Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2228889 C 2007/11/13

(11)(21) **2 228 889**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1996/08/22
(87) Date publication PCT/PCT Publication Date: 1997/03/06
(45) Date de délivrance/Issue Date: 2007/11/13
(85) Entrée phase nationale/National Entry: 1998/02/05
(86) N° demande PCT/PCT Application No.: IB 1996/000831
(87) N° publication PCT/PCT Publication No.: 1997/008274
(30) Priorité/Priority: 1995/08/24 (US08/518,774)

(51) Cl.Int./Int.Cl. *B01J 35/10* (2006.01),
B01J 23/85 (2006.01), *C10G 45/08* (2006.01)
(72) Inventeur/Inventor:
SHERWOOD, DAVID EDWARD, JR., US
(73) Propriétaire/Owner:
TEXACO DEVELOPMENT CORPORATION, US
(74) Agent: SMART & BIGGAR

(54) Titre : PROCEDE D'HYDROCONVERSION AU MOYEN D'UN CATALYSEUR A REPARTITION DE DIMENSIONS DE PORES SPECIFIQUE, SANS AJOUT DE SILICE
(54) Title: HYDROCONVERSION PROCESS EMPLOYING A CATALYST WITH SPECIFIED PORE SIZE DISTRIBUTION AND NO ADDED SILICA

(57) Abrégé/Abstract:

A process for hydroconverting a hydrocarbon feed containing components boiling above 1000 °F (538 °C), sulphur, metals and carbon residue into product containing decreased levels of components having a boiling point greater than 1000 °F (538 °C), decreased levels of sulphur, particularly decreased sulphur contents in the unconverted 1000 °F+ (538 °C+) boiling point products and reduced sediment, which comprises: contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤ 0.5 wt.% of silica, no silicon containing components being intentionally added, and bearing 2.2-6 wt.% of a Group VIII metal oxide, 7-24 wt.% of a Group VIB metal oxide and 0.0-2.0 wt.% of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-98 cc/g, and a Pore Diameter Distribution wherein 27.0-34.0 % of the TPV are macropores of diameter > 250 Å, 66.0-73.0 % of the TPV are micropores of diameter 250 Å, 55-64.5 % of the Pore Volume in pores with diameters < 250 Å are micropores of diameter within ± 25 Å of a pore mode by volume of 110-130 Å, and < 0.05 cc/g of micropore volume are micropores with diameters < 80 Å.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} :
C10G 45/08, B01J 35/10

A1

(11) International Publication Number: **WO 97/08274**

(43) International Publication Date: 6 March 1997 (06.03.97)

(21) International Application Number: PCT/IB96/00831

(22) International Filing Date: 22 August 1996 (22.08.96)

(30) Priority Data:
08/518,774 24 August 1995 (24.08.95) US

(71) Applicant: TEXACO DEVELOPMENT CORPORATION [US/US]; 2000 Westchester Avenue, White Plains, NY 10650 (US).

(72) Inventor: SHERWOOD, David, Edward; 1010 Twentieth Street, Beaumont, TX 77706 (US).

(81) Designated States: CA, JP, MX, PL, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HYDROCONVERSION PROCESS EMPLOYING A CATALYST WITH SPECIFIED PORE SIZE DISTRIBUTION AND NO ADDED SILICA

(57) Abstract

A process for hydroconverting a hydrocarbon feed containing components boiling above 1000 °F (538 °C), sulphur, metals and carbon residue into product containing decreased levels of components having a boiling point greater than 1000 °F (538 °C), decreased levels of sulphur, particularly decreased sulphur contents in the unconverted 1000 °F+ (538 °C+) boiling point products and reduced sediment, which comprises: contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing $\leq$ 0.5 wt.% of silica, no silicon containing components being intentionally added, and bearing 2.2-6 wt.% of a Group VIII metal oxide, 7-24 wt.% of a Group VIB metal oxide and 0.0-2.0 wt.% of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-98 cc/g, and a Pore Diameter Distribution wherein 27.0-34.0 % of the TPV are macropores of diameter > 250 Å, 66.0-73.0 % of the TPV are micropores of diameter 250 Å, 55-64.5 % of the Pore Volume in pores with diameters < 250 Å are micropores of diameter within ± 25 Å of a pore mode by volume of 110-130 Å, and < 0.05 cc/g of micropore volume are micropores with diameters < 80 Å.

HYDROCONVERSION PROCESS EMPLOYING A CATALYST WITH SPECIFIED PORE SIZE DISTRIBUTION AND NO ADDED SILICA

This invention relates to a process for hydrotreating a hydrocarbon feed. More particularly, it relates to a hydroconversion process employing a catalyst with a specified pore size distribution and a method of impregnation/finishing which achieves improved levels of hydrodesulphurisation, particularly improved sulphur removal from the unconverted 1000°F (538°C) products, and reduced sediment make and which allows operations at higher temperatures and higher levels of hydroconversion of feedstock components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C) and additional hydrodesulphurisation.

As is well known to those skilled in the art, it is desirable to convert heavy hydrocarbons, such as those having a boiling point above about 1000°F (538°C), into lighter hydrocarbons which are characterised by higher economic value. It is desirable to treat hydrocarbon feedstocks, particularly petroleum residue, to achieve other goals including hydrodesulphurisation (HDS), carbon residue reduction (CRR), and hydrodemetallation (HDM) - the latter particularly including removal of nickel compounds (HDNi) and vanadium compounds (HDV).

These processes typically employ hydrotreating catalysts with specified ranges of pores having relatively small diameters (i.e. micropores, herein defined as pores having diameters less than 250Å) and pores having relatively large diameters (i.e. macropores, herein defined as pores having diameters greater than 250Å).

One approach to developing improved catalysts for petroleum resid processing has involved enlarging the micropore diameters of essentially monomodal catalysts (having no significant macroporosities) to overcome diffusion limitations. Early petroleum distillate hydrotreating catalysts generally were monomodal catalysts with very small micropore diameters (less than say 100Å) and rather broad pore size distributions. First generation petroleum resid hydrotreating catalysts were developed by introducing a large amount of macroporosity into a distillate hydrotreating catalyst pore structure to overcome the diffusion resistance of large molecules. Such catalysts, which are considered fully bimodal HDS/HDM catalysts, are typified by United States Patents 4,746,419, 4,395,328, 4,395,329, and 4,089,774, discussed below.

U.S. 4,746,419 (Peck *et al.*) discloses an improved hydroconversion process for the hydroconversion of heavy hydrocarbon feedstocks containing asphaltenes, metals, and sulphur compounds, which process minimises the production of carbonaceous insoluble solids and catalyst attrition rates. The disclosed process employs a catalyst which has 0.1 to 0.3 cc/g of its pore volume in pores with diameters greater than 1200Å and no more than 0.1 cc/g of its pore volume in pores having diameters greater than 4000Å. The present invention is distinguished from this reference because the prior art discloses only features of macropore size distribution useful for minimising the production of carbonaceous insoluble solids and does not disclose a pore size distribution which would provide additional hydrodesulphurisation activities. By contrast, the catalysts of the present invention require a unique pore size distribution, in addition to a specific method of impregnating/finishing, in order to provide additional hydrodesulphurisation. The present invention gives improved levels of hydrodesulphurisation, particularly improved sulphur removal from the unconverted 1000°F (538°C) products, and reduced sediment make at the same operating conditions compared to operations with a commercial vacuum resid hydroconversion catalyst having a macropore size distribution which satisfies the requirements of this prior art disclosure. The present invention also allows operations at higher temperatures and higher levels of hydroconversion of feedstock components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C) with improved levels of hydrodesulphurisation compared to operations with the prior art vacuum resid hydroconversion catalyst.

U.S. 4,395,328 (Hensley, Jr. *et al.*) discloses a process for the hydroconversion of a hydrocarbon stream containing asphaltenes and a substantial amount of metals, comprising contacting the stream (in the presence of hydrogen) with a catalyst present in one or more fixed or ebullating beds, the catalyst comprising at least one metal which may be a Group VIB or Group VIII metal, an oxide of phosphorus, and an alumina support, where the alumina support material initially had at least 0.8 cc/g of TPV in pores having diameters of 0-1200Å, at least 0.1 cc/g of TPV is in pores having diameters of 1200-50,000Å, a surface area in the range of 140-190 m^2/g, and the support material was formed as a composite comprising alumina and one or more oxides of phosphorus into a shaped material and was thence heated with steam to increase the average pore diameter of the catalyst support material prior to impregnation with active metals. The present invention is distinguished from this reference because the support of the present invention does not contain one or more oxides of phosphorus, is not heated with steam to increase the average pore diameter, and requires a higher surface area of about 229-307 m^2/g and there is a much more precise definition of pore volume distribution.

U.S. 4,395,329 (Le Page *et al.*) discloses a hydrorefining process of a high metal-containing feedstock employing a catalyst containing alumina, a metal from group VI and a metal from the iron group, the catalyst having a Total Surface Area of 120-200 m^2/g, a Total Pore Volume of 0.8-1.2 cc/g, and a Pore Diameter Distribution whereby 0-10% of the Total Pore Volume is present as micropores with diameters less than 100Å, 35-60% of the Total Pore Volume is in pores with diameters of 100-600Å, and 35-55% of the Total Pore Volume is present as macropores of diameter greater than 600Å. The present invention is distinguished from this reference because the prior art requires 35-55% of the TPV in pores with a diameter >600Å and the catalysts of the present invention have only about 17-27% of the TPV in pores greater than 600Å.

U.S. 4,089,774 (Oleck *et al.*) discloses a process for the demetallation and desulphurisation of a hydrocarbon oil comprising contacting the oil with hydrogen and a catalyst, the catalyst comprising a Group VIB metal and an iron group metal (i.e. iron, cobalt, or nickel) on a porous support, and having a surface area of 125-210 m^2/g and TPV of 0.4-0.65 cc/g with at least 10% TPV in pores having diameters less than 30Å, at least 50% of pore volume accessible to mercury being in pores having diameters of 30-150Å, and at least

16.6% of pores accessible to mercury being in pores having diameters greater than 300Å. The present invention is distinguished from this reference because the prior art requires a relatively low Total Pore Volume of only 0.4-0.65 cc/g, whereas, the catalysts of the present invention require much higher Total Pore Volumes of 0.82-0.98 cc/g.

U.S. 5,221,656, to Clark *et al.* discloses a hydroprocessing catalyst comprising at least one hydrogenation metal selected from the group consisting of the Group VIB metals and Group VIII metals deposited on an inorganic oxide support, said catalyst characterised by a surface area of greater than about 220 m^2/g, a pore volume of 0.23-0.31 cc/g in pores with radii greater than about 600Å (i.e. in pores with diameters greater than 1200Å), an average pore radius of about 30-70Å in pores with radii less than about 600Å (i.e. an average pore diameter of about 60-140Å in pores with diameters less than about 1200Å), and an incremental pore volume curve with a maximum at about 20-50Å radius (i.e. at about 40-100Å diameter). In the present invention, pores having a diameter greater than 1200Å are only about 0.12-0.20 cc/g and the incremental pore volume curve has a maximum (i.e. Pore Mode) at 110-130Å.

A recent approach to developing improved catalysts for petroleum resid processing has involved the use of catalysts having micropore diameters intermediate between the above described monomodal HDS and HDM catalysts, as well as sufficient macroporosities so as to overcome the diffusion limitations for petroleum bottoms HDS (i.e. sulphur removal from hydrocarbon product of a hydrotreated petroleum resid having a boiling point greater than 1000°F (538°C)) but limited macroporosities to limit poisoning of the interiors of the catalyst particles. Catalysts with micropore diameters intermediate between the above described monomodal HDS and HDM catalysts with limited macroporosities include those of United States Patents 4,941,964, 5,047,142, 5,399,259 and 5,545,602, discussed below.

U.S. 4,941,964 discloses a process for the hydrotreatment of a sulphur- and metal-containing feed which comprises contacting said feed with hydrogen and a catalyst in a manner such that the catalyst is maintained at isothermal conditions and is exposed to a uniform quality of feed, the catalyst comprising an oxide of a Group VIII metal, an oxide of a Group VIB metal and 0-2.0 weight % of an oxide of phosphorus on a porous alumina support, having a surface area of 150-210 m^2/g and a Total Pore Volume (TPV) of 0.50-0.75 cc/g such that 70-85% TPV is in pores having diameters of 100-160Å and 5.5-22.0% TPV is in pores having diameters of greater than 250Å.

U.S. 5,047,142 discloses a catalyst composition useful in the hydroprocessing of a sulphur and metal-containing feedstock comprising an oxide of nickel or cobalt and an oxide of molybdenum on a porous alumina support in such a manner that the molybdenum gradient of the catalyst has a value of less than 6.0 and 15-30% of the nickel or cobalt is in an acid extractable form, having a surface area of 150-210 m^2/g, a Total Pore Volume (TPV) of 0.50-0.75 cc/g, and a pore size distribution such that less than 25% TPV is in pores having diameters less than 100Å, 70.0-85.0% TPV is in pores having diameters of 100-160Å and 1.0-15.0% TPV is in pores having diameters greater than 250Å.

U.S. 5,399,259 discloses a process for the hydrotreatment of a sulphur-, metals- and asphaltenes-containing feed which comprises contacting said feed with hydrogen and a catalyst in a manner such that the catalyst is maintained at isothermal conditions and is exposed to a uniform quality of feed, the catalyst comprising 3-6 wt % of an oxide of a Group VIII metal, 14.5-24 wt % of an oxide of a Group VIB metal and 0-6 wt % of an oxide of phosphorus on a porous alumina support, having a surface area of 165-230 m^2/g and a Total Pore Volume (TPV) of 0.5-0.8 cc/g such that less than 5% of TPV is in pores with diameters less than about 80Å, at least 65% of the pore volume in pores with diameters less than 250Å is in pores with diameters +/-20Å of a Pore Mode of about 100-135Å and 22-29% TPV is in pores having diameters of greater than 250Å. The present invention is distinguished from this reference because the prior art requires a relatively low Total Pore Volume of only 0.5-0.8 cc/g, whereas the catalysts of the present invention require much higher Total Pore Volumes of 0.82-0.98 cc/g.

In United States Patent No. 5,435,908, there is disclosed a hydrotreating process employing, as catalyst, a porous alumina support with pellet diameters of 0.032-0.038 inches (0.81-0.96 mm) bearing 2.5-6 wt % of a Group VIII non-noble metal oxide, 13-24 wt % of a Group VIB metal oxide, less than or equal to 2.5 wt % of silicon oxide, typically about 1.9-2 wt % of intentionally added silica oxide, and 0-2 wt % of a phosphorus oxide, preferably less than about 0.2 wt % of a phosphorus oxide, with no phosphorus-containing components intentionally added during the catalyst preparation, said catalyst having a Total Surface Area of 165-210 m^2/g, a Total Pore Volume of 0.75-0.95 cc/g, and a Pore Diameter Distribution whereby 14-22% of the Total Pore Volume is present as macropores of diameter $\geq$1000Å, 22-32% of the Total Pore Volume is present as pores of diameter $\geq$250Å, 68-78% of the Total Pore Volume is present as pores of diameter $\leq$250Å, 26-35% of the Total Pore Volume is present as mesopores of diameters $\geq$200Å, 34-69% of the Total Pore Volume is present as secondary micropores of diameters 100-200Å, 5-18% of the Total Pore Volume is present as primary micropores of diameter $\leq$100Å, and $\geq$57% of the micropore volume is present as micropores of diameter within $\pm$20Å of a pore mode by volume of 100-145Å. By contrast, the present invention employs, as catalyst, a nominally pure porous alumina support with pellet diameters of 0.032-0.044 inches (0.81-1.12 mm), preferably 0.039-0.044 inches (0.99-1.12 mm), bearing 2.2-6 wt % of a Group VIII non-noble metal oxide, 7-24 wt % of a Group VIB metal oxide, less than or equal to 0.5 wt % of silicon oxide (e.g. silica: SiO_2), preferably less than or equal to 0.41 wt % of silica, with no silicon containing components intentionally added during catalyst preparation, and 0-2 wt % of a phosphorus oxide, preferably less than 0.2 wt % of a phosphorus oxide, most preferably less than 0.1 wt % of a phosphorus oxide, with no phosphorus-containing components intentionally added during the catalyst preparation, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume of 0.82-0.98 cc/g, and a Pore Diameter Distribution whereby 27.0-34.0% of the Total Pore Volume is present as macropores of diameter greater than 250Å, 66.0-73.0% of the Total Pore Volume is present as micropores of diameter less than 250Å, 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, and less than or equal to 0.05 cc/g of micropore volume is present in micropores with diameters less than 80Å. In the present case, the catalysts have only 46.5-56.5% of the micropore volume in pores with diameters ≤200Å present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å.

None of the above-identified catalyst types in the art have been found to be effective for achieving all of the desired improved process needs. Early catalysts in the art addressed the need for improved hydrodesulphurisation and/or hydrodemetallation as measured in the total liquid product.

One recent line of catalyst development, as typified by United States Patent Nos. 5,397,456 and 5,514,273 has been to develop hydroconversion catalysts for the improved hydroconversion of feedstocks components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C). The most recent developments of hydroconversion catalysts have been to develop hydroconversion catalysts with slightly improved bottoms HDS activities and some slight degree of sediment control allowing the use of some higher temperatures. Although the above-described hydroconversion catalysts give improved levels of hydroconversion of feedstocks components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C), they do not give the desired levels of sulphur removal obtained from the below-described petroleum bottoms HDS catalysts and these hydroconversion catalysts still make some amount of sediment.

A second line of catalyst development, as typified by United States Patents 4,941,964 and 5,047,142, has been to develop improved catalysts for petroleum bottoms HDS (i.e. selective sulphur removal from the unconverted hydrocarbon product having a boiling point greater than 1000°F (538°C) from a hydroprocess operating with significant hydroconversion of feedstocks components (e.g. petroleum resids) having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C)). More recent developments of petroleum bottoms HDS catalysts have been to develop petroleum bottoms HDS catalysts with some degree of sediment control allowing the use of some higher temperatures.

It would be desirable if a catalyst were available which provided improved hydrodesulphurisation, particularly improved bottoms HDS, and no sediment make and which could also withstand operation at much higher temperatures, so that it would be possible to attain a much higher levels of hydroconversion without the undesirable formation of sediment. Undesirable low levels of hydroconversion represent a problem which is particularly acute for those refiners who operate vacuum resid hydroprocessing units at or near their sediment limit. Such refiners, in the absence of sediment, would raise temperature and thus hydroconversion levels. It would be most desirable to operate at high temperatures, high levels of hydroconversion and hydrodesulphurisation, particularly high levels of bottoms hydrodesulphurisation, and minimal sediment make.

It is an object of this invention to provide a process for hydroconverting a charge hydrocarbon feed, particularly, to hydroconvert feedstock components having boiling points greater than 1000°F (538°C) into products having boiling points less than 1000°F (538°C) while simultaneously removing high amounts of sulphur from the unconverted 1000°F+ (538°C+) product stream. It is also an object of this invention to provide low Existent and Accelerated IP Sediment values in the 650°F+ (343°C+) boiling point product (Discussed below under "Sediment Measurement"). It is also an object of this invention to allow the use of much higher operating temperatures to produce more highly hydroconverted product with improved, lower levels of sulphur, particularly lower levels of sulphur in the unconverted 1000°F+ (538°C+) product stream, and minimal sediment. Other objects will be apparent to those skilled in the art.

In accordance with certain of its aspects, this invention is directed to a process for hydroprocessing a charge hydrocarbon feed containing components boiling above 1000°F (538°C), and sulphur, metals, and carbon residue which comprises contacting said charge hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a nominally pure, porous alumina support, bearing 2.2-6 wt % of a Group VIII non-noble metal oxide, 7-24 wt % of a Group VIB metal oxide, less than or equal to 0.5 wt % of silicon oxide (e.g. silica: SiO_2), preferably less than or equal to 0.41 wt % of silica, with no silicon containing components intentionally added during catalyst preparation and 0-2 wt % of a phosphorus oxide, preferably less than 0.2 wt % of a phosphorus oxide, most preferably less than 0.1 wt % of a phosphorus oxide, with no phosphorus-containing components intentionally added during the catalyst preparation, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume of 0.82-0.98 cc/g, and a Pore Diameter Distribution whereby 27.0-34.0% of the Total Pore Volume is present as macropores of diameter greater than 250Å, 66.0-73.0% of the Total Pore Volume is present as micropores of diameter less than 250Å, 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume (i.e. that micropore diameter where maximum mercury intrusion occurs: dV/dD MAX) of 110-130Å, and less than or equal to 0.05 cc/g of micropore volume is present in micropores with diameters less than 80Å, thereby forming hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals, and carbon residue; and

recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C), and of sulphur, metals, and carbon residue,

recovering said hydroprocessed product containing decreased content of sulphur in the portion of the hydroprocessed product boiling above 1000°F (538°C), and

recovering said hydroprocessed product containing decreased content of sediment in the portion of the hydroprocessed product boiling above 650°F (343°C).

According to one aspect of the present invention, there is provided a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals, and carbon residue which comprises: contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å, thereby forming hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue, and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C), and of sulphur, metals and carbon residue, and recovering said hydroprocessed product containing decreased content of sediment in the portion of the hydroprocessed product boiling above 650°F (343°C).

According to another aspect of the present invention, there is provided in a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue, an improvement which allows operations at a temperature 10°F (5.6°C) higher than normal hydrotreating conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 5 wt %, and reduces Existent IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.02 wt % which comprises contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

According to still another aspect of the present invention, there is provided in a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue, an improvement which allows operations at a temperature 20°F (11.1°C) higher than normal hydrotreating process conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 13.5 wt %, and reduces Accelerated IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.32 wt % which comprises contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

According to yet another aspect of the present invention, there is provided a hydrotreating catalyst characterised by stability at up to 10°F (5.6°C) over normal hydrotreating process conditions consisting essentially of: a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

According to a further aspect of the present invention, there is provided a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals, and carbon residue which comprises: contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å, thereby forming hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue, and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C), and of sulphur, metals and carbon residue, and recovering said hydroprocessed product containing decreased content of sediment in the portion of the hydroprocessed product boiling above 650°F (343°C).

According to yet a further aspect of the present invention, there is provided in a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue, an improvement which allows operations at temperature 10°F (5.6°C) higher than normal hydrotreating conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 5 wt %, and reduces Existent IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.02 wt % which comprises contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

According to still a further aspect of the present invention, there is provided in a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue, an improvement which allows operations at a temperature 20°F (11.1°C) higher than normal hydrotreating process conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 13.5 wt %, and reduces Accelerated IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.32 wt % which comprises contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

According to another aspect of the present invention, there is provided a hydrotreating catalyst characterised by stability at up to 10°F (5.6°C) over normal hydrotreating process conditions consisting essentially of: a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide, said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

The catalyst of the present invention allows operation at about +10°F (+5.6°C) and about +5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst. The catalyst of the present invention also allows operation at about +20°F (+11.1°C) and about +13.5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst. This constitutes a substantial economic advantage.

DESCRIPTION OF THE INVENTION

Feedstock

The hydrocarbon feed which may be charged to the process of this invention may include heavy, high boiling petroleum cuts typified by gas oils, vacuum gas oils, petroleum cokes, residual oils, vacuum resids, etc. The process of this invention is particularly useful to treat high boiling oils which contain components boiling above 1000°F (538°C) to convert them to products boiling below 1000°F (538°C). The charge may be a petroleum fraction having an initial boiling point of above 650°F (343°C) characterised by presence of an undesirable high content of components boiling above 1000°F (538°C), and sulphur, carbon residue and metals; and such charge may be subjected to hydrodesulphurisation (HDS). In particular, the charge may be undiluted vacuum resid.

A typical charge which may be utilised is an Arabian Medium/Heavy Vacuum Resid having the properties shown in Table I below:

It is a particular feature of the process of this invention that it may permit treating of hydrocarbon charge, particularly those containing components boiling above about 1000°F (538°C), to form product which is characterised by an increased content of components boiling below 1000°F (538°C) and by decreased content of undesirable components typified by sulphur, metals, and carbon residue. It is another feature of the process of the present invention that it provides improved sulphur removal from the unconverted 1000°F (538°C) products. It is another feature of the process of the present invention that it provides the above mentioned improvements with little or no sediment formation as measured by the Existent and Accelerated IP

Sediment values of the 650°F+ (343°C+) boiling point product. It is another feature of the process of the present invention that it allows operations at higher temperatures with consequent higher levels of 1000°F+ to 1000°F- (538°C+ to 538°C-) than may be achieved with the use of first generation catalysts.

TABLE I

Property	Value
API Gravity	4.8
1000°F+ (538°C+), vol%	87.5
1000°F+ (538°C+), wt%	88.5
1000°F- (538°C-), wt%	11.5
Sulphur, wt %	5.1
Total Nitrogen, wppm	4480
Hydrogen, wt %	10.27
Carbon, wt %	84.26
Alcor MCR, wt %	22.2
Kinematic Viscosity, cSt	
@ 212°F (100°C)	2430
@ 250°F (121°C)	410
@ 300°F (149°C)	117
Pour Point, °F (°C)	110
n-C_5 Insolubles, wt %	28.4
n-C_7 Insolubles, wt %	9.96
Toluene Insolubles, wt %	0.02
Asphaltenes, wt %	9.94
Metals, wppm	
Ni	49
V	134
Fe	10
Cu	3
Na	49
Total Metals wppm	245
Chloride, wppm	28

Sediment Measurement

It is a particular feature of the catalyst of this invention that it permits operation to be carried out under conditions which yield a substantially decreased content of sediment in the product stream leaving hydrotreating.

The charge to a hydroconversion process is typically characterised by a very low sediment content of 0.01 weight percent (wt %) maximum. Sediment is typically measured by testing a sample by the Shell Hot Filtration Solids Test (SHFST). See Jour. Inst. Pet. (1951) 37 pages 596-604 Van Kerknoort *et al.* Typical hydroprocessing processes in the art commonly yield Shell Hot Filtration Solids of above about 0.17 wt % and as high as about 1 wt % in the 650°F+ (343°C+) product recovered from the bottoms flash drum (BFD). Production of large amounts of sediment is undesirable in that it results in deposition in downstream units which in due course must be removed. This of course requires that the unit be shut down for an undesirable long period of time. Sediment is also undesirable in the products because it deposits on and inside various pieces of equipment downstream of the hydroprocessing unit and interferes with proper functioning of e.g. pumps, heat exchangers, fractionating towers, etc.

Very high levels of sediment formation (e.g. 1 wt %), however, are not usually experienced by those refiners who operate vacuum resid hydroprocessing units at moderate conversion levels of feedstock components having boiling points greater than 1000°F (538°C) into products having boiling points less than 1000°F (538°C) (say, 40-65 volume percent - vol% - conversion) and at relatively low but still undesirable values of sediment (e.g. a sediment limit of 0.17 wt %). Many refiners operate at this relatively low but still undesirable value of sediment in order to minimise the above described equipment fouling. Such refiners, in the absence of sediment, would raise temperature and thus hydroconversion levels. It would be most desirable to operate at high temperatures, high levels of hydroconversion and hydrodesulphurisation, particularly high levels of bottoms hydrodesulphurisation, and minimal sediment make.

In the present invention, the IP 375/86 test method for the determination of total sediment has been very useful. The test method is described in ASTM Designation D 4870-92. The IP 375/86 method was designed for the determination of total sediment in residual fuels and is very suitable for the determination of total sediment in the 650°F+ (343°C+) boiling point product. The 650°F+ (343°C+) boiling point product can be directly tested for total sediment which is designated as the "Existent IP Sediment value." It has been found that the Existent IP Sediment Test gives essentially equivalent test results as the Shell Hot Filtration Solids Test described above.

However, it has been noted that even 650°F+ (343°C+) boiling point products that give low Existent IP Sediment values, may produce additional sediment upon storage. Thus, a more severe test for sediment has been developed. In this modified test, 50 grams of 650°F+ (343°C+) boiling point product are heated to about 90°C and mixed with about 5 cm^3 of reagent grade hexadecane. The mixture is aged for about one hour at about 100°C. The resultant sediment is then measured by the IP 375/86 test method. The values obtained from this modified test are designated the "Accelerated IP Sediment values."

As it is recommended that the IP 375/86 test method be restricted to samples containing less than or equal to about 0.4 to 0.5 wt % sediment, sample size is reduced when high sediment values are observed. This leads to fairly reproducible values for even those samples with very large sediment contents.

It will be noted that catalysts of this invention, characterised by (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å, - are particularly advantageous in that they permit attainment of product hydrocarbon streams containing the lowest content of sediment at highest conversion, while producing product characterised by low sulphur, carbon residue and metals contents. It is a feature of the catalyst of this invention that it permits attainment of hydrotreated product with ≤0.17 wt % sediment, as measured by the Existent IP Sediment test in the portion of the hydroprocessed product boiling above 650°F (343°C), typically as low as 0.02 wt % in operations at about +10°F (+5.6°C) and about +5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst, and typically 0.17 wt % in operations at about +20°F (+11.1°C) and about +13.5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst.

It is another feature of the catalyst of this invention that it permits attainment of hydrotreated product with ≤0.32 wt % sediment, as measured by the Accelerated IP Sediment test in the portion of the hydroprocessed product boiling above 650°F (343°C), typically as low as 0.17 wt % in operations at about +10°F (+5.6°C) and about +5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst, and typically 0.32 wt % in operations at about +20°F (+11.1°C) and about +13.5 wt % 1000°F (538°C) conversion compared to operations with a first generation H-OIL catalyst.

Reaction Conditions

In the practice of the process of this invention (as typically conducted in a single-stage Robinson reactor in pilot plant operations), the charge hydrocarbon feed is contacted with hydrogen at isothermal hydrotreating conditions in the presence of catalyst. Pressure of operation may be 1500-10,000 psig (10.4-69 MPa), preferably 1800-2500 psig (12.4-17.3 MPa), say 2250 psig (15.5 MPa). Hydrogen is charged to the Robinson Reactor at a rate of 2000-10,000 SCFB (360-1800 m^3/m^3), preferably 3000-8000 SCFB (540-3240 m^3/m^3), say 7000 SCFB (1260 m^3/m^3). Liquid Hourly Space Velocity (LHSV) is typically 0.1-1.5, say 0.56 volumes of oil per hour per volume of liquid hold-up in the reactor. Temperature of operation is typically 700-900°F (371-482°C), preferably 750-875°F (399-468°C), say (404°C). Operation is essentially isothermal. The temperature may typically vary throughout the bed by less than about 20°F (11.1°C).

In another more preferred embodiment of the process of the present invention, the liquid and gaseous effluent from the previously described first-stage Robinson reactor is routed to a second-stage Robinson reactor containing the same weight of catalyst as had been loaded to the first-stage Robinson reactor and which is operated at essentially the same temperature and pressure as the first-stage Robinson reactor. The difference in average temperature between the first- and second-stage reactors is 0-30°F (0-16.7°C), preferably 0-15°F (0-8.3°C), say 0°F (0°C). No additional hydrogen is normally injected to the second-stage Robinson reactor. The liquid effluent passes through the second-stage Robinson reactor at a similar LHSV to that of the first-stage Robinson reactor. The liquid effluent from the first-stage Robinson reactor is uniformly contacted with the hydrogen-containing gaseous effluent and the second loading of catalyst at isothermal conditions in the second-stage Robinson reactor. No attempt is made to maintain constant catalytic activity by periodic or continuous withdrawal of portions of used catalyst and replacement of the withdrawn material with fresh catalyst in the two-stage Robinson reactor system. The catalyst begins as fresh catalyst and accumulates catalyst age generally expressed in barrels per pound. The average temperature is defined as the average of the temperatures of the first- and second-stage reactors. Average temperature of operation is typically 700-900°F (371-482°C), preferably 750-875°F (399-468°C), say 760°F (404°C). Overall, the hydrocarbon charge passes through the entire process system (i.e. the first- and second-stage Robinson reactors) at an overall LHSV of 0.05-0.75, say 0.28 volumes of oil per hour per volume of liquid hold-up in the reactor.

In general, reaction may be carried out in one or more continuously stirred tank reactors (CSTRs), such as Robinson reactors, in which the catalyst is exposed to a uniform quality of feed.

In one particularly preferred embodiment of the present invention, a sulphur-and metal-containing hydrocarbon feedstock is catalytically hydroprocessed using the H-OIL (TM) Process configuration. H-OIL is a proprietary ebullated bed process (co-owned by Hydrocarbon Research, Inc. and Texaco Development Corporation) for the catalytic hydrogenation of residua and heavy oils to produce upgraded distillate petroleum products and an unconverted bottoms product particularly suited for blending to a low sulphur fuel oil. The ebullated bed system operates under essentially isothermal conditions and allows for exposure of catalyst particles to a uniform quality of feed.

In the H-OIL Process, a catalyst is contacted with hydrogen and a sulphur- and metal-containing hydrocarbon feedstock by means which insures that the catalyst is maintained at essentially isothermal conditions and exposed to a uniform quality of feed. Preferred means for achieving such contact include contacting the feed with hydrogen and the catalyst in a single ebullated bed reactor, or in a series of two to five ebullated bed reactors, with a series of two ebullated bed reactors being particularly preferred. This hydroprocessing process is particularly effective in achieving high levels of hydrodesulphurisation with vacuum residua feedstocks.

In the H-OIL Process, the hydrocarbon charge is admitted to the first-stage reactor of a two-stage ebullated bed H-OIL unit in the liquid phase at 650-850°F (343-454°C), preferably 700-825°F (371-441°C) and 1000-3500 psia (6.9-24.2 MPa), preferably 1500-3000 psia (10.4-20.7 MPa). Hydrogen gas is admitted to the first-stage reactor of a two-stage ebullated bed H-OIL unit in amount of 2000-10,000 SCFB (360-1800 m^3/m^3), preferably 3000-8000 SCFB (540-1440 m^3/m^3). The hydrocarbon charge passes through the first-stage ebullated bed reactor at a LHSV of 0.16-3.0 hr^{-1}, preferably 0.2-2 hr^{-1}. During operation, the catalyst bed is expanded to form an ebullated bed with a defined upper level. Operation is essentially isothermal with a typical maximum temperature difference between the inlet and outlet of 0-50°F (0-27.8°C), preferably 0-30°F (0-16.7°C). The liquid and gaseous effluent from the first-stage reactor is then routed to the second-stage reactor of the two-stage H-OIL unit which is operated at essentially the same temperature and pressure as the first-stage reactor. The difference in average temperature between the first- and second-stage reactors is 0-30°F (0-16.7°C), preferably 0-15°F (0-8.3°C). Some additional hydrogen may optionally be injected to the second-stage reactor to make up for the hydrogen consumed by reactions in the first-stage reactor.

In the H-OIL process, constant catalytic activity is maintained by periodic or continuous withdrawal of portions of used catalyst and replacement of the withdrawn material with fresh catalyst. Fresh catalyst is typically added at the rate of 0.05-1.0 pounds per barrel of fresh feed, preferably 0.20-0.40 pounds per barrel of fresh feed. An equal volume of used catalyst is withdrawn and discarded to maintain a constant inventory of catalyst on the volume basis. The catalyst replacement is performed such that equal amounts of fresh catalyst are added to the first-stage reactor and the second-stage reactor of a two-stage H-OIL unit.

Catalyst Support

The catalyst support is alumina. Although the alumina may be alpha, beta, theta, or gamma alumina, gamma alumina is preferred.

The charge alumina which may be employed in practice of this invention may be available commercially from catalyst suppliers or it may be prepared by variety of processes typified by that wherein 85-90 parts of pseudoboehmite alumina is mixed with 10-15 parts of recycled fines. In preparing the present catalyst, no silicon containing components, particularly silicon oxide (i.e. silica: SiO2), are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions. It is within the concept of this invention that during catalyst preparation, a small amount of silicon containing components may be unintentionally introduced as a contaminant, however, the finished catalyst is required to contain only ≤0.5 wt % of silica, preferably ≤0.41 wt % of silica.

Acid is added and the mixture is mulled and then extruded in an Auger type extruder through a die having cylindrical holes sized to yield a calcined substrate having a diameter of 0.032-0.044 inches (0.81-1.12 mm), preferably 0.039-0.044 inches (0.99-1.12 mm). Extrudate is air-dried to a final temperature of typically 250-275°F (121-135°C) yielding extrudates with 20-25% of ignited solids. The air-dried extrudate is then calcined in an indirect fired kiln for 0.5-4 hours in an atmosphere of air and steam at typically about 1000-1150°F (538-621°C).

Catalysts of the Present Invention - Pore Size Distribution

The catalyst which may be employed is characterised by Total Surface Area (TSA), Total Pore Volume (TPV), and (Pore Diameter Distribution (Pore Size Distribution PSD). The Total Surface Area is 195-230 m^2/g, preferably 200-225 m^2/g, say 209 m^2/g. The total Pore Volume (TPV) may be 0.82-0.98, preferably 0.82-0.90, say 0.84 cc/g.

Less than 0.05 cc/g of micropore volume is present in micropores with diameters less than 80Å.

Micropores of diameter in the range of less than 250Å are present in an amount of about 66.0-73.0% of the Total Pore Volume, say 70.8 %TPV. 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å. 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å.

The amount of Total Pore Volume in the range of 55-115Å is only about 20-35% and preferably 28.9%.

The Pore Size Distribution is such that 27.0-34.0% of the Total Pore Volume, and preferably about 29.2% is present as macropores of diameter greater than 250Å.

The amount of Total Pore Volume in pores with a diameter greater than 600Å is only about 17-27% and preferably 20.9 %TPV.

The amount of Total pore Volume in pores having a diameter greater than 1200Å is only about 0.12-0.20 cc/g and preferably 0.14 cc/g.

It should be noted that the percentages of the pores in the finished catalyst are essentially the same as in the charge gamma alumina substrate from which it is prepared, although the Total Surface Area of the finished catalyst may be 75-85%, say 81.3% of the charge gamma alumina substrate from which it is prepared (i.e. 75-85% of a support surface area of 229-307

m^2/g, say 257 m^2/g). It should also be noted that the Median Pore Diameter by Surface Area from mercury porosimetry of the finished catalyst is essentially the same as that of the charge gamma alumina substrate from which it is prepared.

It is also noted that the Pore Size Distribution (percent of total) in the finished catalyst may be essentially the same as in the charge alumina from which it is prepared (unless the majority of the pore volume distribution in a given range is near a "break-point" - e.g. 80Å or 250Å, in which case a small change in the amount of pores of a stated size could modify the reported value of the pore volume falling in a reported range). The Total Pore Volume, of the finished catalyst may be 75%-98%, say 81.3% of the charge alumina from which it is prepared.

Catalysts of the Present Invention - Metals Loadings

The alumina charge extrudates may be loaded with metals to yield a product catalyst containing a Group VIII non-noble metal oxide in an amount of 2.2-6 wt %, preferably 3.0-3.9 wt %, say 3.6 wt % and a Group VIB metal oxide in amount of 7-24 wt %, preferably 12.5-15.5 wt %, say 15.1 wt %.

The Group VIII metal may be a non-noble metal such as iron, cobalt, or nickel. This metal may be loaded onto the alumina typically from a 10%-30%, say 15% aqueous solution of a water-soluble salt (e.g. a nitrate, acetate, oxalate etc.). The preferred metal is nickel, employed as about a 12.3 wt % aqueous solution of nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$.

The Group VIB metal can be chromium, molybdenum, or tungsten. This metal may be loaded onto the alumina typically from a 10%-40%, say 20% aqueous solution of a water-soluble salt. The preferred metal is molybdenum, employed as about a 16.3 wt % aqueous solution of ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The molybdenum is supported on the alumina support in such a manner that the molybdenum gradient of the catalyst has a value of less than 5.0, discussed below.

It is a feature of the catalyst of the invention that it contains 0-2 wt % of a phosphorus oxide, preferably less than 0.2 wt % of a phosphorus oxide, most preferably less than 0.1 wt % of a phosphorus oxide, with no phosphorus-containing components intentionally added during the catalyst preparation.

As described above, no silicon containing components, particularly silicon oxide (i.e. silica: SiO2), are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, however, silica may be present in very small amounts, typically up to 0.5 wt % of silica, preferably less than or equal to 0.41 wt % of silica.

These catalyst metals are impregnated onto the preferably pure alumina support according to the procedures described in United States Patent 5,047,142.

A necessary and essential feature of the catalyst composition of the present invention is that 10-40% of the Group VIII metal present in the catalyst (with nickel preferably being the sole Group VIII metal) is acid extractable. The amount of acid extractable Group VIII metal in the catalyst (with nickel preferably being the sole Group VIII metal) is preferably in the range of 15-40%, most preferably 25-35% of the total Group VIII metal present in the catalyst. It is believed that the final calcination temperature during preparation of the catalyst determines the percentage of free Group VIII metal oxide (which is acid extractable) in the total catalyst composition.

Another feature of the catalyst composition of the present invention is that the ratio of the measured hydrodesulphurisation (HDS) microactivity rate constant k of the catalyst of the present invention to the measured HDS microactivity rate constant k of a standard hydroprocessing catalyst (namely, Criterion HDS-1443B, a commercially available, state-of-the-art catalyst for use in hydroprocessing resid oils), has a value of $\geq$0.5, preferably $\geq$1.03, most preferably $\geq$1.5. As used in this description, the phrase "HDS microactivity" means the intrinsic hydrodesulphurisation activity of a catalyst in the absence of diffusion, as measured according to the HDS Microactivity (HDS-MAT) Test, described as follows. In the HDS-MAT Test, a given catalyst is ground to a 30-60 mesh (0.0071-0.013 mm) fraction and presulphided at 750°F (399°C) with a gas stream containing 10% H_2S/90% H_2. The catalyst is then exposed to a sulphur-containing feed, namely benzothiophene, which acts as a model sulphur compound probe, at reaction temperature and with flowing hydrogen for approximately 4 hours. Samples are taken periodically and analysed by gas chromatography for the conversion of benzothiophene to ethylbenzene, thereby indicating the hydrodesulphurisation properties of the catalyst being tested. The activity is calculated on both a catalyst weight and catalyst volume basis to account for any density differences between catalysts. The conditions for a typical HDS-MAT Test are as follows:

Temperature:	about 550°F (about 288°C)
Pressure:	about atmospheric
Feedstock:	about 0.857 molar Benzothiophene in reagent grade normal heptane
Space Velocity:	4 hr^{-1}
Catalyst Charge:	0.5 gram

The kinetics of the reactor used in the HDS-MAT Test are first order, plug flow. At the above stated temperature and space velocity, the rate constant, k, may be expressed as

$$k = \ln (1/1\text{-HDS})$$

where HDS is the fractional hydrodesulphurisation value obtained for a given catalyst at the above stated conditions. A commercially available, state-of-the-art catalyst sold for use in hydroprocessing resid oils (Criterion HDS-1443B catalyst) was evaluated with the HDS-MAT Test under the above stated conditions and was found to have a %HDS value of 73% on a weight basis and a corresponding rate constant k value of 1.3093. The catalysts of the present invention require that the ratios of the measured HDS-MAT rate constant k, relative to that obtained with Criterion HDS-1443B, have values of preferably ≥1.03, most preferably ≥1.5: the catalysts of U.S. Patent No. 5,047,142 are required to have values >1.0, preferably >1.5.

It is another feature of the catalyst composition of the present invention that the oxide of molybdenum, preferably MoO_3, is distributed on the above described porous alumina support in such a manner that the molybdenum gradient is <5. As used in this description, the phrase "molybdenum gradient" means the ratio of molybdenum/aluminum atomic ratio observed on the exterior surfaces of catalyst pellets relative to the molybdenum/aluminum atomic ratio observed on surfaces of a sample of the same catalyst which has been ground to a fine powder, the atomic ratios being measured by X-Ray photoelectron spectroscopy (XPS), sometimes referred to as Electron Spectroscopy for Chemical Analysis (ESCA). It is theorised that the molybdenum gradient is strongly affected by the impregnation of molybdenum on the catalyst support and the subsequent drying of the catalyst during its preparation. ESCA data were obtained on an ESCALAB MKII instrument available from V. G. Scientific Ltd., which uses a 1253.6 eV magnesium X-Ray source.

In the following Table II, the catalyst of Example I was prepared by using an alumina support prepared without silica and then impregnating/finishing with a low final calcination temperature. Examples II and III were made in commercial equipment by the same formula as Example I. Examples I-III are the most preferred catalysts of the present invention. Example IV was made by the same formula as Example I but in this instance, the catalyst was finished with a somewhat higher calcination temperature designed to meet the minimum HDS-MAT requirements (C 0.5g @ 555°F (290.6°C) and Relative k values) and the minimum nickel extraction requirements (wt % acid extractable nickel). Example IV is a preferred catalyst of the present invention. Examples V and VI were made by the same formula as Example I but the catalysts were finished at high calcination temperature. Examples V and VI are less preferred catalysts of the present invention. Example VII* is a catalyst with similar catalytic metals loadings but which does contain silica (i.e. as in United States Patent No. 5,545,602.

Table II

Analyses of Catalyst Samples*

	Present Invention		Present Invention — Preferred Types				Present Invention Less Preferred Types		
	Broad Ranges	Preferred Ranges	Example I	Example II	Example III	Example IV	Example V	Example VI	Example VII*
Metals									
Molybdenum (as MoO_3)	7-24	12.5-15.5	15.1	15.1	15.3	NA	(15.3)	14.4	(14.0)
Nickel (as NiO)	2.2-6	3.0-3.9	3.6	3.6	3.5	NA	(3.4)	3.3	(3.1)
Silicon (as SiO_2)	≤0.5 (None added)	≤0.41 (None added)	0.41	0.24	0.26	NA	NA	0.17	(2.1)
Phosphorus (as P_2O_5)	≤0.2 (None added)	≤0.2 (None added) Most preferably ≤0.1	<0.2	0.09	<0.02	NA	NA	<0.02	(0.0)
Surface Area (N_2, BET) m^2/g	195-230	200-225	209	212	215	205	207	224	199
Pore Size Distribution (Hg)**									
TPV cc/g	0.82-0.98	0.82-0.90	0.84	0.87	0.86	0.87	0.88	0.95	0.87
PV, cc/g > 1200 Å	~0.12-0.20	~0.12-0.20	0.14	0.17	0.18	0.12	0.16	0.15	0.15
PV, cc/g >600 Å % of TPV	~17-27	~17-27	20.9	23.1	23.8	18.2	21.5	20.1	22.0
PV, cc/g >250 Å % of TPV	27.0-34.0	27.0-34.0	29.2	29.7	29.7	27.1	30.3	28.5	29.6
PV, cc/g <80Å	<0.05	<0.05	0.02	0.02	0.03	0.01	0.01	0.02	0.03
Pore Mode (dV/dD MAX from Hg)	110-130	110-130	111	111	116	116	111	111	116

PV, ±25Å from dV/dD MAX, % of PV <250 Å	55-64.5	55-64.5	60.2	61.9	57.0	58.3	58.4	60.8	65.6
PV, ±20Å from dV/dD MAX, % of PV <200 Å	46.5-56.5	49-56.1	54.8	56.1	49.9	53.6	54.2	55.9	69.2
PV, cc/g 55-115 Å % of TPV	~20-35	~20-35	28.9	30.3	26.0	22.0	23.5	28.9	23.7
PV, cc/g >1000 Å % of TPV	~14-22	~14-22	18.1	20.7	21.7	15.2	18.5	16.9	18.9
Median Pore Diameter (by Surface Area from Hg), Å	~115-130	~115-130	116	115	118	124	122	120	120
Impregnation Characteristics									
HDS-MAT C 0.5g @ 550°F (288°C)	≥49	≥74	91	90	88.5	74	68	54	62
HDS-MAT, Relative k***	≥0.5	≥1.03 most preferably ≥1.5	1.84	1.76	1.65	1.03	0.87	0.59	0.74
Nickel Extraction, wt %	10-40	15-40 most preferably 25-35	(30.0)	(30.2)	(28.0)	(15.2)	(13.6)	(12)	(13.0)
ESCA Molybdenum Gradient	<5	<5	1.6	3.2	2.1	1.4	1.4	1.5	2.8
Average Pellet Diameter, Inches (mm)	0.032-0.044 (0.81-1.12)	0.039-0.044 (0.99-1.12)	0.041 (1.04)	0.043 (1.09)	0.044 (1.12)	0.039 (0.99)	0.040 (1.02)	0.043 (1.09)	0.040 (1.02)

---

* Values in parentheses obtained at Cytec Industries Stamford Research Laboratories.

** Contact angle = 130°; surface tension = 484 dynes/cm.

*** As described in U.S. Patent No. 5,047,142.

In the following Table III, the broad ranges for the catalysts of this invention and the preferred ranges for the catalysts of this invention are listed (including: Total Pore Volume in cc/g; Pore Volume occupied by pores falling in designated ranges - as a volume% of Total Pore Volume (%TPV) or as a volume % of the Pore Volume in micropores with diameters less than 250Å - i.e. % of Pore Volume in the micropores- or in cc of Pore Volume per gram of catalyst; Pore Mode by volume from mercury porosimetry (dV/dD MAX); Pore Volume falling within ± 25Å of dV/dD MAX in the less than 250Å region; and, Surface Area in m^2/g). The remaining columns list properties and references for other hydroprocessing catalysts in the art.

Table III

	Present Invention		Selected	U.S. Patent No./
	Broad Ranges	Preferred Ranges	Art Ranges	Application Serial No. Reference
Metals				
Molybdenum (as MoO_3)	7-24	12.5-15.5		
Nickel (as NiO)	2.2-6	3.0-3.9		
Silicon (as SiO_2)	≤0.5 (None added)	≤0.41 (None added)	≤2.5; typically 1.9-2.0	5,435,908; 08/425,971
Phosphorus (as P_2O_5)	≤0.2 (None added)	≤0.2 (None added) Most preferably ≤0.1	<0.2 (None added)	5,435,908; 08/425,971
Surface Area (N_2, BET) m^2/g	195-230	200-225	140-190	4,395,328
			240-310	5,397,456
Pore Size Distribution (Hg)**				
TPV cc/g	0.82-0.98	0.82-0.90	0.4-0.65	4,089,774
			0.5-0.75	4,941,964
			0.5-0.75	5,047,142
			0.5-0.75	5,397,456
			0.5-0.8	5,399,259
PV, cc/g >1200 Å	~0.12-0.20	~0.12-0.20	0.23-0.31	5,221,656
PV, cc/g >600 Å % of TPV	~17-27	~17-27	35-55	4,395,329
PV, cc/g >250 Å % of TPV	27.0-34.0	27.0-34.0	5.5-22.0	4,941,964
			1.0-15.0	5,047,142
			11-18	5,397,456
PV, cc/g <80 Å	<0.05	<0.05		
Pore Mode (dV/dD MAX from Hg)	110-130	110-130	40-100	5,221,656

PV, ±25Å from dV/dD MAX, % of PV <250 Å	55-64.5	55-64.5	≥65	5,399,259
PV, ±20Å from dV/dD MAX, % of PV <200 Å	46.5-56.5	49-56.1	≥57	5,435,908; 08/425,971
PV, cc/g 55-115 Å % of TPV	~20-35	~20-35	63-78 50-62.8	5,397,456 08/130,472
PV, cc/g >1000 Å % of TPV	~14-22	~14-22	14-22	5,435,908; 08/425,971
Median Pore Diameter (by Surface Area from Hg), Å	~115-130	~115-130		
Impregnation Characteristics				
HDS-MAT C 0.5g @ 550°F (288°C)	≥49	≥74		
HDS-MAT, Relative k^{***}	≥0.5	≥1.03 most preferably ≥1.5		
Nickel Extraction, wt %	10-40	15-40 most preferably 25-35	15-30	5,047,142
ESCA Molybdenum Gradient	<5	<5		
Average Pellet Diameter, Inches (mm)	0.032-0.44 (0.81-1.12)	0.039-0.044 (0.99-1.12)	0.032-0.038 0.81-0.97)	5,435,908; 08/425,971

---

* Values in parentheses obtained at Cytec Industries Stamford Research Laboratories.

** Contact angle = 130°; surface tension = 484 dynes/cm.

*** As described in U.S. Patent No. 5,047,142.

The catalyst may be evaluated in a two-stage Robinson Reactor, a Continuously Stirred Tank Reactor (CSTR) which evaluates catalyst deactivation at conditions simulating those of a two-stage H-OIL ebullated bed Unit. The feedstock is an Arabian Medium/Heavy Vacuum Resid of the type set forth above. Evaluation is carried out for six or more weeks to a catalyst age of 2.73 or more barrels per pound.

Preferred Embodiment

In practice of the process of this invention, the catalyst, preferably in the form of extruded cylinders of 0.039-0.044 inches (0.99-1.1 mm) in diameter and about 0.15 inches (3.8 mm) in length, may be placed within the first- and second-stage reactors of a two-stage H-OIL Unit. The hydrocarbon charge is admitted to the lower portion of the first-stage reactor bed in the liquid phase at 650-850°F (343-454°C), preferably 700-825°F (371-441°C) and 1000-3500 psia (6.9-24.2 MPa), preferably 1500-3000 psia (10.4-20.7 MPa). Hydrogen gas is admitted to the first-stage reactor of the two-stage ebullated bed H-OIL unit in amount of 2000-10,000 SCFB (360-1800 m^3/m^3), preferably 3000-8000 SCFB (540-1440 m^3/m^3). The hydrocarbon charge passes through the first-stage ebullated bed reactor at a LHSV of 0.16-3.0 hr^{-1}, preferably 0.2-2 hr^{-1}. During operation, the first-stage reactor catalyst bed is expanded to form an ebullated bed with a defined upper level. Operation is essentially isothermal with a typical maximum temperature difference between the inlet and outlet of 0-50°F (0-27.8°C), preferably 0-30°F (0-16.7°C). The liquid and gaseous effluent from the first-stage reactor is admitted to the lower portion of the second-stage reactor of the two-stage H-OIL unit which is operated at essentially the same temperature and pressure as the first-stage reactor. The difference in average temperature between the first- and second-stage reactors is 0-30°F (0-16.7°C), preferably 0-15°F (0-8.3°C). Some additional hydrogen may optionally be injected to the second-stage reactor to make up for the hydrogen consumed by reactions in the first-stage reactor. During operation, the second-stage reactor catalyst bed is also expanded to form an ebullated bed with a defined upper level. Constant catalytic activity is maintained by periodic or continuous withdrawal of portions of used catalyst and replacement of the withdrawn material with fresh catalyst. Fresh catalyst is typically added at the rate of 0.05-1.0 pounds per barrel of fresh feed, preferably 0.20-0.40 pounds per barrel of fresh feed. An equal volume of used catalyst is withdrawn and discarded to maintain a constant inventory of catalyst on the volume basis. The catalyst replacement is performed such that equal amounts of fresh catalyst are added to the first-stage reactor and the second-stage reactor of a two-stage H-OIL unit.

In a less preferred embodiment, the reaction may be carried out in one or more continuously stirred tank reactors (CSTR) which also provides essentially isothermal conditions.

During passage through the reactor, preferably containing an ebullated bed, the hydrocarbon feedstock is converted to lower boiling products by the hydrotreating/hydrocracking reaction.

<u>Practice of the Present Invention</u>

In a typical embodiment, employing a two-stage Robinson reactor pilot unit, a charge containing 60-95 wt %, say 88.5 wt % boiling above 1000°F (538°C) may be converted to a hydrotreated product containing only 32-50 wt %, say 47.0 wt % boiling above 1000°F (538°C). The sulphur of the original charge is 3-7 wt %, typically 5.1 wt %; the sulphur content of the unconverted 1000°F+ (538°C+) component in the product is 0.5-3.5 wt %, typically 1.8 wt %. In another embodiment, employing a two-stage Robinson reactor pilot Unit operating at +10°F (+5.6°C) over normal operating temperatures and at a larger value of catalyst age, a charge containing 60-95 wt %, say 88.5 wt % boiling above 1000°F (538°C) may be converted to a hydrotreated product containing only 26-41 wt %, say 38.5 wt % boiling above 1000°F (538°C). The sulphur content of the unconverted 1000°F+ (538°C+) component in the product is 0.5-3.5 wt %, typically 2.1 wt %. In both embodiments, the Existent IP sediment values of the 650°F+ (343°C+) product leaving the reactor are extremely small; ≤ 0.02 wt %. In both embodiments, the Accelerated IP sediment values are relatively small; ≤0.17 wt %.

In another embodiment, employing a two-stage Robinson reactor pilot unit operating at +20°F (+11.1°C) over normal operating temperatures and at a larger value of catalyst age, a charge containing 60-95 wt %, say 88.5 wt % boiling above 1000°F (538°C) may be converted to a hydrotreated product containing only 21-32 wt %, say 30.3 wt % boiling above 1000°F (538°C). The sulphur content of the unconverted 1000°F+ (538°C+) component in the product is 0.5-3.5 wt %, typically 2.3 wt %. In this embodiment, the Existent IP sediment value of the 650°F+ (343°C+) product leaving the reactor is high (i.e. 0.17 wt %). This Existent IP sedimentation level, however, is similar to that experienced with first generation catalysts at normal operating temperatures and lower (i.e. -13.5 wt %) hydroconversion of feedstock components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C). The Accelerated IP sediment value of the 650°F+ (343°C+) product leaving the reactor is still relatively low (i.e. 0.32 wt %). This Accelerated IP sedimentation level is only about 44% of that experienced with first generation catalysts at normal operating temperatures and lower (i.e. -13.5 wt %) hydroconversion of feedstock components having a boiling point greater than 1000°F (538°C) to products having a boiling point less than 1000°F (538°C).

ADVANTAGES OF THE INVENTION

It will be apparent to those skilled in the art that this invention is characterised by advantages including the following:

(a) It gives no sediment versus an undesirable level with a commercially available first generation nickel/molybdenum H-OIL catalyst when both catalysts are compared at normal operating temperatures;

(b) It allows an increase in reaction temperature and thus allows operations at higher (i.e. up to 66.2) wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion levels;

(c) It permits improved levels of carbon residue reduction and nickel and vanadium removal at all (i.e. 46.9-66.2) wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion levels; and,

(d) It permits an improved level of sulphur removal as seen in the observed hydrodesulphurisation (HDS) of the total liquid product and the substantially improved, lower level of sulphur in the unconverted 1000°F (538°C) stream at all (i.e. 46.9-66.2) wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion levels.

Practice of the process of this invention will be apparent to those skilled in the art from the following wherein all parts are parts by weight unless otherwise stated.

DESCRIPTION OF SPECIFIC EMBODIMENTS

Best Known Mode Reactor Data

Equal amounts of Example I catalyst are placed within the reaction vessels (the first-stage and second-stage Robinson Reactors). The hydrocarbon charge (i.e. the undiluted Arabian Medium/Heavy vacuum resid, described in Table I) is admitted in liquid phase to the first-stage Robinson reactor at 760°F (404°C) and 2250 psig (15.5 MPa). Hydrogen gas is admitted to the first-stage Robinson reactor in the amount of 7000 SCFB (1260 m^3/m^3). The hydrocarbon charge passes through the first-stage Robinson reactor at a Liquid Hourly Space Velocity (LHSV) of 0.56 volumes of oil per hour per volume of liquid hold up. This is equivalent to a Catalyst Space Velocity (CSV) of 0.130 barrels of hydrocarbon charge per pound of catalyst per day. The hydrocarbon feed is uniformly contacted with hydrogen and catalyst at isothermal conditions in the first-stage Robinson reactor. The liquid and gaseous effluent from the first-stage Robinson reactor is then routed to the second-stage Robinson reactor which is operated at essentially the same temperature and pressure as the first-stage Robinson reactor. The difference in average temperature between the first- and second-stage reactors is nominally 0°F (0°C). No additional hydrogen is injected to the second-stage Robinson reactor. The liquid effluent passes through the second-stage Robinson reactor at a Liquid Hourly Space Velocity (LHSV) of 0.56 volumes of liquid effluent per hour per volume of liquid hold up. This is equivalent to a Catalyst Space Velocity (CSV) of 0.130 barrels of liquid effluent per pound of catalyst per day. The liquid effluent from the first-stage Robinson reactor is uniformly contacted with the hydrogen-containing gaseous effluent and the second loading of catalyst at isothermal conditions in the second-stage Robinson reactor. No attempt is made to maintain constant catalytic activity by periodic or continuous withdrawal of portions of used catalyst and replacement of the withdrawn material with fresh catalyst in the two-stage Robinson reactor system. The catalyst begins as fresh catalyst and accumulates catalyst age generally expressed in barrels per pound. The average temperature is defined as the average of the temperatures of the first- and second-stage reactors. Overall, the hydrocarbon charge passes through the entire process system (i.e. the first- and second-stage Robinson reactors) at an overall LHSV of 0.28 volumes of oil per hour per volume of liquid hold up. This is equivalent to an overall CSV of 0.065 barrels of hydrocarbon charge per pound of catalyst per day. As will be discussed below, the temperatures of the first- and second-stage reactors may be raised to higher levels with the catalyst of the present invention.

Product is collected and analysed over a range of catalyst age from 0.60 to 1.18 barrels per pound (corresponding approximately to the 9th to 18th days of the evaluation) to yield the averaged data shown in Table IV below:

From the Table, it is apparent that the process of the present invention permits increasing the conversion of materials boiling above 1000°F (538°C) by 46.9 wt %; and sulphur, carbon residue, and metals are removed.

TABLE IV	
Property	Value
% Sulphur Removal	78.0
% Carbon Residue Reduction	58.0
% Ni Removal	71.0
% V Removal	95.0
% Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt % Basis)	46.9
% Kinetically Adjusted Hydroconversion (to 0.0650 bbl/lb/day and 760°F (404°C) of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials) (wt % Basis)	46.8

Upon distillation to recover (1) a first cut from the initial boiling point to 650°F (343°C), (2) a second cut from 650-1000°F (343-538°C), and (3) a third cut above 1000°F (538°C), the following is noted:

TABLE V	
Cut #	Product
<u>Cut 1 : up to 650°F (343°C)</u>	
Specific Gravity, g/cc	0.84
Sulphur, wt %	0.1
<u>Cut 2 : 650-1000°F (343-538°C)</u>	
Specific Gravity, g/cc	0.93
Sulphur, wt %	0.6
<u>Cut 3 : 1000°F+ (538°C+)</u>	
Specific Gravity, g/cc	1.02
Sulphur, wt %	1.8

From the above Table V, it is apparent that the Sulphur content is decreased in all of the product fractions (from 5.1 wt % in the feed).

Upon distillation to recover (4), a cut which boils at temperatures of about 650°F (343°C) and higher, the following is noted:

TABLE VI	
Cut #	Product
Cut 4 : 650°F+ (343°C+)	
Existent IP Sediment, wt %	0.01
Accelerated IP Sediment, wt %	0.01

From the above Table, it is apparent that the process of the present invention can operate at about 46.9 % conversion of feed components with boiling points greater than 1000°F (538°C) to products with boiling points less than 1000°F (538°C) without making any sediment (as measured by both the Existent and Accelerated IP sediment tests).

EXAMPLE A

COMPARISON TO FIRST GENERATION CATALYST

Comparative data between the Example I catalyst of the present invention and a first generation nickel/molybdenum H-OIL catalyst (Criterion HDS-1443B), collected under virtually identical reactor conditions, are given in Table VII. The process of the present invention is superior in that it gives:

(a) No sediment versus an undesirable level with a commercially available first generation nickel/molybdenum H-OIL catalyst (as measured by both the Existent and Accelerated IP sediment tests);

(b) Improved levels of carbon residue reduction and nickel and vanadium removal; and,

(c) An improved level of sulphur removal as seen in the observed hydrodesulphurisation (HDS) of the total liquid product and the substantially improved, lower level of sulphur in the unconverted 1000°F (538°C) stream.

It is noted that a lower level of 1000°F+ to 1000°F- (538°C+ to 538°C-) wt % conversion is obtained with the catalyst of the present invention even once the data from both catalysts are kinetically adjusted to the target CSV and temperature at catalyst ages of 0.60 through 1.18 barrels per pound.

TABLE VII

EXAMPLE A

Two-Stage Robinson Reactor Catalyst Test Results
Single-Pass, Pure Resid, No Diluent, Once Through Hydrogen

Age = 0.60 to 1.18 Barrels Per Pound

Catalyst	Example I	1st Generation 9HDS-1443B
CSV (Bbl/Lb/Day)	0.066	0.064
Temperature/°F(°C) (Average both stages)	760.5 (404.7)	760.8 (404.9)
Cut 4: (650°F+ (343°C+))		
Existent IP Sediment (wt %)	0.01	0.16
Accelerated IP Sediment (wt %)	0.01	0.67
Total Liquid Product		
% Sulphur Removal	78	76
% Carbon Residue Reduction	58	53
% Nickel Removal	71	64
% Vanadium Removal	95	90
% Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	46.9	52.9
Kinetically Adjusted (CSV and T)		
% Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	46.8	52.5
Cut 1 : up to 650°F (343°C)		
Specific Gravity (g/cc)	0.84	0.84
Sulphur (wt %)	0.10	0.10
Cut 2 : 650-1000°F (343-538°C)		
Specific Gravity (g/cc)	0.93	0.93
Sulphur (wt %)	0.60	0.70
Cut 3 : 1000°F+ (538°C+)		
Specific Gravity (g/cc)	1.02	1.03
Sulphur (wt %)	1.80	2.20

* Criterion HDS-1443B H-OIL catalyst.

** 1st order CSTR kinetics (assuming equal rate constants for the 1st- and 2nd- stage reactors); Activation Energy = 65 kcal/mole.

EXAMPLE B

DATA AT +10°F (+5.6°C)

In the evaluation of the Example I catalyst of the present invention, reactor temperatures were raised about 10°F (5.6°C) over a period of 2.0 days to a final temperature of approximately 770°F (410°C) (i.e. the first-stage, second-stage, and average temperatures). Product was collected and analysed over a range of catalyst age from 1.57 to 2.16 barrels per pound (corresponding approximately to the 24th to 33rd days of the evaluation). Comparative data between the catalyst of the present invention operating at about +10°F (+5.6°C) compared to the first generation nickel/molybdenum H-OIL catalyst (Criterion HDS-1443B) at the same catalyst ages are given in Table VIII. The process of the present invention is superior in that it gives:

(a) Low Existent IP sediment at 57 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion *versus* an undesirable level with the first generation nickel/molybdenum H-OIL catalyst operating at only 53 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion;

(b) Relatively low Accelerated IP sediment at 57 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion *versus* a very high level with the first generation nickel/molybdenum H-OIL catalyst operating at only 53 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion;

(c) An improved level of 1000°F+ to 1000°F- (538°C+ to 538°C-) wt % conversion by the observed data and once the data from both catalysts are kinetically adjusted to the target CSV;

(d) Improved levels of carbon residue reduction and nickel and vanadium removal; and,

(e) An improved level of sulphur removal as seen in the observed hydrodesulphurisation (HDS) of the total liquid product and the substantially improved, lower level of sulphur in the unconverted 1000°F+ (538°C+) stream.

The catalyst of the present invention, besides giving low sediment results for the 650°F+ (343°C+) boiling cut, also showed improved operability. The evaluation went smoothly at both 760°F (404°C) and 770°F (710°C). On the other hand, the first generation catalyst evaluation showed evidence of plugging due to accumulated sediment during the course of its evaluation. Operations with the first generation catalyst became somewhat erratic at about 1.54 bbl/pound catalyst age and the unit had to be shut down and partially cleaned out before the evaluation of the first generation catalyst could be completed. With so much trouble due to sediment, it was felt that temperatures could not be raised any higher with the first generation catalyst.

TABLE VIII

EXAMPLE B

Two-Stage Robinson Reactor Catalyst Test Results
Single-Pass, Pure Resid, No Diluent, Once Through Hydrogen

Age = 1.57 to 2.16 Barrels Per Pound
(Temperature increased by 10°F (5.6°C) for Example I)

Catalyst	Example I	1st Generation 9HDS-1443B
CSV (Bbl/Lb/Day)	0.066	0.065
Temperature/°F(°C) (Average both stages)	770.0 (410)	760.8 (404.9)
Cut 4: (650°F+ (343°C+))		
Existent IP Sediment (wt %)	0.02	0.15
Accelerated IP Sediment (wt %)	0.17	0.59
Total Liquid Product		
% Sulphur Removal	76	71
% Carbon Residue Reduction	58	53
% Nickel Removal	73	63
% Vanadium Removal	95	88
% Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	56.5	52.8
Kinetically Adjusted (CSV only) % Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	57.0	51.9
Cut 1 : up to 650°F (343°C)		
Specific Gravity (g/cc)	0.84	0.84
Sulphur (wt %)	0.10	0.20
Cut 2 : 650-1000°F (343-538°C)		
Specific Gravity (g/cc)	0.93	0.93
Sulphur (wt %)	0.90	0.90
Cut 3 : 1000°F+ (538°C+)		
Specific Gravity (g/cc)	1.04	1.04
Sulphur (wt %)	2.10	2.50

* Criterion HDS-1443B H-OIL catalyst.

** 1st order CSTR kinetics (assuming equal rate constants for the 1st- and 2nd- stage reactors); Activation Energy = 65 kcal/mole.

EXAMPLE C

DATA AT +20°F (+11.1°C)

In the evaluation of the Example I catalyst of the present invention, reactor temperatures were raised an additional 10°F (5.6°C) over a period of three days to a final temperature of approximately 780°F (416°C) (i.e. the first-stage, second-stage, and average temperatures). Product was collected and analysed over a range of catalyst age from 2.51 to 2.73 barrels per pound (corresponding approximately to the 39th to 42nd days of the evaluation). Comparative data between the catalyst of the present invention operating at about +20°F (+11.1°C) compared to the first generation nickel/molybdenum H-OIL catalyst (Criterion HDS-1443B) at the same catalyst ages are given in Table IX. The process of the present invention is superior in that it gives:

(a) About the same Existent IP sediment at 66 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion *versus* that experienced with the first generation nickel/molybdenum H-OIL catalyst operating at only 53 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion;

(b) Relatively low Accelerated IP sediment at 66 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion *versus* a very high level with the first generation nickel/molybdenum H-OIL catalyst operating at only 53 wt % 1000°F+ to 1000°F- (538°C+ to 538°C-) conversion;

(c) A greatly improved level of 1000°F+ to 1000°F- (538°C+ to 538°C-) wt % conversion by the observed data and once the data from both catalysts are kinetically adjusted to the target CSV;

(d) Improved levels of carbon residue reduction and nickel and vanadium removal; and,

(e) An improved level of sulphur removal as seen in the observed hydrodesulphurisation (HDS) of the total liquid product and the substantially improved, lower level of sulphur in the unconverted 1000°F+ (538°C+) stream.

It was noted that the specific gravity of the unconverted 1000°F+ (538°C+) stream was slightly higher with the catalyst of the present invention operating at about +20°F (+11.1°C) compared to the level obtained with the first generation H-OIL catalyst when both were at catalyst ages of 2.51 to 2.73 barrels per pound.

The catalyst of the present invention continued to show good operability. The evaluation went smoothly at 760°F (404°C), 770°F (410°C), and 780°F (416°C). The end of the run represented one of the highest conversion levels that had ever been successfully run in the two-stage Robinson reactor. The +20°F (+11.1°C) portion of the run lasted about ten days and lined-out data were collected on the last seven days. It cannot be said that the catalyst of the present invention could run indefinitely at +20°F (+11.1°C) (corresponding to +13.5 wt % 1000°F+ to 1000°F- (538+°C to 538°C-) bp conversion) compared to the HDS-1443B catalyst. The run terminated due to problems in the recovery section.

As discussed above, the first generation catalyst evaluation showed evidence of plugging due to accumulated sediment early in the course of the run. Operations became somewhat erratic at about 1.54 bbl/pound catalyst age and the unit had to be shut down and partially cleaned out before the evaluation of the first generation catalyst could be completed (this represented the same age at which the temperature on the catalyst of the present invention could first be raised with no trouble). Additional plugging incidents (presumably caused by high sedimentation) occurred at roughly 3 and 3.5 bbl/lb catalyst age thereby terminating the evaluation of the first generation HDS-1443B catalyst. Note again, that the entire evaluation of the first generation HDS-1443B catalyst was performed at a relatively low temperature (760°F (404°C)) and a relatively low level of 1000°F+ to 1000°F- (538°C+ to 538°C-) bp conversion (52 to 53 w%). With so much operability trouble, it was felt that temperatures could not be raised any higher with the first generation HDS-1443B catalyst.

TABLE IX

EXAMPLE C

Two-Stage Robinson Reactor Catalyst Test Results
Single-Pass, Pure Resid, No Diluent, Once Through Hydrogen

Age = 2.51 to 2.73 Barrels Per Pound
(Temperature increased by 20°F (11.1°C) for Example I)

Catalyst	Example I	1st Generation 9HDS-1443B
CSV (Bbl/Lb/Day)	0.066	0.064
Temperature/°F(°C) (Average both stages)	779.5 (415.3)	759.8 (404.3)
Cut 4: (650°F+ (343°C+))		
Existent IP Sediment (wt %)	0.17	0.13
Accelerated IP Sediment (wt %)	0.32	0.73
Total Liquid Product		
% Sulphur Removal	77	67
% Carbon Residue Reduction	62	50
% Nickel Removal	76	61
% Vanadium Removal	96	87
% Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	65.8	52.0
Kinetically Adjusted (CSV only) % Hydroconversion of 1000°F+ to 1000°F- (538°C+ to 538°C-) Materials (wt %)	66.2	52.7
Cut 1 : up to 650°F (343°C)		
Specific Gravity (g/cc)	0.84	0.85
Sulphur (wt %)	0.20	0.20
Cut 2 : 650-1000°F (343-538°C)		
Specific Gravity (g/cc)	0.93	0.93
Sulphur (wt %)	1.00	1.00
Cut 3 : 1000°F+ (538°C+)		
Specific Gravity (g/cc)	1.06	1.04
Sulphur (wt %)	2.30	2.70

* Criterion HDS-1443B H-OIL catalyst.

** 1st order CSTR kinetics (assuming equal rate constants for the 1st- and 2nd- stage reactors); Activation Energy = 65 kcal/mole.

CLAIMS:

1. A process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals, and carbon residue which comprises:

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å,

thereby forming hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue, and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C), and of sulphur, metals and carbon residue, and

recovering said hydroprocessed product containing decreased content of sediment in the portion of the hydroprocessed product boiling above 650°F (343°C).

2. A process as claimed in claim 1, wherein said Group VIB metal oxide is molybdenum oxide in an amount of 12.5-15.5 wt %.

3. A process as claimed in claim 1 or 2, wherein said Group VIII metal oxide is nickel oxide in an amount of 3.0-3.9 wt %.

4. A process as claimed in any one of claims 1 to 3, wherein the content of SiO_2 is ≤ 0.41 wt %.

5. A process as claimed in any one of claims 1 to 4, wherein the phosphorus oxide is P_2O_5 present in the amount <0.1 wt % with no phosphorus containing components intentionally added during the catalyst preparation.

6. A process as claimed in any one of claims 1 to 5, wherein said Total Surface Area is 200-225 m^2/g.

7. A process as claimed in any one of claims 1 to 6, wherein said Total Pore Volume is 0.82-0.90 cc/g.

8. In a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed

product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue,

an improvement which allows operations at a temperature 10°F (5.6°C) higher than normal hydrotreating conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 5 wt %, and reduces Existent IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.02 wt % which comprises

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

9. In a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue,

an improvement which allows operations at a temperature 20°F (11.1°C) higher than normal hydrotreating process conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 13.5 wt %, and reduces Accelerated IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.32 wt % which comprises

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about

0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

10. A hydrotreating catalyst characterised by stability at up to 10°F (5.6°C) over normal hydrotreating process conditions consisting essentially of:

a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon containing components are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

11. A hydrotreating catalyst as claimed in claim 10, wherein said Group VIB metal oxide is molybdenum oxide in an amount of 12.5-15.5 wt %.

12. A hydrotreating catalyst as claimed in claim 10 or 11, wherein said Group VIII metal oxide is nickel oxide in an amount of 3.0-3.9 wt %.

13. A hydrotreating catalyst as claimed in any one of claims 10 to 12, wherein the content of SiO_2 is ≤0.41 wt %.

14. A process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals, and carbon residue which comprises:

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii)

27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å,

thereby forming hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue,

and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C), and of sulphur, metals and carbon residue, and

recovering said hydroprocessed product containing decreased content of sediment in the portion of the hydroprocessed product boiling above 650°F (343°C).

15. A process as claimed in claim 14, wherein said Group VIB metal oxide is molybdenum oxide in an amount of 12.5-15.5 wt %.

16. A process as claimed in claim 14 or 15, wherein said Group VIII metal oxide is nickel oxide in an amount of 3.0-3.9 wt %.

17. A process as claimed in any one of claims 14 to 16, wherein the content of SiO_2 is ≤0.41 wt %.

18. A process as claimed in any one of claims 14 to 17, wherein the phosphorus oxide is P_2O_5 present in the amount <0.1 wt % with no phosphorus containing components intentionally added during the catalyst preparation.

19. A process as claimed in any one of claims 14 to 18, wherein said Total Surface Area is 200-225 m^2/g.

20. A process as claimed in any one of claims 14 to 19, wherein said Total Pore Volume is 0.82-0.90 cc/g.

21. In a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue,

an improvement which allows operations at temperature 10°F (5.6°C) higher than normal hydrotreating conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 5 wt %, and reduces Existent IP Sediment Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.02 wt % which comprises

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group

VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

22. In a process for hydrotreating a charge hydrocarbon feed containing components boiling above 1000°F (538°C) and sulphur, metals and carbon residue to form hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and sulphur, metals and carbon residue and recovering said hydroprocessed product containing decreased content of components boiling above 1000°F (538°C) and of sulphur, metals and carbon residue,

an improvement which allows operations at a temperature 20°F (11.1°C) higher than normal hydrotreating process conditions, increases conversion of components boiling above 1000°F (538°C) to product boiling below 1000°F (538°C) by 13.5 wt %, and reduces Accelerated IP Sediment

Test values in the portion of the hydroprocessed product boiling above 650°F (343°C) to 0.32 wt % which comprises

contacting said hydrocarbon feed with hydrogen at isothermal hydroprocessing conditions in the presence of, as catalyst, a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

23. A hydrotreating catalyst characterised by stability at up to 10°F (5.6°C) over normal hydrotreating process conditions consisting essentially of:

a porous alumina support containing ≤0.5 wt % of silica, wherein no silicon oxide are intentionally added to the alumina, alumina support, impregnating solution or impregnating solutions, and bearing 2.2-6 wt % of a Group VIII metal oxide, 7-24 wt % of a Group VIB metal oxide and 0.0-2.0 wt % of a phosphorus oxide,

said catalyst having a Total Surface Area of 195-230 m^2/g, a Total Pore Volume (TPV) of 0.82-0.98 cc/g, and a Pore Diameter Distribution wherein (i) about 0.12-0.20 cc/g of pores in the ≥1200Å range, (ii) about 17-27% of TPV in pores in the ≥600Å range, (iii) 27.0-34.0% of the TPV in pores having a diameter of ≥250Å, (iv) 66.0-73.0% of the TPV in micropores of diameter less than 250Å, (v) 55-64.5% of the micropore volume is present as micropores of diameter within ±25Å of a pore mode by volume of 110-130Å, (vi) 46.5-56.5% of the micropore volume in pores with diameters ≤200Å is present as micropores of diameter within ±20Å of a pore mode by volume (i.e. dV/dD MAX) of 110-130Å, (vii) about 20-35% of the TPV in pores having a diameter of 55-115Å, and (viii) less than 0.05 cc/g micropore volume in micropores with diameters less than 80Å.

24. A hydrotreating catalyst as claimed in claim 23, wherein said Group VIB metal oxide is molybdenum oxide in an amount of 12.5-15.5 wt %.

25. A hydrotreating catalyst as claimed in claim 23 or 24, wherein said Group VIII metal oxide is nickel oxide in an amount of 3.0-3.9 wt %.

26. A hydrotreating catalyst as claimed in any one of claims 23 to 25, wherein the content of SiO_2 is ≤0.41 wt %.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS