and a combination thereof and optionally phosphorous.

3. The catalyst of claim 1 wherein the pore size distribution is selected from the group consisting of from about 0.064 cc/g to about 0.2 cc/g of the total pore volume of the support in pores having a diameter greater than 350Å; from about 0.4 cc/g to about 0.8 cc/g of the total pore volume of the support in pores having a diameter in the range of about 200Å to about 500Å; from about 0.04 cc/g to about 0.2 cc/g of the total pore volume of the support in pores having a diameter above 1500Å; and combinations thereof.

4. The catalyst of claim 1 wherein: the precipitated alumina support has a total pore volume of greater than 0.8 cc/g and a BET surface area of about 80 to about 180 m²/g.

5. The catalyst of claim 1 wherein the precipitated alumina comprising the support was prepared by:

(a) adding an acidic compound selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, ammonium sulfate, aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum chlorohydrate, and combinations thereof to water in an amount sufficient to provide a pH of less than 5;

(b) adding an alkaline compound selected from the group consisting of sodium hydroxide, sodium aluminate, aluminum hydroxide, ammonium hydroxide, and combinations thereof, to (a) in an amount sufficient to have a pH of greater than 7 and to precipitate seed alumina, forming a slurry;

(c) repeating steps (a) to (b) at least 1 additional time to provide an alumina-containing slurry having pH greater than 7;

(d) adding an acidic compound selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum chlorohydrate, and combinations thereof to the alumina-containing slurry of step (c) in an amount sufficient to provide an alumina slurry having a pH of less than 5;

(e) adding an alkaline compound selected from the group consisting of sodium hydroxide, sodium aluminate, aluminum hydroxide, ammonium hydroxide, and combinations thereof, to the alumina slurry of step (d) in an amount sufficient to provide a final alumina slurry having a pH of at least about 9; and

(f) recovering the precipitated alumina from the final alumina slurry;

wherein the temperature during steps (a) – (e) is maintained at a temperature of about 15°C to about 72°C.

6. The catalyst of claim 5 wherein the support is prepared by:

(g) drying the precipitated alumina of step (f);

(h) peptizing the dried alumina;

(i) extruding the peptized alumina; and

(j) calcining the extrudate at a temperature ranging from about 700°C to about 1060°C to obtain support particles.

7. The catalyst of claim 5 wherein the temperature during steps (a) – (e) is maintained at a temperature from about 48°C to about 68°C.

8. The catalyst of claim 5 wherein: (i) the acidic compound in any of steps (a), (c) and (d) is selected from the group consisting of aluminum sulfate, aluminum nitrate, ammonium sulfate, aluminum chlorohydrate, and combinations thereof; or (ii) the alkaline compound in any of steps (b), (c) and (e) is selected from the group consisting of sodium aluminate, aluminum hydroxide, sodium hydroxide, ammonium hydroxide and combinations thereof; or (iii) both (i) and (ii).

9. The catalyst of claim 5 wherein the pH in at least one of steps (a), (b), (c), (d) and (e) is controlled as follows:

(a) the pH in (a) ranges from about 2.0 to about 4.5;

(b) the pH in (b) ranges from about 7.5 to about 10;

(c) the alumina-containing slurry pH of step (c) ranges from about 7.5 to about 10;

(d) the alumina slurry pH of step (d) ranges from about 2.0 to about 4.5; and

(e) the final alumina slurry pH of step (e) ranges from about 9 to about 9.5.

10. A process for hydrotreating a heavy hydrocarbon fraction containing a component selected from the group consisting of metals, sulfur, microcarbon residue and mixtures thereof, which process comprises contacting the heavy hydrocarbon fraction with a catalyst of claim 1 under hydrotreating process conditions and reducing the content of a component selected from

the group consisting of metals, sulfur and microcarbon residue in the heavy hydrocarbon fraction compared to the level originally present.

11. The process of claim 10 wherein the heavy hydrocarbon fraction is contacted with the catalyst at a reaction temperature ranging from about 300°C to about 450°C, a hydrogen pressure of about 25 to about 200 bar, a H₂:oil ratio ranging from about 150 to about 1500 Nl/l, and a space velocity from about 0.1 to 5 hr⁻¹.

12. The process of claim 10 wherein the heavy hydrocarbon fraction contains a metal selected from the group consisting of nickel, vanadium and combinations thereof.

13. An alumina support for a hydroconversion catalyst having improved activity and stability in the hydrodemetallation of heavy hydrocarbons, said alumina comprising spherical or substantially spherical particles having a total pore volume in the range from about 0.8 cc/g to about 1.2 cc/g, a surface area from about 80 m²/g to about 180 m²/g and a crystalline structure having a first dimension as measured along a 120 XRD plane and a second dimension as measured along a 020 XRD plane, wherein the ratio of the second dimension to the first dimension is less than 1.0, wherein total pore volume is determined by mercury penetration porosimetry.

14. The catalyst support of claim 13, comprising a total pore volume in the range of from about 0.8 cc/g to about 1.2 cc/g, with greater than 8% of the total pore volume having a diameter greater than 350Å, and 40% or greater of the total pore volume having a diameter in the range of about 200Å to about 500Å and at least 5% of the total pore volume having a diameter above 1500Å, wherein total pore volume and pore volume distribution values are determined by mercury penetration porosimetry.

15. A process of preparing a precipitated alumina composition exhibiting a crystalline structure suitable for use as the catalyst support of claim 1 or claim 13 comprising:

- (a) adding an acidic compound selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, ammonium sulfate, aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum chlorohydrate, and combinations thereof to water in an amount sufficient to provide a pH of less than 5;
- (b) adding an alkaline compound selected from the group consisting of sodium hydroxide, sodium aluminate, aluminum hydroxide, ammonium hydroxide, and combinations thereof, to (a) in an amount sufficient to have a pH of greater than 7 and to precipitate seed alumina, forming a slurry;
- (c) repeating steps (a) to (b) at least 1 additional time to provide an alumina-containing slurry having pH greater than 7;
- (d) adding an acidic compound selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, ammonium sulfate, aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum chlorohydrate, and combinations thereof to the alumina-containing slurry of step (c) in an amount sufficient to provide an alumina slurry having a pH of less than 5;

(e) adding an alkaline compound selected from the group consisting of sodium hydroxide, sodium aluminate, aluminum hydroxide, ammonium hydroxide, and combinations thereof, to the alumina slurry of step (d) in an amount sufficient to provide a final alumina slurry having a pH of at least about 9; and
(f) recovering the precipitated alumina from the final alumina slurry;
wherein the temperature during steps (a) – (e) is maintained at a temperature of about 15°C to about 72°C.

16. The process of claim 15 wherein the temperature during steps (a) – (e) is maintained at from about 48°C to about 68°C.

17. The process of claim 15 wherein: (i) the acidic compound in any of steps (a), (c) and (d) is selected from the group consisting of aluminum sulfate, aluminum nitrate, ammonium sulfate, aluminum chlorohydrate, and combinations thereof; (ii) or the alkaline compound in any of steps (b), (c) and (e) is selected from the group consisting of sodium aluminate, aluminum hydroxide, sodium hydroxide, ammonium hydroxide and combinations thereof; or (iii) both (i) and (ii).

18. The process of claim 17 wherein: (i) the acid compound is aluminum sulfate; or (ii) the alkaline compound is sodium aluminate; or (iii) the acid compound is aluminum sulfate and the alkaline compound is sodium aluminate.

19. The process of claim 15 wherein the pH in at least one of steps (a), (b), (c), (d) and (e) is controlled as follows:

- (a) the pH in step (a) ranges from about 2.0 to about 4.5;
- (b) the pH in step (b) ranges from about 7.5 to about 10;
- (c) the alumina-containing slurry pH of step (c) ranges from about 7.5 to about 10;
- (d) the alumina slurry pH of step (d) ranges from about 2.0 to about 4.5; and
- (e) the final alumina slurry pH of step (e) ranges from about 9 to about 9.5.

20. The process of claim 15 wherein the catalyst support is prepared by:

- (g) drying the precipitated alumina of step (f);
- (h) peptizing the dried alumina;
- (i) extruding the peptized alumina; and
- (j) calcining the extrudate at a temperature ranging from about 700°C to about 1060°C to obtain support particles.