METHOD OF UPGRA OING HEAVY HYDROCARBON STREAMS TO JET PRODUCTS

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ABSTRACT
A process of upgrading a heavy hydrocarbon feedstock comprising contacting a heavy hydrocarbon feedstock with a catalyst in the presence of hydrogen in a reactor system, containing the catalyst as the only catalyst, wherein the catalyst is prepared by sulfiding a catalyst precursor obtained by mixing at reaction conditions, to form a precipitate or cocrystallization at least a Promoter metal compound in solution; at least a Group VIB metal compound in solution; and, at least an organic oxygen containing ligand in solution, and thereby producing a fuel product.
METHOD OF UPGRADING HEAVY HYDROCARBON STREAMS TO JET PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit under 35 USC 120 of U.S. application Ser. No. 11/932,751 with a filing date of Oct. 31, 2007. This application claims priority to and benefits from the foregoing, the disclosure of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a hydroconversion process wherein a hydrocarbon feed comprising aromatic compounds is contacted with hydrogen in the presence of a catalyst composition which catalyst composition comprises at least one Group VIII metal and at least one Group VIIB metal. Specifically, the present invention is directed to a process for converting heavy hydrocarbonaceous feeds to jet products using a single catalyst system.

BACKGROUND OF THE INVENTION

[0003] Heavy hydrocarbon streams, such as FCC Light Cycle Oil (“LCO”), Medium Cycle Oil (“MCO”), and Heavy Cycle Oil (“HCO”), have a relatively low value. Typically, such hydrocarbon streams are upgraded through hydroconversion including hydrotreating and/or hydrocracking.

[0004] Hydrotreating catalysts are well known in the art. Conventional hydrotreating catalysts comprise at least one Group VIII metal component and/or at least one Group VIIB metal component either as a bulk unsupported catalyst or, more commonly, as a catalyst supported on a refractory oxide support. The Group VIII metal component is typically based on a non-noble metal, such as nickel (Ni) and/or cobalt (Co). Group VIIB metal components include those based on molybdenum (Mo) and tungsten (W). The most commonly applied refractory oxide support materials are inorganic oxides such as silica, alumina and silica-alumina. Examples of conventional hydrotreating catalyst are NiMo/alumina, CoMo/alumina and Ni/Al2O3. In some cases, platinum and/or palladium containing catalysts may be employed.

[0005] Hydrotreating catalysts are normally used in processes wherein a hydrocarbon feed is contacted with hydrogen to reduce its content of aromatic compounds, sulfur compounds, and/or nitrogen compounds. Typically, hydroconversion processes wherein reduction of the aromatics content is the main purpose are referred to as hydrogenation or hydrosulfurization processes, while processes predominantly focusing on reducing sulfur and/or nitrogen content are referred to as hydrosulfurization and hydronitrogenation, respectively. Traditionally, the term “hydrotreating” is used to describe hydrosulfurization and hydronitrogenation while the term “hydrofinishing” is used to describe the hydrogenation of aromatics. The present invention follows this tradition of terminologies. Typically, hydrocracking converts feed to lighter products such as naphtha or gas via cracking and dealkylation as well as to low volumetric energy density components via unselctive ring opening. One disadvantage of hydrotreating is that it leads to a higher H2 consumption due to cracking, dealkylation and unselective ring opening. The present invention avoids these disadvantages while producing jet products which not only meet the requirements of the jet specifications but also possess high volumetric energy density.

[0006] The present invention is directed to a method of upgrading heavy hydrocarbon feedstocks with an unsupported catalyst in a fixed bed reactor system. Specifically, the method of the present invention is directed to a method of upgrading heavy hydrocarbon feedstocks to jet products with high volumetric energy density.

DESCRIPTION OF THE RELATED ART

[0007] Marmo, U.S. Pat. No. 4,162,961 discloses a cycle oil that is hydrogenated under conditions such that the product of the hydrogenation process can be fractionated.

[0008] Myers et al., U.S. Pat. No. 4,619,759 discloses the catalytic hydrorefining of a mixture comprised of resid and a light cycle oil that is carried out in a multiple catalyst bed in which the portion of the catalyst bed with which the feedstock is first contacted contains a catalyst which comprises alumina, cobalt, and molybdenum and the second portion of the catalyst bed through which the feedstock is passed after passing through the first portion contains a catalyst comprising alumina to which molybdenum and nickel have been added.

[0009] Kirker et al., U.S. Pat. No. 5,219,814 discloses a moderate pressure hydrocracking process in which highly aromatic, substantially dealkylated feedstock is processed to high octane gasoline and low sulfur distillate by hydrocracking over a catalyst, preferably comprising ultrastable Y and Group VIII metal and a Group VI metal, in which the amount of the Group VIII metal content is incorporated at specified proportion to the framework aluminium content of the ultrastable Y component.

[0010] Kalnes, U.S. Pat. No. 7,005,057 discloses a catalytic hydrocracking process for the production of ultra low sulfur diesel wherein a hydrocarbonaceous feedstock is hydrocracked at elevated temperature and pressure to obtain conversion to diesel boiling range hydrocarbons.

[0011] Barre et al., U.S. Pat. No. 6,444,865 discloses a catalyst, which comprises from 0.1 to 15 wt % of noble metal selected from one or more of platinum, palladium, and iridium, from 2 to 40 wt % of manganese and/or rhenium supported on an acidic carrier, used in a process wherein a hydrocarbon feedstock comprising aromatic compounds is contacted with the catalyst at elevated temperature in the presence of hydrogen.

[0012] Barre et al., U.S. Pat. No. 5,868,921 discloses a hydrocracking distillate fraction that is hydrotreated in a single stage by passing the distillate fraction downwardly over a stacked bed of two hydrotreating catalysts.

[0013] Fujikawa et al., U.S. Pat. No. 6,821,412 discloses a catalyst for hydrotreatment of gas oil containing defined amounts of platinum, palladium and in support of an inorganic oxide containing a crystalline alumina having a crystallite diameter of 20 to 40 Å. Also disclosed is a method for hydrotreating gas oil containing an aromatic compound in the presence of the above catalyst at defined conditions.

[0014] Kirker et al., U.S. Pat. No. 4,968,402 discloses a one stage process for producing high octane gasoline from a highly aromatic hydrocarbon feedstock.

[0015] Brown et al., U.S. Pat. No. 5,520,799 discloses a process for upgrading distillate feeds. Hydrotreating catalyst is placed in a reaction zone, which is usually a fixed bed reactor under reactive conditions and low aromatic diesel and jet fuel are produced.
[0016] Soled et al., U.S. Pat. No. 6,162,350 discloses a slurry hydrosprocessing process for upgrading hydrocarbon feedstock with a bulk mixed metal catalyst preferentially comprised of Ni—Mo—W.

[0017] Haluska et al., U.S. Pat. No. 6,755,963 discloses a slurry hydrosprocessing process for upgrading hydrocarbon resid feedstock with a bulk mixed metal catalyst comprised of one or more Group VIII metals and one or more Group VIB metals.

[0018] Riley et al., U.S. Pat. No. 6,582,590 discloses a multistage slurry hydrosprocessing process for upgrading hydrocarbon feedstock with a bulk mixed metal catalyst comprised of one or more Group VIII metals and at least two Group VIB metals.

[0019] Riley et al., U.S. Pat. No. 7,229,548 discloses a slurry hydrosprocessing process for upgrading a naphtha feedstock to a naphtha product with less than about 10 ppm of nitrogen and less than about 15 ppm sulfur using a bulk mixed metal catalyst comprised of one or more Group VIII metals and at least two Group VIB metals.

[0020] Riley et al., U.S. Pat. No. 6,929,738 discloses a two stage slurry hydrosprocessing process for hydrodesulfurization of high sulfur (greater than about 3,000 ppm sulfur) distillates with a bulk mixed metal catalyst comprised of one or more Group VIII metals and at least two Group VIB metals.

[0021] Hou et al., U.S. Pat. No. 6,712,955 and Riley et al., U.S. Pat. No. 6,783,665 discloses a slurry hydrosprocessing process for upgrading hydrocarbon feedstock with a bulk mixed metal catalyst comprised of one or more Group VIII metals and at least two Group VIB metals.

[0022] Demmin et al., U.S. Pat. No. 6,620,313 discloses a Ni—Mo—W catalyst used in a multi step process to hydros-process a raffinate feedstock.

SUMMARY OF THE INVENTION

In one embodiment of the invention, there is provided a process for upgrading hydrocarbon feedstocks, which process comprises contacting a heavy hydrocarbon feedstock with a catalyst in the presence of hydrogen in a reactor system, containing said catalyst as the only catalyst, wherein the catalyst, is prepared from a catalyst of the general formula:

\[ \text{A}_i(M^{x+y}_i)(OH)_j(L)^p(M^{2x+y}_2)_{(2)} \]

wherein

[0024] A is at least one of an alkali metal cation, an ammonium, an organic amonium and a phosphonium cation,

[0025] M^{x+y}_i is at least a Group VIII metal,

[0026] X is at least an organic oxygen-containing ligand,

[0027] M^{2x+y}_2 is at least a Group VIB metal,

[0028] and wherein M^{x+y}_i:M^{2x+y}_2 has an atomic ratio of 100:1 to 1:100; and thereby producing a fuel product.

[0029] In one embodiment of the present invention, there is provided a process of upgrading a heavy hydrocarbon feedstock comprising contacting a heavy hydrocarbon feedstock with a catalyst in the presence of hydrogen in a reactor system, at hydrosprocessing conditions, containing said catalyst as the only catalyst, wherein the catalyst is prepared by sulfiding a catalyst precursor obtained by mixing at reaction conditions, to form a precipitate or gel, at least a Promoter metal compound in solution; at least a Group VIB metal compound in solution; and, at least an organic oxygen containing ligand in solution, and thereby producing a fuel product.

[0030] The process according to the invention can achieve increased hydrocarbon productivity through an increase in the conversion of lower value hydrocarbon streams to higher quality products in a single reactor system.

[0031] The process of the invention is desirably practiced with a light cycle oil (LCO) feedstock and a catalyst comprising nickel, molybdenum, and tungsten to produce jet products.

DETAILED DESCRIPTION OF THE INVENTION

[0032] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

Definitions

[0033] FCC—The term “FCC” refers to fluid catalytic crack-er, -ing, or -ed.

[0034] As used herein, the terms “feedstock” and “feedstream” are interchangeable.

[0035] As used herein, “hydrosprocessing” is meant any process that is carried out in the presence of hydrogen, including, but not limited to, hydrogenation, hydrofinishing, hydrocracking, hydrodesulfurization, hydrosulfurization, hydrodemetallation, hydrodearomatization, hydrosomerization, hydrosyngas and hydrocracking including selective hydro-ring-opening. Depending on the type of hydrosprocessing and the reaction conditions, the products of hydrosprocessing may show improved viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization, etc.

[0036] Energy density—refers to the heat of combustion of a fuel, which is released during its combustion. The amount of heat released depends on whether the water formed during combustion remains in the vapor phase or is condensed to a liquid. If the water is condensed to the liquid phase, it gives up its heat of vaporization in the process. In this case, the released heat is called gross heat of combustion. The net heat of combustion is lower than the gross heat of combustion because the water remains in the gaseous phase (water vapor). The net heat of combustion is the appropriate value for comparing fuels since engines exhaust water as vapor. The net volumetric energy density describes the net energy density of a fuel on the volumetric basis and is often given in Btu per gallon, for example, 125,000 Btu per gallon for a jet fuel and 130,000 Btu per gallon for a diesel.

[0037] LHSV—refers to liquid hourly space velocity, which is the volumetric rate of the liquid feed (i.e., the volume of the liquid feed at 60°F per hour) divided by the volume of the catalyst, and is given in hr⁻¹.

[0038] The Periodic Table referred to herein is the Table approved by IUPAC and the U.S. National Bureau of Standards, an example is the Periodic Table of the Elements by Los Alamos National Laboratory’s Chemistry Division of October 2001.

[0039] The term “Group VIB metal” refers to chromium, molybdenum, tungsten, and combinations thereof in their elemental, compound, or ionic form.
The term “Group IIB metal” refers to zinc, cadmium, mercury and combinations thereof in their elemental, compound, or ionic form.

The term “Group IIA metal” refers to beryllium, magnesium, calcium, strontium, barium, radium, and combinations thereof in their elemental, compound, or ionic form.

The term “Group IVA metal” refers to germanium, tin or lead, and combinations thereof in their elemental, compound, or ionic form.

The term “Group VIII metal” refers to iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and combinations thereof in their elemental, compound, or ionic form.

As used herein, the term “phosphonium” refers to a cation with the chemical formula PH₄⁺ or to organic phosphorus-containing cations.

The term “oxonate” refers to monomeric oxonates and polyoxometallates. As used herein, the term “mixture” refers to a physical combination of two or more substances. The “mixture” can be homogeneous or heterogeneous and in any physical state or combination of physical states.

The term “reagent” refers to a raw material that can be used in the manufacture of the catalyst precursor of the invention. When used in conjunction with a metal, the term “metal” does not mean that the reagent is in the metallic form, but is present as a metal compound.

As used herein the term “carboxylate” refers to any compound containing a carboxyate or carboxylic acid group in the deprotonated or protonated state.

As used herein, the term “ligand” may be used interchangeably with “chelating agent” (or chelator, or chelant), referring to an additive that combines with metal ions, e.g., Group VIB and/or Promoter metals, forming a larger complex, e.g., a catalyst precursor.

As used herein, the term “organic” means containing carbon, and wherein the carbon can be from biological or non-biological sources.

As used herein, the term “organic oxygen-containing ligand” refers to any compound comprising at least one carbon atom, at least one oxygen atom, and at least one hydrogen atom wherein said oxygen atom has one or more electron pairs available for co-ordination to the Promoter metal(s) or Group VIB metal ion. In one embodiment, the oxygen atom is negatively charged at the pH of the reaction. Examples of organic oxygen-containing ligands include, but are not limited to, carboxylic acids, carboxylates, aldehydes, ketones, the enolate forms of aldehydes, the enolate forms of ketones, hemiacetals, and the o xo anions of hemiacetals.

The term “cogel” refers to a hydroxide co-precipitate (or precipitate) of at least two metals containing a water rich phase. “Cocelation” refers to the process of forming a cogel or a precipitate.

A. Overview

In one embodiment, the present invention is directed to a process of upgrading heavy hydrocarbons comprising:

(a) Preparing a catalyst by sulfidation of a catalyst precursor in which the catalyst precursor comprises at least one Promoter metal hydroxide, at least one Group VIB metal oxonate, and at least one oxygen containing co-ordinating ligand; and

(b) Reacting a heavy hydrocarbon feedstock with the catalyst in the presence of hydrogen in a fixed bed reactor;

B. Feed

Heavy hydrocarbon feedstock may be upgraded to a product having a boiling point range within jet boiling point ranges. The hydrocarbon feedstock comprises FCC effluent, including FCC light, medium and heavy cycle oil; fractions of jet and diesel fuels; coker product; coal liquifed oil; the product from the heavy oil thermal cracking process; the product from heavy oil hydrotreating and/or hydrocracking; straight run cut from a crude unit; or mixtures thereof, and having a major portion of the feedstock having a boiling range of from about 250°F to about 1200°F, and preferably from
about 300°F to about 1000°F. The term “major portion” as used in this specification and the appended claims, shall mean at least 50 wt%.

0062] Typically, the feedstock may comprise at least 20 wt% ring-containing hydrocarbon compounds comprising aromatic moieties, naphthenic moieties or both, up to 3 wt% sulfur and up to 1 wt% nitrogen. Preferably, the feedstock may comprise at least 40 wt% ring-containing hydrocarbon compounds. More preferred, the feedstock may comprise at least 60 wt% ring-containing hydrocarbon compounds.

C. Catalyst

0063] In one embodiment of the present invention, the catalyst employed is prepared from a catalyst precursor which may be sulfided thereby producing an active catalyst which is used to produce the jet fuel product of the present invention.

0064] Catalyst Precursor Formula: A catalyst precursor, the charge-neutral catalyst precursor composition is of the general formula AvI(MP)(OH)(L)nyZx(MVIBo4), wherein:

0065] A is one or more monovalent cationic species. In one embodiment, A is at least one of an alkali metal cation, an ammonium, an organic ammonium and a phosphonium cation; MP is at least a Promoter metal with an oxidation state of +2 or +4 depending on the Promoter metal(s) being employed. MP is selected from Group VIII, Group IIB, Group IIA, Group IVA and combinations thereof. In one embodiment wherein MP is at least a Group VIII metal, MP has an oxidation state of +2.

0066] L is one or more oxygen-containing ligands, and L has a neutral or negative charge n<0.

0067] MVIBo is at least a Group VIB metal having an oxidation state of +6;

0068] MP:MVIBo has an atomic ratio between 100:1 and 1:100;

v = 2+2x+y+z = 0; and

0 ≤ x ≤ P; 0 ≤ y ≤ 2; 0 ≤ Z.

0069] In one embodiment, L is selected from carboxylates, carboxylic acids, aldehydes, ketones, the enolate forms of aldehydes, the enolate forms of ketones, and hemiacetals, and combinations thereof.

0070] In one embodiment, A is selected from monovalent cations such as NH4+, other quaternary ammonium ions, organic phosphonium cations, alkali metal cations, and combinations thereof.

0071] In one embodiment where both molybdenum and tungsten are used as the Group VIB metals, the molybdenum to tungsten atomic ratio (Mo:W) is in the range of about 10:1 to 1:10. In another embodiment, the ratio of Mo:W is between about 1:1 and 1:5. In an embodiment where molybdenum and tungsten are used as the Group VIB metals, the charge-neutral catalyst precursor is of the formula AvI(MP)(OH)(L)nyZx(MoWt04). In yet another embodiment, where molybdenum and tungsten are used as the Group VIB metals, chromium can be substituted for some or all of the tungsten with the ratio of (Cr+W):Mo in the range of about 10:1 to 1:10. In another embodiment, the ratio of (Cr+W):Mo is between 1:1 and 1:5. In an embodiment where molybdenum, tungsten, and chromium are the Group VIB metals, the charge-neutral catalyst precursor is of the formula AvI(MP)(OH)(L)nyZx(MoWt04).

0072] In one embodiment, the Promoter metal MP is at least a Group VIII metal with MP having an oxidation state of +2 and the catalyst precursor of the formula AvI(MP)(OH)(L)nyZx(MVIBo4) to have (v-2+2x+y+z)*=0.

0073] In one embodiment, the Promoter metal MP is a mixture of two Group VIII metals such as Ni and Co. In yet another embodiment, MP is a combination of three metals such as Ni, Co and Fe.

0074] In one embodiment wherein MP is a mixture of two Group IIB metals such as Zn and Cd, the charge-neutral catalyst precursor is of the formula AvI(ZnCd)(OH)(L)nyZx(MVIBo4). In yet another embodiment, MP is a combination of three metals such as Zn, Cd, and Hg, the charge-neutral catalyst precursor is of the formula AvI(ZnCdHg)(OH)(L)nyZx(MVIBo4).

0075] In one embodiment wherein MP is a mixture of two Group IIA metals such as Mg and Ca, the charge-neutral catalyst precursor is of the formula AvI(MgCa)(OH)(L)nyZx(MVIBo4). In another embodiment wherein MP is a combination of three Group IIA metals such as Mg, Ca and Ba, the charge-neutral catalyst precursor is of the formula AvI(MgCaBa)(OH)(L)nyZx(MVIBo4).

0076] Promoter Metal Component MP: In one embodiment, the Promoter metal (MP) compound is in a solution state, with the whole amount of the Promoter metal compound dissolved in a liquid to form a homogeneous solution. In another embodiment, the Promoter metal is partly present as a solid and partly dissolved in the liquid. In a third embodiment, it is completely in the solid state.

0077] The Promoter metal compound MP can be a salt or mixtures of metal salts selected from nitrates, hydrated nitrates, chlorides, hydrated chlorides, sulphates, hydrated sulphates, formates, acetates, hypophosphites, and mixtures thereof.

0078] In one embodiment, the Promoter metal MP is a nickel compound which is at least partly in the solid state, e.g., a water-insoluble nickel compound such as nickel carbonate, nickel hydroxide, nickel phosphate, nickel sulphate, nickel formate, nickel sulphide, nickel molybdate, nickel tungstate, nickel oxide, nickel alloys such as nickel-molybdenum alloys, Raney nickel, or mixtures thereof.

0079] In one embodiment, the Promoter metal MP is selected from the group of IIB and VIA metals such as Zn, Cd, Hg, and the combinations thereof, in their elemental, compound, or ionic form. In yet another embodiment, the Promoter metal MP further comprises at least one of Ni, Co, Fe and combinations thereof, in their elemental, compound, or ionic form.

0080] In one embodiment, the Promoter metal compound is a zinc compound which is at least partly in the solid state, e.g., a zinc compound poorly soluble in water such as zinc carbonate, zinc hydroxide, zinc phosphate, zinc sulphate, zinc formate, zinc sulphide, zinc molybdate, zinc tungstate, zinc oxide, zinc alloys such as zinc-molybdenum alloys.

0081] In an embodiment, the Promoter metal is a Group IIA metal compound, selected from the group of magnesium, calcium, strontium and barium compounds which are at least partly in the solid state, e.g., a water-insoluble compound such as a carbonate, hydroxide, phosphate, phosphite, sulphide, molybdate, tungstate, oxide, or mixtures thereof.

0082] In one embodiment, the Promoter metal compound is a tin compound which is at least partly in the solid state, e.g., a tin compound poorly soluble in water such as stannic
acid, tin phosphate, zinc formate, tin acetate, tin molybdate, tin tungstate, tin oxide, tin alloys such as tin-molybdenum alloys.

Group VIB Metal Component:

[0083] The Group VIB metal (MVIB) compound can be added in the solid, partially dissolved, or solution state. In one embodiment, the Group VIB metal compound is selected from molybdenum, chromium, tungsten components, and combinations thereof. Examples of such compounds include, but are not limited to, alkali metal, alkaline earth, or ammonium metalates of molybdenum, tungsten, or chromium, (e.g., ammonium tungstate, meta-, peri-, hexa-, or polytungstate, ammonium chromate, ammonium molybdate, iso- peroxo-, di-, tri-, tetra-, hepta-, octa-, or tetradecamolybdate, alkali metal heptamolybdates, alkali metal orthomolybdates, or alkali metal isomolybdates), ammonium salts of phosphomolybdic acids, ammonium salts of phosphotungstic acids, ammonium salts of phosphochromic acids, molybdic (di- and tri) oxide, tungsten (di- and tri) oxide, chromic or chromic oxide, molybdenum carbide, molybdenum nitride, aluminum molybdate, molybdc acid, chromic acid, tungstic acid, Mo—P heteropolyanion compounds, W—Si heteropolyanion compounds, W—P heteropolyanion compounds, W—Si heteropolyanion compounds, Ni—Mo—W heteropolyanion compounds. Co—Mo—W heteropolyanion compounds, or mixtures thereof, added in the solid, partially dissolved, or solute state.

Chelating Agent (Ligand) L:

[0084] In one embodiment, the catalyst precursor composition comprises at least a non-toxic organic oxygen containing ligand with an LD50 rate (as single oral dose to rats) of greater than 500 mg/kg. In a second embodiment, the organic oxygen containing ligand L has an LD50 rate of >700 mg/kg. In a third embodiment, organic oxygen containing chelating agent has an LD50 rate of >1000 mg/kg. As used herein, the term “non-toxic” means the ligand has an LD50 rate (as single oral dose to rats) of greater than 500 mg/kg. As used herein the term “at least an organic oxygen containing ligand” means the composition may have more than one organic oxygen containing ligand in some embodiments, and some of the organic oxygen containing ligand may have an LD50 rate of <500 mg/kg, but at least one of the organic oxygen containing ligands has an LD50 rate of >500 mg/kg.

[0085] In one embodiment, the oxygen-containing chelating agent L is selected from the group of non-toxic organic acid addition salts such as formic acid, acetic acid, propionic acid, maleic acid, fumaric acid, succinic acid, tartaric acid, citric acid, oxalic acid, glycolic acid, aspartic acid, alkane sulfonic acids such as methane sulfonic acid and ethane sulfonic acid, aryl sulfonic acid, aromatic sulfonic acids such as benzene sulfonic acid and p-toluene sulfonic acid and arylcarboxylic acids such as benzoic acid. In one embodiment, the oxygen-containing chelating agent L is maleic acid (LD of 708 mg/kg).

[0086] In another embodiment, the non-toxic chelating agent L is selected from the group of glycic acid (having an LD50 of 1950 mg/kg), lactic acid (LD50 of 3543 mg/kg), tartaric acid (LD50 of 7500 mg/kg), malic acid (LD50 of 1600 mg/kg), citric acid (LD50 of 5040 mg/kg), gluconic acid (LD50 of 10380 mg/kg), methoxy-acetic acid (LD50 of 3200 mg/kg), ethoxy-acetic acid (LD50 of 1292 mg/kg), malonic acid (LD 50 of 1310 mg/kg), succinic acid (LD 50 of 500 mg/kg), fumaric acid (LD50 of 10700 mg/kg), and glyoxylic (LD 50 of 3000 mg/kg). In yet another embodiment, the non-toxic chelating agent is selected from the group of organic sulfur compounds including but not limited to mercapto-succinic acid (LD 50 of 800 mg/kg) and thio-diglycolic acid (LD 50 of 500 mg/kg).

[0087] In yet another embodiment, the oxygen containing ligand L is a carboxylate containing compound. In one embodiment, the carboxylate compound contains one or more carboxylate functional groups. In yet another embodiment, the carboxylate compound comprises monokarboxylic acids, but not limited to, formate, acetate, propionate, butyrate, pentanoate, and hexanoate and dicarboxylic acids including, but not limited to, oxalate, malonate, succinate, glutarate, adipate, maleate, maleic acid, or combinations thereof. In yet another embodiment, the carboxylate compound comprises maleate.

[0088] The organic oxygen containing ligands can be mixed with the Promoter metal containing solution or mixture, the Group VIB metal containing solution or mixture, or a combination of the Promoter metal and Group VIB metal containing precipitates, solutions, or mixtures. The organic oxygen containing ligands can be in a solution state, with the whole amount of the organic oxygen containing ligands dissolved in a liquid such as water. The organic oxygen containing ligands can be partially dissolved and partially in the solid state during mixing with the Promoter metal(s), Group VIB metal(s), or combinations thereof.

Methods for Making Hydroprocessing Catalyst Precursor:

[0089] The preparation method allows systematic varying of the composition and structure of the catalyst precursor by controlling the relative amounts of the elements, the types of the reagents, and the length and severity of the various reactions and reaction steps.

[0090] The order of addition of the reagents used in forming the catalyst precursor may be in various ways. For example, organic oxygen containing ligand can be combined with a mixture of Promoter metals and Group VIB metals prior to precipitation or cogelation. The organic oxygen containing ligand can be mixed with a solution of a Promoter metal, and then added to a solution of one or more Group VIB metals. The organic oxygen containing ligand can be mixed with a solution of one or more Group VIB metals and added to a solution of one or more Promoter metals.

Forming a Precipitate or Cogel with Group VIB Promoter Metals:

[0091] In one embodiment, the process, the first step is a precipitation or cogelation step, which involves reacting in a mixture the Promoter metal compound in solution and the Group VIB metal compound in solution to obtain a precipitate or cogel. The precipitation or cogelation is carried out at a temperature and pH which the Promoter metal compound and the Group VIB metal compound precipitate or form a cogel. An organic oxygen containing ligand in solution or at least partially in solution is then combined with the precipitate or cogel to form an embodiment of the catalyst precursor.

[0092] In one embodiment, the temperature at which the catalyst precursor is formed is between 50-150° C. If the temperature is below the boiling point of the protic liquid, such as 100° C. in the case of water, the process is generally carried out at atmospheric pressure. Above this temperature, the reaction is generally carried out at increased pressure, such as in an autoclave. In one embodiment, the catalyst precursor is formed at a pressure of between about 0 to 3000
In a second embodiment, the catalyst precursor is formed at a pressure of between about 100 to 1000 psig.

[0093] The pH of the mixture can be changed to increase or decrease the rate of precipitation or coagulation, depending on the desired characteristics of the product. In one embodiment, the mixture is kept at its natural pH during the reaction step(s). In another embodiment, the pH is maintained in the range of between about 0-12. In another embodiment, the pH is maintained in the range of between about 4-10. In a further embodiment, the pH is maintained in the range of between about 7-10. Changing the pH can be done by adding base or acid to the reaction mixture, or adding compounds, which decompose upon temperature increase into hydroxide ions or H+ ions that respectively increase or decrease the pH. Examples include urea, nitrites, ammonium hydroxide, mineral acids, organic acids, mineral bases, and organic bases.

[0094] In one embodiment, the reaction of Promoter metal component(s) is carried out with water-soluble metal salts, e.g., zinc, molybdenum and tungsten metal salts. The solution can further comprise other Promoter metal component(s), e.g., cadmium or mercury compounds such as Cd(NO3)2 or (CH3CO2)2Cd, Group VIII metal components including cobalt or iron compounds such as Co(NO3)2 or (CH3CO2)2Co, as well as other Group VI B metal component(s) such as chromium.

[0095] In one embodiment, the reaction of Promoter metal component(s) is carried out with water-soluble tin, molybdenum and tungsten metal salts. The solution can further comprise other Group IV A metal component(s), e.g., lead compounds such as Pb(NO3)2 or (CH3CO2)2Pb, as well as other Group VI B metal compounds such as chromic compounds.

[0096] The reaction is carried with the appropriate metal salts resulting in precipitate or cogel combinations of nickel/molybdenum/tungsten, cobalt/molybdenum/tungsten, nickel/molybdenum, nickel/tungsten, cobalt/molybdenum, cobalt/tungsten, or nickel/cobalt/molybdenum/tungsten. An organic oxygen containing ligand can be added prior to or after precipitation or cogelation of the Group VIII and/or Group VI B metal components.

[0097] The metal precursors can be added to the reaction mixture in solution, suspension or a combination thereof. If soluble salts are added as such, they will dissolve in the reaction mixture and subsequently be precipitated or cogelled. The solution can be heated optionally under vacuum to effect precipitation and evaporation of the water.

[0098] After precipitation or cogelation, the catalyst precursor can be dried to remove water. Drying can be performed under atmospheric conditions or under an inert atmosphere such as nitrogen, argon, or vacuum. Drying can be effected at a temperature sufficient to remove water but not removal of organic components. Preferably drying is performed at about 120°C until a constant weight of the catalyst precursor is reached.

Characterization of the Catalyst Precursor:

[0099] Characterization of the charge-neutral catalyst precursor can be performed using techniques known in the art, including, but not limited to, powder x-ray diffraction (PXRD), elemental analysis, surface area measurements, average pore size distribution, average pore volume. Porosity and surface area measurements can be performed using BJH analysis under B.E.T. nitrogen adsorption conditions.

Characteristics of the Catalyst Precursor:

[0100] In one embodiment, the catalyst precursor has an average pore volume of 0.05-5 ml/g as determined by nitrogen adsorption. In another embodiment, the average pore volume is 0.1-4 ml/g. In a third embodiment, the average pore volume is 0.1-3 ml/g.

[0101] In one embodiment, the catalyst precursor has a surface area of at least 10 m²/g. In a second embodiment, the catalyst precursor has a surface area of at least 50 m²/g. In a third embodiment, the catalyst precursor has a surface area of at least 150 m²/g.

[0102] In one embodiment, the catalyst precursor has an average pore size, as defined by nitrogen adsorption, of 2-50 nanometers. In a second embodiment, the catalyst precursor has an average pore size, as defined by nitrogen adsorption, of 3-30 nanometers. In a third embodiment, the catalyst precursor has an average pore size, as defined by nitrogen adsorption, of 4-15 nanometers.

Shaping Process:

[0103] In one embodiment, the catalyst precursor composition can generally be directly formed into various shapes depending on the intended commercial use. These shapes can be made by any suitable technique, such as by extrusion, pelletizing, beading, or spray drying. If the amount of liquid of the bulk catalyst precursor composition is so high that it cannot be directly subjected to a shaping step, a solid-liquid separation can be performed before shaping.

Addition of Pore forming Agents

[0104] The catalyst precursor can be mixed with a pore forming agent including, but not limited to steric acid, polyethylene glycol polymers, carbohydrate polymers, methacrylates, and cellulose polymers. For example, the dried catalyst precursor can be mixed with cellulose containing materials such as methylcellulose, hydroxypropylcellulose, or other cellulose ethers in a ratio of between 100:1 and 10:1 (wt. % catalyst precursor to wt. % cellulose) and water added until a mixture of extrudable consistency is obtained. Examples of commercially available cellulose based pore forming agents include but are not limited to: methocel (available from Dow Chemical Company), avicel (available from FMC Biopolymer), and porcel (available from Porocel). The extrudable mixture can be extruded and then optionally dried. In one embodiment, the drying can be performed under an inert atmosphere such as nitrogen, argon, or vacuum. In another embodiment, the drying can be performed at elevated temperatures between 70 and 200°C. In yet another embodiment, the drying is performed at 120°C.

Optional Component—Diluent:

[0105] The term diluent may be used interchangeably with binder.

[0106] In one embodiment, a diluent is optionally included in the process for making the catalyst. Generally, the diluent material to be added has less catalytic activity than the catalyst prepared from the catalyst precursor composition (without the diluent) or no catalytic activity at all. Consequently, by adding a diluent, the activity of the catalyst can be reduced. Therefore, the amount of diluent to be added in the process of the invention generally depends on the desired activity of the
The diluent can be added to the Promoter metal(s), Promoter metal containing mixtures, Group VIb metal(s) or metal containing mixtures either simultaneously or one after the other. Alternatively, the Promoter and Group VIb metal mixtures can be combined together and subsequently a diluent can be added to the combined metal mixtures. It is also possible to combine part of the metal mixtures either simultaneously or one after the other, to subsequently add the diluent and to finally add the rest of the metal mixtures either simultaneously or one after the other. Furthermore, it is also possible to combine the diluent with metal mixtures in the solute state and to subsequently add a metal compound at least partly in the solid state. The organic oxygen containing ligand is present in at least one of the metal containing mixtures.

In one embodiment, the diluent is composited with a Group VIb metal and/or a Promoter metal, prior to being composited with the bulk catalyst precursor composition and/or prior to being added during the preparation thereof. Compositing the diluent with any of these metals in one embodiment is carried out by impregnation of the solid diluent with these materials.

Diluent materials include any materials that are conventionally applied as a diluent or binder in hydroprocessing catalyst precursors. Examples include silica, silica-alumina, such as conventional silica-alumina, silica-coated alumina and alumina-coated silica, alumina such as (pseudo)boehmite, or gibbsite, titania, zirconia, cationic clays or anionic clays such as saponite, bentonite, kaoline, sepiolite or hydrotalcite, or mixtures thereof. In one embodiment, binder materials are selected from silica, colloidal silica doped with aluminum, silica-alumina, alumina, titanic, zirconia, or mixtures thereof.

These diluents can be applied as such or after precipitation. It is also possible to apply precursors of these diluents that, during the process, are converted into any of the above-described diluents. Suitable precursors are, e.g., alkali metal alumimates (to obtain an alumina diluent), water glass (to obtain a silica diluent), a mixture of alkali metal alumimates and water glass (to obtain a silica alumina diluent), a mixture of sources of a di-, tri-, and/or tetravalent metal such as a mixture of water-soluble salts of magnesium, aluminum and/or silicic acid or transform, aluminum sulfate, or mixtures thereof.

Other Optional Components:

If desired, other materials, including other metals can be added in addition to the components described above. These materials include any material that is added during conventional hydroprocessing catalyst precursor preparation. Suitable examples are phosphorus compounds, boric compounds, additional transition metals, rare earth metals, fillers, or mixtures thereof. Suitable phosphorus compounds include ammonium phosphate, phosphoric acid, or organic phosphorus compounds. Phosphorus compounds can be added at any stage of the process steps. Suitable additional transition metals that can be added to the process steps include are, e.g., rhenium, ruthenium, rhodium, iridium, chromium, vanadium, iron, cobalt, platinum, palladium, and copper. In one embodiment, the additional metals are applied in the form of water-insoluble compounds. In another embodiment, the additional metals are added in the form of water-soluble compounds. Apart from adding these metals during the process, it is also possible to composite the final catalyst precursor composition therewith the optional materials. It is, e.g., possible to impregnate the final catalyst precursor composition with an impregnation solution comprising any of these additional materials.

Sulfiding Agent Component:

The charge-neutral catalyst precursor of the general formula $A[M^{2+}]_{2}/(OH)_{2}(L)^{5}$, $L[M^{4+}O_{4}]$ can be sulfided to form an active catalyst. In one embodiment, the sulfiding agent is in the form of a solution, which, under prevailing conditions, is decomposable into hydrogen sulfide. In one embodiment, the sulfiding agent is present in an amount in excess of the stoichiometric amount required to form the sulfided catalyst from the catalyst precursor. In another embodiment, the amount of sulfiding agent represents a sulfur to Group VIb metal mole ratio of at least 3 to 1 to produce a sulfided catalyst from the catalyst precursor.

In one embodiment, the sulfiding agent is selected from the group of ammonium sulfide, ammonium polysulfide ([(NH$_4$)$_2$S]$_n$), thiosulfatate ([(NH$_4$)$_2$S$_2$O$_7$]), thiosulfate (Na$_2$S$_2$O$_7$), thiourea (CS$_2$H$_4$O, carbon disulfide, dimethyl disulfide (DMDS), dimethyl sulfide (DMS), tertiarybutyl polysulfide (PSTB) and tertiarymethyl polysulfide (PSTM), and the like. In another embodiment, the sulfiding agent is selected from alkali- and/or alkaline-earth metal sulfides, alkali- and/or alkaline-earth metal hydrogen sulfides, and mixtures thereof. The use of sulfiding agents containing alkali- and/or alkaline earth metals can require an additional separation process step to remove the alkali- and/or alkaline earth metals from the spent catalyst.

In one embodiment, the sulfiding agent is ammonium sulfide in aqueous solution, which aqueous ammonium sulfide solution can be synthesized from hydrogen sulfide and ammonia refinery off-gases. This synthesized ammonium sulfide is readily soluble in water and can easily be stored in aqueous solution in tanks prior to use. Since the ammonium sulfide solution is denser than resin, it can be separated easily in a settler tank after reaction.

The sulfiding agent can be elemental sulfur mixed with the catalyst precursor during or prior to extrusion. The elemental sulfur can be co-extruded with the catalyst precursor to form active catalyst in situ during hydro treatment.

In one embodiment, hydrocarbon feedstock is used as a sulfur source for performing the sulfidation of the catalyst precursor. Sulfidation of the catalyst precursor by a hydrocarbon feedstock can be performed in one or more hydro treating reactors during hydro treatment.

Sulfiding Step:

Sulfiding of the catalyst precursor to form the catalyst can be performed prior to introduction of the catalyst into the hydro treating reactor, or in situ in the reactor. In one embodiment, the catalyst precursor is converted into an active catalyst upon contact with the sulfiding agent at a temperature ranging from 70°C to 500°C, from 10 minutes to 5 days, and under a H$_2$-containing gas pressure. If the sulfidation temperature is below the boiling point of the sulfiding agent, such as 60-70°C, in the case of ammonium sulfide solution, the process is generally carried out at atmospheric pressure. Above the boiling temperature of the sulfiding agent/optional
components, the reaction is generally carried out at an increased pressure, such as in an autoclave.

[0118] In one embodiment, the sulfidation is carried out at a temperature ranging from room temperature to 400°C and for \( \frac{1}{2} \) hr to 24 hours. In another embodiment, the sulfidation is at 150°C to 300°C. In yet another embodiment, the sulfidation is between 300-400°C under pressure. In a fourth embodiment, the sulfidation is with an aqueous ammonium sulfide solution at a temperature between 0 and 50°C, and in the presence of at least a sulfur additive selected from the group of thiodiazoles, thio acids, thio amides, thiocyanates, thio esters, thio phenols, thiosemicarbazides, thioureas, mercapto alcohols, and mixtures thereof.

[0119] In one embodiment of the present invention, the catalyst of the present invention optionally can include an additional structural support material such as a refractory metal oxide material such as for example silica, alumina, magnesia, titania, etc. and mixtures thereof. The structural support can be in any form including for example monolith, spheres, or hollow cylinders. More specifically the metal oxide material can include “supports” such as alumina, silica, silica-alumina, silicate, alumino-silicate, magnesia, zeolite, active carbon, titanium oxide, thorium oxide, clay and any combination of these supports. In one embodiment of the present invention preferably, the invention’s catalyst can contain between 50% and 95% by weight of structural support. In one embodiment of the present invention, the preferred support was zirconia.

D. Process Conditions and Equipment

[0120] In one embodiment, the heavy hydrocarbon feedstream is reacted with the catalyst in the presence of hydrogen in a fixed bed reactor system. The fixed bed reactor system comprises at least one reactor. Additionally, more than one reactor may be employed in either series or parallel or both. Each reactor employed uses the catalyst described herein. By optimizing the Group VIII and Group VIb metal components and ratios, these catalysts used in the process of this invention can be located in a single reactor to convert LCO in one reactor directly to jet products.

[0121] The reaction zone comprises the catalyst in a fixed bed. The heavy hydrocarbon feedstock is fed to the reaction zone, which has a temperature of from about 300°F to about 900°F, thereby producing a reaction product. In a preferred embodiment the feedstock is LCO and the reaction products are jet fuel products.

[0122]Typically, the contacting of the hydrocarbon feedstock takes place in the reactor wherein the feedstock is contacted with the catalyst. The reaction occurs at pressures ranging from 100 psig to 3000 psig, hydrogen feed LHSV (Liquid Hourly Space Velocity) ranging from 0.1 to 10 h⁻¹, and a ratio of hydrogen to hydrocarbon ranging from about 400-20,000 SCF/bbl. If a higher conversion of the hydrocarbon feedstock is desirable, then the process optionally includes a separation stage for recovering at least a portion of the product which may contain unconverted feedstock. At least a portion of the product stream is then, optionally, recycled to the reactor system. In case the catalyst is deactivated by coke deposit or other poisons, the catalyst activity can be rejuvenated via regeneration. Processes which are suitable for regeneration are known to those skilled in the art.

[0123] Treating the hydrocarbon feed at the above conditions can substantially remove most of the sulfur and nitrogen compounds as well as partially hydrogenate the aromatic compounds to give a final aromatics content below 25% providing hydrocarbon products that are low in sulfur and nitrogen and within jet fuel specifications. More specifically, the inventive method can reduce the amount of sulfur to less than about 15 wppm, more preferably less than about 10 wppm and most preferably less than about 5 wppm. It also can reduce the amount of nitrogen to less than about 10 wppm, more preferably less than about 5 wppm and most preferably less than about 1 wppm.

E. Product

[0124] The method employed in the present invention upgrades heavy hydrocarbon feedstocks to jet fuel products. It has been discovered that the present method employed produces jet fuel products that have a net heat of combustion of greater than at least 125,000 Btu/gal, preferably the net heat of combustion is greater than at least 127,000 Btu/gal, more preferably 128,500 Btu/gal, even more preferably 129,500 Btu/gal. Furthermore, the product meets the specifications for jet fuel. Specifically, the product has a freezing point below -40°C for jet fuel. The product has a smoke point greater than 18 mm. The product has a viscosity of less than 8 cSt at ≈20 degrees Celsius. The product has a density of less than 0.840 g/cc at ≈20 degrees Celsius.

[0125] Other embodiments will be obvious to those skilled in the art.

EXAMPLES

[0126] The following examples are presented to illustrate specific embodiments of this invention and are not to be construed in any way as limiting the scope of the invention.

Example 1

Catalyst Precursor Formation

[0127] A catalyst precursor of the formula \((NH_4)_x\left[\text{Ni}_{4-6}(\text{OH})_{2-8}(\text{H}_2\text{O})_{2-6}\right]\) was prepared as follows: 52.96 g of ammonium heptamolybdate (NH_4)_6Mo_7O_{40}·4H_2O was dissolved in 2.4 L of deionized (DI) water at room temperature. The pH of the resulting solution was within the range of 5-6. 73.98 g of ammonium metatungstate powder was then added to the above solution and stirred until completely dissolved. 90 ml of concentrated (NH_4)OH was added to the solution with constant stirring. The resulting molybdate/tungstate solution was stirred for 10 minutes and the pH monitored. The solution had a pH in the range of 9-10. A second solution was prepared containing 174.65 g of Ni(NO_3)_2·6H_2O dissolved in 150 ml of deionized water and heated to 90°C, thereby producing a hot nickel solution which was then slowly added over 1 hr to the molybdate/tungstate solution. The resulting mixture was heated to 91°C and stirred for another 30 minutes. The pH of the solution was in the range of 5-6. A blue-green precipitate formed and the precipitate was collected by filtration. The precipitate was dispersed into a solution of 10.54 g of maleic acid dissolved in 1.8 L of DI water and heated to 70°C. The resulting slurry was stirred for 50 min. at 70°C, filtered to produce a precipitate which was collected and vacuum dried at room temperature overnight. The material was then further dried at 120°C for 12 hr. The resulting material has a typical XRD pattern with a broad peak at 2.5 Å, denoting an amorphous Ni—OH containing material. Surface area measurements were within the range of 50-150 m²/g and an average
pore volume within the range of 0.1-0.2 cc/g with an average pore size of 5-50 nm as measured by BET method.

Example 2

Sulfidation

[0128] 6.5 cc of the catalyst precursor of Example 1 was placed in a tubular reactor and first purged with 700 cc/min \( \text{N}_2 \) at 100°F. overnight. Then the temperature was increased to 450°F. in 4 hours. After having been held at 450°F. in this \( \text{N}_2 \) flow for 1 hour, it was switched to 700 cc/min \( \text{H}_2 \) and the pressure was increased to 800 psig. It’s held at 450°F. and 800 psig in 700 cc/min \( \text{H}_2 \) for 1 hour. Then the sulfiding feed containing 6 wt. % DMDS (dimethyl disulfide) in n-heptane was introduced at 36 cc/hr at 800 psig, 450°F. and 700 cc/min \( \text{H}_2 \) and it was held for 2 hours under these conditions. Subsequently the temperature was increased from 450°F. to 650°F. in 4 hours and it was held at 650°F. for 2 hours. With the sulfiding feed still on, the temperature was dropped from 650°F. to 300°F. as soon as possible. Then the sulfiding feed was stopped. The pressure was increased to the pre-selected reaction pressure such as 1000 psig and the \( \text{H}_2 \) rate was adjusted to 77.2 cc/min. At this stage, the FCC LCO was started with a rate of 6.5 cc/hr at a \( \text{H}_2 \) rate of 77.2 cc/min, 1000 psig and 300°F. Subsequently the reactor temperature was increased from 300°F. to a pre-selected reaction temperature such as 600°F. at a rate of 1°F./min. Then the reaction proceeded at 6.5 cc/hr feed, 77.2 cc/min \( \text{H}_2 \), 600°F. and 1000 psig.

Example 3

Catalysts

[0129] The following catalysts were used in the example of the invention or in the comparative examples.

[0130] (1) The catalyst of the invention is hereinafter referred to as Ni—Mo—W, which was prepared according to Examples 1 and 2.

[0131] (2) A hydrotreating catalyst comprising molybdenum and nickel supported on an alumina base is hereinafter referred to as Ni—Mo.

[0132] (3) A hydrofinishing catalyst comprising platinum and palladium supported on a mixed silica-alumina/alumina base is hereinafter referred to as Pt—Pd.

Example 4

Feedstock

[0133] Table 1 discloses the properties of the feedstock used in the present invention. The feedstock is a light cycle oil (LCO) product from the Fluid Catalytic Cracking unit in a refinery. The feedstock was also analyzed with simulated distillation. The results of the simulated distillation are listed in Table 2. This feedstock has not been hydrotreated.

Example 5

Upgrade of LCO to Jet Fuels with Ni—Mo—W Catalyst of the Present Invention as a Single Catalyst in a Single Fixed Bed Reactor

[0134] The FCC LCO feed, as described in Table 1 and Table 2 in Example 4, was hydroprocessed in a single fixed bed reactor at a feed rate of 6.5 cc/hr over 6.5 cc of the Ni—Mo—W catalyst of the present invention, as described in

Example 3. The reactor temperature was 600°F. and the reactor pressure was 1000 psig. Hydrogen feed rate was 77.2 cc/min.

[0135] The catalytic results are also listed in Table 1. The results from the simulated distillation are also listed in Table 2. The results indicate that the jet specifications are met.

Comparative Example 1

Upgrade of LCO to Jet Fuels with Ni—Mo Catalyst as a Single Catalyst in One Single Fixed Bed Reactor

[0136] The FCC LCO feed, as described in Table 1 and Table 2 in Example 4, was hydrotreated in a fixed bed reactor at a feed rate of 11.2 cc/hr over 5.9 g of the Ni—Mo catalyst described in Example 3 to compare with Ni—Mo—W catalyst of the invention described in Example 5. In this comparative example, the temperature was 660°F. and the pressure was 1700 psig. Hydrogen rate was 300 cc/min.

[0137] The catalytic results are also listed in Table 1. The results from the simulated distillation are also listed in Table 2. The results indicate that the jet product prepared with such a Ni—Mo catalyst does not meet the jet specifications and demonstrate the advance of Ni—Mo—W catalyst of the present invention described in Example 5, especially due to its high activity at a low pressure of 1000 psig and a low temperature of 600°F.

Comparative Example 2

Upgrade of LCO to Jet Fuels with Ni—Mo Hydrotreating and Pt—Pd Hydrofinishing catalysts in Two Fixed Bed Reactors

[0138] In Comparative Example 1, the FCC LCO feed described in Table 1 and Table 2 in Example 4 was hydrotreated in a fixed bed reactor at a feed rate of 11.2 cc/hr over 5.9 g of the Ni—Mo catalyst described in Example 3. The resulting hydrotreating product produced in this first reactor was then hydrofinished in a second fixed bed reactor at a feed rate of 4 cc/hr over 4.7 g of platinum/palladium hydrotreating catalyst described in Example 3. The temperature of this second reactor containing Pt/Pd catalyst was 550°F. and the pressure was 1000 psig. Hydrogen rate was 100 cc/min. Thus, a jet product is produced via a two-stage hydrotreating/hydrofinishing reactor system with each stage containing one catalyst.

[0139] The properties of the jet product produced from this two stage reactor system containing two catalysts are also listed in Table 1. The reaction product was also analyzed with simulated distillation. The results of the simulated distillation are also listed in Table 2.

[0140] The results show the improvement of jet fuel properties using such a two-stage hydroprocess which combines Ni—Mo and Pt/Pd catalysts, as demonstrated, for example, by the improved smoke point with still a high net heat of combustion of 128,781 Btu/gallon. By comparison to Example 5 which employs only a single Ni—Mo—W catalyst in a single reactor, the process of Comparative Example 2 is undesirable because a hydrotreating catalyst is used in one reactor and a hydrofinishing catalyst is used in another reactor to produce a high energy density jet fuel product. It may be economically disadvantageous to use more than one catalyst and more than one reactor to upgrade LCO to a high energy density jet fuel product.
What is claimed is:

1. A process of upgrading a heavy hydrocarbon feedstock comprising:

   contacting a heavy hydrocarbon feedstock with a catalyst in the presence of hydrogen in a reactor system, containing said catalyst as the only catalyst, wherein the catalyst is prepared from a catalyst of the general formula:

   \[ A_{x}(M^8)^{y}(OH)_{z}(L)^{p}(M^{10})O_a \]

   wherein

   A is at least one of an alkali metal cation, an ammonium, an organic ammonium and a phosphonium cation,

   \( M^8 \) is at least a Group VIII metal,

   L is one or more oxygen-containing ligands, having a neutral or negative charge wherein \( \alpha \leq 0 \),

   \( M^{10} \) is at least a Group VIB metal,

   wherein \( M^8: M^{10} \) has an atomic ratio of 100:1 to 1:100, and wherein \( 0 \leq \alpha \leq -2/\alpha \), \( 0 \leq \alpha \leq 2/\alpha \), \( 0 \leq \alpha \leq 2 \), and \( 0 \leq \alpha \);

   and thereby producing a fuel product.

2. The process of claim 1 wherein the heavy hydrocarbon feedstock comprises FCC effluent, including FCC light, medium and heavy cycle oil; fractions of jet and diesel fuels; coker product; coal liquefied oil; the product from the heavy oil thermal cracking process; the product from heavy oil hydrocracking; straight run cut from a crude unit; or mixtures thereof.

3. The process of claim 1 wherein the fuel product has a net heat of combustion of greater than 125,000 Btu/gal.

4. The process of claim 1 wherein the catalyst is unsupported.

5. The process of claim 1 wherein the catalyst is supported.

6. The process of claim 1 wherein the temperature of the fuel product is below −40 degrees Celsius.

7. The process of claim 1 wherein the smoke point of the fuel product is greater than 18 mm.

8. The process of claim 1 wherein the density of the fuel product at 20 degrees Celsius is equal to or below 0.840 g/cc.

9. The process of claim 1 wherein the viscosity of the fuel product at −20 degrees Celsius is below 8 cSt.

10. The process of claim 1 wherein the fuel product is a jet fuel product.

11. A process of upgrading a heavy hydrocarbon feedstock comprising contacting a heavy hydrocarbon feedstock with a catalyst in the presence of hydrogen in a reactor system, at hydroprocessing conditions, containing said catalyst as the only catalyst, wherein the catalyst is prepared by sulfiding a catalyst precursor obtained by mixing at reaction conditions, to form a precipitate or clogel, at least a Promotor metal compound in solution; at least a Group VIB metal compound in solution; and at least an organic oxygen containing ligand in solution, and thereby producing a fuel product.

12. The process of claim 12 wherein the heavy hydrocarbon feedstock comprises FCC effluent, including FCC light, medium and heavy cycle oil; fractions of jet and diesel fuels; coker product; coal liquefied oil; the product from the heavy oil thermal cracking process; the product from heavy oil hydrocracking; straight run cut from a crude unit; or mixtures thereof.

13. The process of claim 12 wherein the fuel product has a net heat of combustion of greater than 125,000 Btu/gal.

14. The process of claim 12 wherein the fuel product is a jet fuel product.

15. The process of claim 12 wherein the catalyst is unsupported.
16. The process of claim 12 wherein the catalyst is supported.
17. The process of claim 12 wherein the freezing point of the fuel product is below –40 degrees Celsius.
18. The process of claim 12 wherein the smoke point of the fuel product is greater than 8 mm.
19. The process of claim 12 wherein the flash point of the fuel product is greater than 38 degrees Celsius.
20. The process of claim 12 wherein the density of the fuel product at 20 degrees Celsius is equal to or below 0.840 g/cc.
21. The process of claim 12 wherein the fuel product is a jet fuel product.
22. A product prepared by the process of claim 1.
23. A product prepared by the process of claim 12.
24. The process of claim 1 wherein the feedstock comprises at least 20 wt. % ring-containing hydrocarbon compounds comprising aromatic moieties, naphthenic moieties or both.
25. The process of claim 4 wherein the feedstock comprises at least 20 wt % ring-containing hydrocarbon compounds comprising aromatic moieties, naphthenic moieties or both.

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