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

d) 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 has a total pore volume from about 0.5 to about 1.1 cubic centimeters per gram, at least 70% of the total pore volume in pores having a diameter of about 70 Å to about 130 Å, less than 5% of the total pore volume in pores having 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.

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 at least 79% of the total pore volume is in pores having a diameter between about 70 Å and about 130 Å.

11. The support of claim 6 wherein from about 0.40 % to about 1.5% of the total pore volume is in pores having a diameter above 1000 Å.

12. The support of claim 6, wherein the pore volume and pore size distribution properties as determined by mercury penetration porosimetry are obtained using a mercury porosimeter at a pressure from about atmospheric pressure to about 4000 bar, with a contact angle, $\theta = 140°$ and a mercury surface tension of 0.49 N/m at 25°C.

13. A method for preparing a catalyst for hydrodesulfurization of residuum hydrocarbon feedstocks which method comprises: impregnating a porous extruded support with an aqueous

solution containing 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, phosphorous and combinations thereof, 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 one of claim 5 or claim 6.

14. A catalyst produced by the method according to claim 13.

15. 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, phosphorous and combinations thereof,

c) wherein the support has a total pore volume 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 in pores having 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.

16. The catalyst of claim 15 wherein the calcined support comprises at least 90 wt % of the co-precipitated titania alumina.

17. The catalyst of claim 15 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.

18. The catalyst of claim 17 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.

19. The catalyst of claim 15 wherein at least 79% of the total pore volume of the support is in pores having a diameter between about 70 Å and about 130Å.

20. The catalyst of claim 15 wherein from about 0.40 % to about 1.5% of the total pore volume of the support is in pores having a diameter above 1000 Å.

21. The catalyst of claim 15 wherein said at least one catalytic agent comprises a metal selected from the group consisting of cobalt, nickel, molybdenum, phosphorous and combinations thereof.

22. The catalyst of claim 15 wherein the pore volume and pore size distribution properties of the support are determined by mercury penetration porosimetry using a mercury porosimeter at a pressure from about atmospheric pressure to about 4000 bar, with a contact angle, $\theta = 140°$ and a mercury surface tension of 0.49 N/m at 25°C.

23. A process for hydrotreating sulfur containing residuum hydrocarbon feedstocks, which process comprises contacting said residuum feedstocks with a catalyst of claim 15 under hydrodesulfurization process conditions and producing a hydrotreated residuum hydrocarbon fraction having a reduced sulfur content compared to the residuum hydrocarbon feedstock.

24. The process of claim 23 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}.

25. The process of claim 23 wherein the residuum hydrocarbon has a microcarbon residue (MCR) content and the MCR content is reduced in the hydrotreated residuum hydrocarbon fraction simultaneously with the reduction in sulfur.

26. A process of reducing the microcarbon residue (MCR) content of a residuum hydrocarbon feedstock comprising contacting a residuum hydrocarbon feedstock having a MCR content with the catalyst of claim 15 under hydrodesulfurization process conditions and producing a residuum hydrocarbon fraction having a reduced MCR content as compared to the MCR content of the residuum hydrocarbon feedstock.

27. The process of claim 26 wherein the residuum hydrocarbon feedstock contains sulfur, and wherein the residuum hydrocarbon fraction has a reduced content of sulfur as compared to the residuum hydrocarbon feedstock.

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}.