CLAIMS

1. A process for preparing a porous support material for supporting catalytically active metals suitable for the hydrodesulfurization of residuum hydrocarbon fractions under hydrotreating conditions, which process comprises:

(a) preparing a co-precipitated titania alumina powder having 5 wt % or less titania, based on the total weight of the titania alumina powder;

(b) peptizing the titania alumina powder;

(c) extruding the titania alumina powder to form a titania alumina extrudate; and calcining the extrudate at a temperature from about 500°C to about 900°C for about 1 hour to about 3 hours to obtain a titania alumina support having 5 wt % or less titania, based on the total weight of the support, wherein the support is characterized as having:

(i) a total pore volume from about 0.5 to about 1.1 cubic centimeters per gram;

(ii) at least 70% of the total pore volume in pores having a diameter of about 70 Å to about 130 Å;

(iii) less than 5% of the total pore volume in pores having a diameter above 300 Å, as determined by nitrogen porosimetry; and

(iv) less than 2% of the total pore volume in pores having a diameter above 1000 Å, as determined by mercury penetration porosimetry.

2. The process of claim 1 wherein the support comprises at least 90 wt % of co-precipitated titania alumina.

3. The process of Claim 1 wherein the co-precipitated titania alumina powder is formed by co-precipitating aluminum sulfate and titanium sulfate with sodium aluminate while using an amount of titanium sulfate sufficient to provide a final support comprising titania alumina.

4. The process of claim 1 wherein the support is calcined at a temperature from about 650°C to about 870°C.

5. A catalyst support prepared by the process according to claim 1.

6. A catalyst support comprising a co-precipitated titania alumina having 5 wt % or less titania based on the total weight of the titania alumina, said support having a total pore volume in the range of from about 0.5 to about 1.0 cubic centimeters per gram, at least 70% of the total pore volume in pores having a diameter between about 70 Å and about 130 Å, less than 5% of the total pore volume have pores in a diameter above 300 Å, as determined by nitrogen porosimetry, and less than 2% of the total pore volume in pores having a diameter above 1000 Å, as determined by mercury penetration porosimetry.

7. The support of claim 6 wherein the amount of titania present in the titania alumina is an amount less than 5 wt %, based on the total weight of the titania alumina.

8. The support of claim 7 wherein the amount of titania present in the titania alumina is an amount from about 0.3 to about 4.5 wt % titania, based on the total weight of the titania alumina.

9. The support of claim 6 wherein the support comprises at least 90 wt % co-precipitated titania alumina.

10. The support of claim 6 wherein: (a) at least 79% of the total pore volume is in pores having a diameter between about 70 Å and about 130 Å; or (b) from about 0.40 % to about 1.5% of the total pore volume is in pores having a diameter above 1000 Å; or both (a) and (b).

11. A method for preparing a catalyst for hydrodesulfurization of residuum hydrocarbon feedstocks which method comprises: impregnating a porous extruded support with an aqueous solution comprising at least one catalytic agent or catalytic agent precursor selected from the group consisting of a compound of Group 6 metals of The Periodic Table, Group 9 metals of the Periodic Table, Group 10 metals of The Periodic Table, and combinations thereof, and optionally phosphorous, said compounds being thermally decomposable to their corresponding metal oxides, and thereafter drying and calcining the resulting impregnated support to provide a supported catalyst, said support having been prepared by the process of claim 1.

12. A catalyst produced by the method according to claim 11.

13. A catalyst suitable for use in hydrodesulfurization of residuum hydrocarbon feedstocks comprising:

(a) a support comprising a co-precipitated titania alumina having 5 wt % or less titania based on the total weight of the titania alumina; and

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

wherein the support is characterized as having:

(i) a total pore volume of from about 0.5 to about 1.0 cubic centimeters per gram;

(ii) at least 70% of the total pore volume in pores having a diameter between about 70 Å and about 130 Å;

(iii) less than 5% of the total pore volume in pores having a diameter above 300 Å, as determined by nitrogen porosimetry; and

(iv) less than 2% of the total pore volume in pores having a diameter above 1000 Å, as determined by mercury penetration porosimetry.

14. The catalyst of claim 13 wherein the calcined support comprises at least 90 wt % of the co-precipitated titania alumina.

15. The catalyst of claim 13 wherein the amount of titania present in the co-precipitated titania alumina is an amount less than 5 wt %, based on the total weight of the titania alumina.

16. The catalyst of claim 15 wherein the amount of titania present in the co-precipitated titania alumina is an amount from about 0.3 to about 4.5 wt % titania, based on the total weight of the titania alumina.

17. The catalyst of claim 13 wherein: (a) at least 79% of the total pore volume of the support is in pores having a diameter between about 70 Å and about 130Å; or (b) from about 0.40 % to about 1.5% of the total pore volume is in pores having a diameter above 1000 Å; or both (a) and (b).

18. The catalyst of claim 13 wherein said at least one catalytic agent comprises a metal selected from the group consisting of cobalt, nickel, molybdenum, and combinations thereof, and optionally phosphorous.

19. A process for hydrotreating residuum hydrocarbon feedstocks comprising at least one of sulfur or microcarbon residue (MCR), which process comprises contacting said residuum feedstocks with a catalyst of claim 13 under hydrodesulfurization process conditions and producing a hydrotreated residuum hydrocarbon fraction having a reduced sulfur content or a reduced MCR content or both a reduced sulfur and a reduced MCR content compared to the residuum hydrocarbon feedstock.

20. The process of claim 19 wherein the residuum hydrocarbon feedstock is contacted with the catalyst at a reaction temperature from about 300°C to about 450°C, a hydrogen pressure of about 120 bar to about 200 bar, a H_2:oil ratio ranging from about 250 Nl/l to about 1400 N1/1, and a space velocity from about 0.2 hr^{-1} to about 2.0 hr^{-1}.

CLAIMS

1. A process for preparing a porous support material for supporting catalytically active metals suitable for the hydrodesulfurization of residuum hydrocarbon fractions under hydrotreating conditions, which process comprises:

(a) preparing a co-precipitated titania alumina powder having 5 wt % or less titania, based on the total weight of the titania alumina powder, wherein the titania alumina is co-precipitated from an aqueous alumina and titanyl salt composition at a temperature of 63°C to 80°C;

(b) peptizing the titania alumina powder;

(c) extruding the titania alumina powder to form a titania alumina extrudate; and

calcining the extrudate at a temperature from about 500°C to about 900°C for about 1 hour to about 3 hours to obtain a titania alumina support having 5 wt % or less titania, based on the total weight of the support, wherein the support is characterized as having:

(i) a total pore volume from about 0.5 to about 1.1 cubic centimeters per gram as determined by nitrogen porosimetry;

(ii) at least 70% of the total pore volume in pores having a diameter of about 70 Å to about 130 Å as determined by nitrogen porosimetry;

(iii) less than 5% of the total pore volume in pores having a diameter above 300 Å, as determined by nitrogen porosimetry; and

(iv) less than 2% of the total pore volume in pores having a diameter above 1000 Å, as determined by mercury penetration porosimetry.

2. The process of claim 1 wherein the support comprises at least 90 wt % of co-precipitated titania alumina.

3. The process of claim 1 wherein the co-precipitated titania alumina powder is formed by co-precipitating aluminum sulfate and titanyl sulfate with sodium aluminate while using an amount of titanium sulfate sufficient to provide a final support comprising titania alumina.

4. The process of claim 1 wherein the support is calcined at a temperature from about 650°C to about 870°C.

5. A catalyst support prepared by the process according to claim 1.

6. A catalyst support comprising a titania alumina extrudate formed from a peptized co-precipitated titania alumina powder having 5 wt % or less titania based on the total weight of the titania alumina, said support having a total pore volume in the range of from about 0.5 to about 1.0 cubic centimeters per gram as determined by nitrogen porosimetry, at least 70% of the total pore volume in pores having a diameter between about 70 Å and about 130 Å as determined by nitrogen porosimetry, less than 5% of the total pore volume have pores in a diameter above 300 Å as determined by nitrogen porosimetry, and less than 2% of the total pore volume in pores having a diameter above 1000 Å as determined by mercury penetration porosimetry.

7. The support of claim 6 wherein the amount of titania present in the titania alumina is an amount less than 5 wt %, based on the total weight of the titania alumina.

8. The support of claim 7 wherein the amount of titania present in the titania alumina is an amount from about 0.3 to about 4.5 wt % titania, based on the total weight of the titania alumina.

9. The support of claim 6 wherein the support comprises at least 90 wt % co-precipitated titania alumina.

10. The support of claim 6 wherein: (a) at least 79% of the total pore volume is in pores having a diameter between about 70 Å and about 130 Å; or (b) from about 0.40 % to about 1.5% of the total pore volume is in pores having a diameter above 1000 Å; or both (a) and (b).

11. A method for preparing a catalyst for hydrodesulfurization of residuum hydrocarbon feedstocks which method comprises: impregnating a porous extruded support with an aqueous solution comprising at least one catalytic agent or catalytic agent precursor selected from the group consisting of a compound of Group 6 metals of The Periodic Table, Group 9 metals of the Periodic Table, Group 10 metals of The Periodic Table, and combinations thereof, and optionally phosphorous, said compounds being thermally decomposable to their corresponding metal oxides, and thereafter drying and calcining the resulting impregnated support to provide a supported catalyst, said support having been prepared by the process of claim 1.

12. A catalyst produced by the method according to claim 11.

13. A catalyst suitable for use in hydrodesulfurization of residuum hydrocarbon feedstocks comprising:

(a) a support comprising a titania alumina extrudate formed from a peptized co-precipitated titania alumina powder having 5 wt % or less titania based on the total weight of the titania alumina; and

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

wherein the support is characterized as having:

(i) a total pore volume of from about 0.5 to about 1.0 cubic centimeters per gram as determined by nitrogen porosimetry;

(ii) at least 70% of the total pore volume in pores having a diameter between about 70 Å and about 130 Å as determined by nitrogen porosimetry;

(iii) less than 5% of the total pore volume in pores having a diameter above 300 Å as determined by nitrogen porosimetry; and

(iv) less than 2% of the total pore volume in pores having a diameter above 1000 Å as determined by mercury penetration porosimetry.

14. The catalyst of claim 13 wherein the calcined support comprises at least 90 wt % of the co-precipitated titania alumina.

15. The catalyst of claim 13 wherein the amount of titania present in the co-precipitated titania alumina is an amount less than 5 wt %, based on the total weight of the titania alumina.

16. The catalyst of claim 15 wherein the amount of titania present in the co-precipitated titania alumina is an amount from about 0.3 to about 4.5 wt % titania, based on the total weight of the titania alumina.

17. The catalyst of claim 13 wherein: (a) at least 79% of the total pore volume of the support is in pores having a diameter between about 70 Å and about 130Å; or (b) from about 0.40 % to about 1.5% of the total pore volume is in pores having a diameter above 1000 Å; or both (a) and (b).

18. The catalyst of claim 13 wherein said at least one catalytic agent comprises a metal selected from the group consisting of cobalt, nickel, molybdenum, and combinations thereof, and optionally phosphorous.

19. A process for hydrotreating residuum hydrocarbon feedstocks comprising at least one of sulfur or microcarbon residue (MCR), which process comprises contacting said residuum feedstocks with a catalyst of claim 13 under hydrodesulfurization process conditions and producing a hydrotreated residuum hydrocarbon fraction having a reduced sulfur content or a reduced MCR content or both a reduced sulfur and a reduced MCR content compared to the residuum hydrocarbon feedstock.

20. The process of claim 19 wherein the residuum hydrocarbon feedstock is contacted with the catalyst at a reaction temperature from about 300°C to about 450°C, a hydrogen pressure of about 120 bar to about 200 bar, a H_2:oil ratio ranging from about 250 Nl/l to about 1400 N1/1, and a space velocity from about 0.2 hr^{-1} to about 2.0 hr^{-1}.

21. A catalyst suitable for use in hydrodesulfurization of residuum hydrocarbon feedstocks comprising:

(a) a support comprising a titania alumina extrudate formed from a peptized co-precipitated titania alumina powder having 5 wt % or less titania based on the total weight of the titania alumina;

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

wherein the support has:

(i) less than 5% of a total pore volume in pores having a diameter above 300 Å as determined by nitrogen porosimetry; and

(ii) has less than 2% of a total pore volume in pores having a diameter above 1000 Å as determined by mercury penetration porosimetry.

22. The catalyst of claim 13 or claim 21 wherein phosphorous is present in a concentration in the range of about 0.26 to about 3.0 wt %, calculated as elemental phosphorous based on the weight of the total catalyst composition.

23. The catalyst of claim 22 wherein phosphorous is present in a concentration in the range of about 0.3 to about 1.95 wt %.