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(54) **HYDROGENATION OF SOLID
CARBONACEOUS MATERIALS USING
MIXED CATALYSTS**

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(57) **ABSTRACT**

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This invention encompasses systems and methods for converting solid carbonaceous material to a liquid product, comprising maintaining a solid carbonaceous material in the presence of at least one active source of cobalt and at least one active source of a second metal at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig for a time sufficient to form a liquid product.

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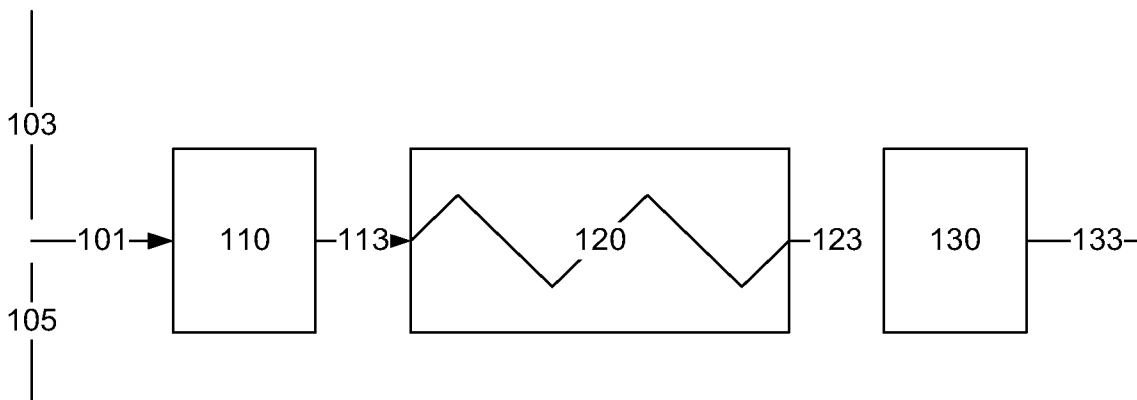


Fig. 1

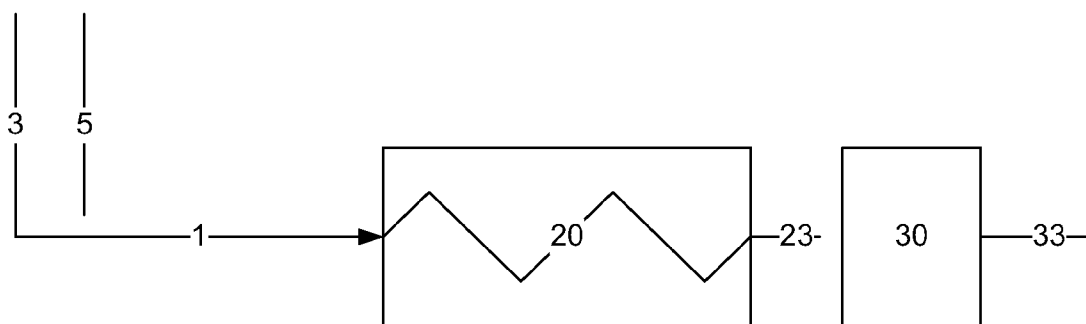


Fig. 2

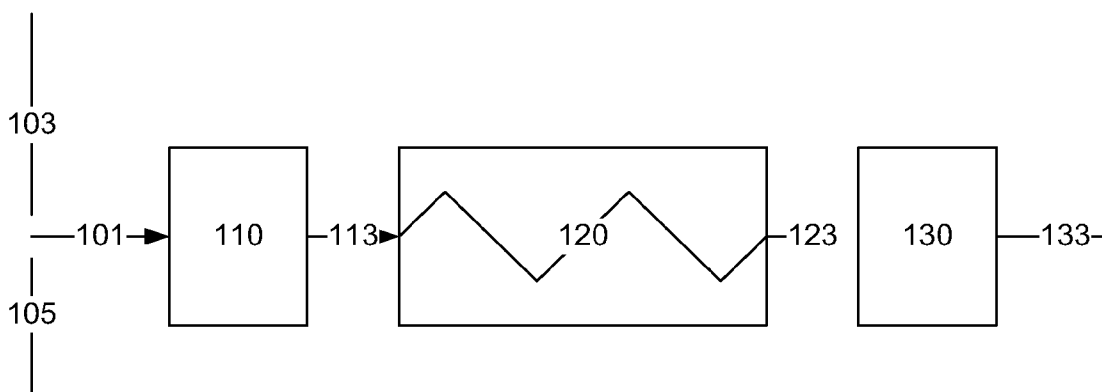


Fig. 3

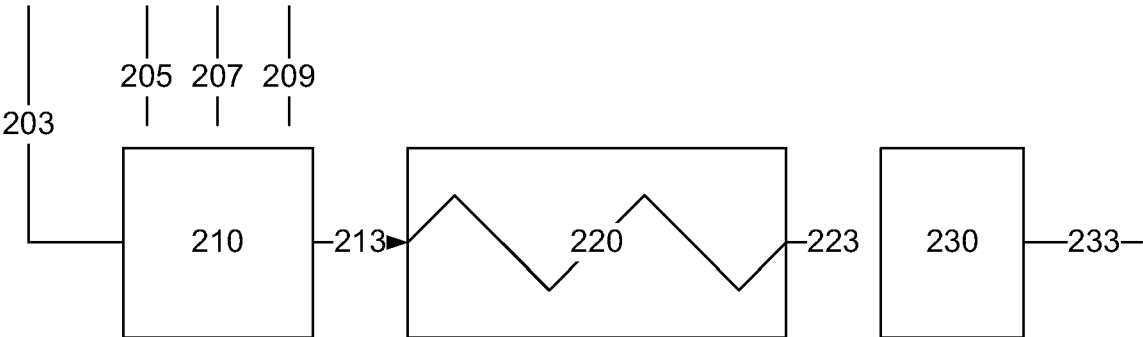
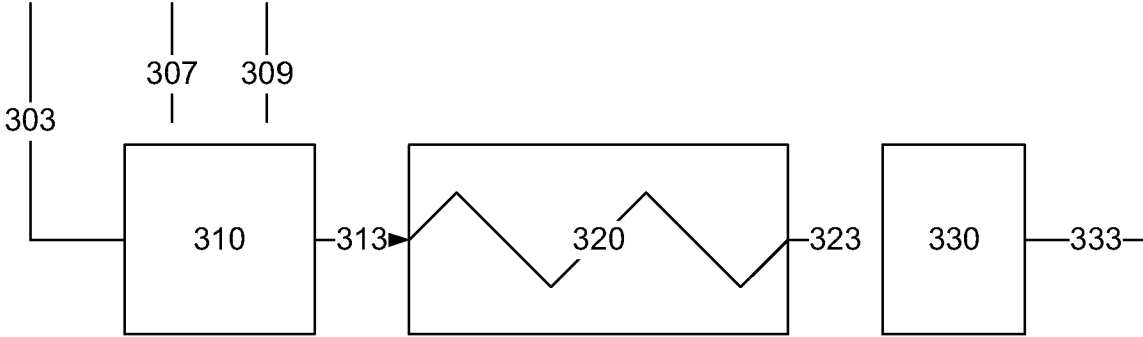


Fig. 4



HYDROGENATION OF SOLID CARBONACEOUS MATERIALS USING MIXED CATALYSTS

TECHNICAL FIELD

[0001] This invention relates to systems and processes for pretreating a carbonaceous material, for liquefying a carbonaceous material, and for improving efficiency of carbonaceous material liquefaction.

BACKGROUND

[0002] Much work has been done over the years on processes for obtaining liquid and gaseous products from solid carbonaceous materials such as coal. The known processes include both catalytic and non-catalytic reactions. In catalytic processes, the hydrocarbonaceous material is typically slurried with a solvent and a catalyst, and is reacted in the presence of molecular hydrogen at elevated temperatures and pressures.

[0003] U.S. Pat. No. 5,246,570, for example, describes a coal liquefaction process in which a mixture of coal, catalyst, and solvent are rapidly heated to a temperature of 600-750° F. in a preheater, and then reacted under coal liquefaction conditions in a liquefaction reaction. U.S. Pat. No. 5,573,556 describes a process for converting a carbonaceous material to normally liquid products comprising heating a slurry that comprises a carbonaceous material, a hydrocarbonaceous solvent, and a catalyst precursor to a temperature sufficient to convert the catalyst precursor to the corresponding catalyst, and introducing the slurry into a liquefaction zone. U.S. Pat. No. 5,783,065 describes a coal liquefaction process comprising impregnating coal particles with a catalyst having hydrogenation or hydrogenolysis activity; introducing the impregnated coal particles for very short periods into a turbulent flow of hydrogen containing gas at a temperature at least about 400° C.; and quenching the temperature of the products to a temperature significantly less than 400° C.

[0004] Such conventional processes leave much room for improving the liquid and/or gas yields of hydroconverted carbonaceous materials, as well as the quality of the liquid and/or gas products that are obtained from such processes. Accordingly, a need remains for improved systems and processes for hydroconversion of carbonaceous materials, as well as improved feed materials for such systems and processes.

SUMMARY OF THE INVENTION

[0005] The present invention relates to a process for converting a solid carbonaceous material to a liquid product, comprising maintaining a solid carbonaceous material in the presence of at least one active source of cobalt and at least one active source of a second metal at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig for a time sufficient to form a liquid product.

[0006] In one aspect, the process comprises preparing a combination of the solid carbonaceous material, at least one hydrocarbonaceous liquid, at least one active source of cobalt and at least one active source of the second metal; and passing the combination to a hydroconversion reaction zone and maintaining the solid carbonaceous material at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig for a time sufficient to convert at

least a portion of the solid carbonaceous material to a liquid product boiling in the temperature range of C₅ to 650° C.

[0007] In a further aspect, the step of preparing the combination comprises preparing a mixture comprising at least one active source of cobalt and at least one active source of a second metal; combining the mixture with coal to form catalyst-containing coal particles; providing a hydrocarbonaceous liquid to the catalyst-containing coal particles to prepare the combination.

[0008] In another aspect, the process of preparing the combination further comprises drying the catalyst-containing coal prior to the step of passing the combination to the hydroconversion reaction zone.

[0009] In a further aspect, the process further comprises pretreating the combination at a pretreatment temperature within the range of 100-350° C. and for a time of between 5 and 600 minutes prior to passing the combination to the hydroconversion reaction zone.

[0010] In a further aspect, before, during or after the step of pretreatment, at least one active source of sulfur is added to the solid carbonaceous material in the preparation of the combination, wherein the atomic ratio of sulfur to metal components is within the range of between 1/1 and 10/1.

[0011] In an aspect, the second metal is iron.

[0012] Several embodiments of the invention, including the above aspects of the invention, are described in further detail as follows. Generally, each of these aspects can be used in various and specific combinations, and with other aspects and embodiments unless otherwise stated herein.

BRIEF DESCRIPTION OF THE DRAWING

[0013] FIG. 1, FIG. 2, FIG. 3 and FIG. 4 illustrate embodiments of the process for converting solid carbonaceous material.

DETAILED DESCRIPTION

[0014] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[0015] The term “catalyst precursor” is used herein to refer to a compound that is transformable into a catalyst via chemical reaction with one or more reagents (such as sulfiding and/or reducing agents, e.g., hydrogen, such as within a hydrocarbon medium) and/or via any other suitable treatment (such as thermal treatment, multi-step thermal treatment, pressure treatment, or any combination thereof) whereby the catalyst precursor at least partially decomposes into a catalyst.

[0016] The term “active source” is used herein to refer to an atomic, molecular, complex or any other form of an element that is a catalyst or a catalyst precursor or that can be converted into a catalyst or catalyst precursor. The active source may be in solution, in slurry or in particle form. When the active source is deposited on the solid carbonaceous material, by, for example, plating, impregnation, coating or washing, a single active source or a mixture of active sources may be deposited on individual particles of the solid carbonaceous material.

[0017] The term “catalytic material” is used to refer to one or more active catalysts or catalyst precursors. The component(s) of catalytic material may be in slurry or particle form. In particle form, single or multiple catalysts may be present on individual particles. Likewise, when the catalytic material

is deposited on the solid carbonaceous material, by, for example, plating, impregnation, coating or washing, a single catalyst, or a mixture of catalysts or precursors making up the catalytic material may be deposited on individual particles of the solid carbonaceous material.

[0018] Unless otherwise specified, coal properties as disclosed herein are on a dry, ash-free (daf) basis, wherein ASTM 3173 is used for moisture determination and ASTM3174 for ash quantification.

[0019] "d" block elements refer to elements of the Periodic Table wherein the d sublevel of the atom is being filled. Examples include iron, molybdenum, nickel, manganese, vanadium, tungsten, cobalt, copper, titanium, chromium, platinum, palladium, cerium, zirconium, zinc and tin.

[0020] Lanthanoid (or lanthanide, or sometimes referred to as rare earths) elements refer to the fifteen elements in the Periodic Table with atomic numbers 57 through 71.

[0021] "Oil dispersible" compound means that the compound scatters or disperses in oil forming a dispersion. In one embodiment, the oil dispersible compound is oil soluble which dissolves upon being mixed with oil.

[0022] For purposes of this disclosure, unless otherwise specified, the catalyst composition is defined as the composition of the active source(s) added to the process, regardless of the form of the catalytic elements during hydroconversion.

[0023] The present invention relates to the composition and preparation procedures of a sulfided cobalt-containing catalyst used for hydroconversion of carbonaceous material including coal, shale oil, vacuum residuum and bio-fuel stock such as lignin. The invention further relates to a hydroconversion process for converting solid carbonaceous material to a liquid product in the presence of a catalyst composition comprising cobalt. In embodiments, the invention further relates to a process for converting a carbonaceous material, comprising pretreating a solid carbonaceous material at a pretreatment temperature and in the presence of at least one active source of cobalt and at least one active source of a second metal; heating the pretreated material in the presence of hydrogen to a conversion temperature which is greater than the pretreatment temperature; and reacting the heated material for a time sufficient to form converted products from the solid carbonaceous material.

Catalyst Formula

[0024] In one embodiment, the catalyst composition as expressed in elemental form is of the general formula $(R^p)_i(M^f)_a(L^u)_b(S^v)_d(C^w)_e(H^x)_f(O^y)_g(N^z)_h$. The formula herein refers to the catalyst solids, constituting the catalyst slurry in oil. In the equation, M and L each represents at least a "d" block element from the Periodic Table such as iron, molybdenum, nickel, manganese, vanadium, tungsten, cobalt, copper, titanium, chromium, platinum, palladium, cerium, zirconium, zinc and tin. M is different from L. R is optional, which represents at least one lanthanoid element from the Periodic Table such as La, Ce, Nd, etc. In another embodiment, R is at least an alkali earth metal such as magnesium.

[0025] Also in the equation, p, t, u, v, w, x, y, z representing the total charge for each of the components (R, M, L, S, C, H, O and N, respectively); $pi+ta+ub+vd+we+xf+yg+zh=0$; R with a subscript i ranging from 0 to 1; M and L with subscripts a and b, with values of a and b respectively ranging from 0 to 5, and $(0 \leq b/a \leq 5)$; S represents sulfur with the value of the subscript d ranging from $0.5(a+b)$ to $5(a+b)$; C represents carbon with subscript e having a value of 0 to $11(a+b)$; H is

hydrogen with the value off ranging from 0 to $7(a+b)$; 0 represents oxygen with the value of g ranging from 0 to $5(a+b)$; and N represents nitrogen with h having a value of 0 to $2(a+b)$.

[0026] In embodiments, M is iron and L is cobalt (or vice versa). In some such embodiments, the catalyst is of the formula $(Fe_xCo_{1-x})_a(S)_d(C)_e(H)_f(O)_g(N)_h$, wherein the cobalt to iron ratio is in the range of 9:1-1:9 (as wt. %). In some such embodiments, the cobalt to iron ratio is in the range of 1:5 to 5:1; or in the range of 1:10 to 1:5.

Pretreatment Process

[0027] In embodiments, the present invention is related to a system and process for pretreating a carbonaceous material, for dispersing one or more catalysts or catalyst precursors into a carbonaceous material, for enhancing the conversion of a carbonaceous material (such as a naturally-occurring solid carbonaceous material, such as coal) to a liquid and/or gaseous product, for producing a carbonaceous material of enhanced reactivity, for improving efficiency of carbonaceous material (such as coal) liquefaction, as measured for example by conversion and liquid yield, and/or for lowering hydrogen consumption during liquefaction of carbonaceous material.

[0028] In one embodiment, such pretreating of a carbonaceous material is performed or accomplished using reaction conditions (or a combination of conditions, such as temperature, pressure, and/or duration of pretreatment) at which substantially no hydroconversion of the carbonaceous material occurs (i.e., wherein less than about 20%, less than about 10% or even less than about 1% of the carbonaceous material is converted) during the pretreatment step. Any suitable process or operating conditions can be utilized to pretreat the carbonaceous material. In one embodiment, the pretreatment composition is heated to a temperature sufficient to cause one or more catalysts or catalyst precursors to disperse into the carbonaceous material, and is maintained, held, and/or kept at this pretreatment temperature for a time or duration sufficient to disperse one or more of the catalysts or catalyst precursors into the carbonaceous material to a desired degree of dispersion, integration, and/or homogeneity. In one embodiment, the pretreatment composition is heated to a temperature of about 100-350° C. (such as about 150-300° C. or even about 180-220° C.). In some such embodiments, the step of pretreating is conducted at a temperature of about 100-350° C. for about 10-360 minutes.

[0029] The pretreatment composition is preferably maintained, kept, and/or held at the pretreatment temperature for a time or duration sufficient to cause swelling of the carbonaceous material and to allow for dispersion (such as complete dispersion and/or homogenous dispersion) of the catalyst or catalyst precursor into the carbonaceous material. In one embodiment, for example, the pretreatment composition is maintained, kept, and/or held at suitable temperature for a suitable duration to cause the total volume of voids of the carbonaceous material (or of each particle of carbonaceous material) to increase by greater than about 5%, or about 25% as compared to the carbonaceous material prior to pretreatment. In one embodiment, in this regard, the pretreatment composition is maintained at the pretreatment temperature for a time of between 5 and 600 minutes, or between 10 and 360 minutes.

[0030] Pretreatment of the carbonaceous material can be performed under any suitable atmosphere. In one embodi-

ment, the pretreatment of carbonaceous material occurs under an inert atmosphere. In another embodiment, the pretreatment occurs under a reducing atmosphere, such as under hydrogen and/or a synthesis gas ("syn-gas") pressure. In some embodiments, for example, the pretreatment is performed at a pressure between atmospheric pressure and about 500 psig, e.g., a pressure of about 100-450 psig, or about 200-350 psig. In other embodiments, the pretreatment occurs under a reducing atmosphere at a pressure defined by the hydroconversion process, such as at a pressure of about 300-5000 psig, such as 500-3500 psig, about 1000-3000 psig, or even about 1500-2600 psig. Any suitable syn-gas can be used in this regard, such as, for example, a syn-gas that comprises a 1:1 to 2:1 mixture of hydrogen with carbon monoxide, and optionally also contains carbon dioxide, methane, and/or other components.

[0031] In one embodiment, such pretreatment is performed or accomplished under conditions sufficient to deposit at least a portion of the catalyst or catalyst precursor onto the solid carbonaceous material during pretreatment. In some such embodiments, one or more catalysts or catalyst precursors and a liquid contact the solid carbonaceous material.

[0032] The pretreatment composition comprising the carbonaceous material, one or more catalyst or catalyst precursors, and a hydrocarbonaceous liquid can be prepared in any suitable manner. In one embodiment, the carbonaceous material, catalyst or catalyst precursor, and hydrocarbonaceous liquid are simply mixed to form a pretreatment composition, and the pretreatment composition is subjected to pretreatment conditions. In another embodiment, the carbonaceous material is contacted with the catalyst or catalyst precursor in the presence of the hydrocarbonaceous liquid, and the pretreatment composition is subjected to pretreatment conditions. In another embodiment, the carbonaceous material is ground in the presence of the one or more catalysts or catalyst precursors and the hydrocarbonaceous liquid, to produce a pretreatment composition in the form of a slurry; and the pretreatment composition is subjected to pretreatment conditions. In another embodiment, the carbonaceous material is ground in the presence of the hydrocarbonaceous liquid to produce a slurry; the one or more catalyst precursors are added to the slurry to form a pretreatment composition; and the pretreatment composition is subjected to pretreatment conditions. In other embodiment, the catalyst or catalyst precursor is added at the start of the pretreatment process. In another embodiment, the catalyst or catalyst precursor is added at intervals throughout a pretreatment process. In other embodiments, at least a portion of the catalyst or catalyst precursor is deposited on the carbonaceous material during pretreatment.

[0033] Following pretreatment of the carbonaceous material, the carbonaceous material and dispersed catalyst or catalyst precursor, optionally together with the hydrocarbonaceous liquid, form an improved feed for a hydroconversion process. Such an improved feed can be used for any suitable hydroconversion process to produce a liquid and/or gaseous product.

Carbonaceous Material

[0034] The carbonaceous material can be any suitable solid carbon containing material, such as any naturally occurring solid, or normally solid, carbon containing material. Specifically, for example, the carbonaceous material can be coal, such as anthracite, bituminous coal, sub-bituminous coal, lignite, or any combination or mixture thereof. The carbon-

aceous material can also be any heteroatom-containing solid carbonaceous material or feed, as well as any heavy hydrocarbonaceous feeds, such as, for example, coal, coke, peat, shale oil and/or a similar material, such as any solid carbonaceous material containing a relatively high ratio of carbon to hydrogen, or combinations or mixtures thereof. In some embodiments, at least a portion of the carbonaceous material is in the form of particles, or finely divided particles, having any suitable size. For example, at least about 50 wt % of the carbonaceous material is in the form of particles having a mean particle diameter of less than about 0.5 inches. In other embodiments, at least greater than 70 wt % of carbonaceous material is in the form of particles having a mean particle diameter in the range of about 0.1 to 0.4 inches. In one embodiment, greater than about 80 wt. % of the carbonaceous material is in the form of particles having a mean diameter less than about 0.25 inches. In another embodiment, greater than 80 wt % of the carbonaceous material is in the form of particles having a mean diameter in the range of 50 microns to 500 microns, such as 100 microns. Such particles can be formed in any suitable manner, such as by grinding at least a portion of the carbonaceous material. In one embodiment, at least a portion of the carbonaceous material is ground in the presence of one or more catalysts or catalyst precursors and the hydrocarbonaceous liquid. In another embodiment, at least a portion of the carbonaceous material is ground in the presence of the hydrocarbonaceous liquid to form a slurry, and (such as subsequently) mixing the slurry with one or more catalysts or catalyst precursors. In other embodiments, the carbonaceous material is ground under an inert or a reducing atmosphere, such as, for example, hydrogen, nitrogen, helium, argon, syn-gas, or any combination or mixture thereof. Any process or equipment may be used to grind the carbonaceous material, such as, for example, a hammer mill, a ball mill (such as a wet ball mill, a conical ball mill, a rubber roller mill), a rod mill, or a combination thereof.

Hydrocarbonaceous Liquid

[0035] The hydrocarbonaceous liquid can be any suitable liquid (such as solvent or diluent) known in the art to be useful for the liquefaction of carbonaceous materials (such as solid carbonaceous materials, such as coal). In one embodiment, the hydrocarbonaceous liquid is a hydrogen donor solvent, such as any compound(s) which functions as a hydrogen donor in hydroconversion conditions. The hydrocarbonaceous liquid can have any suitable hydrogen donatability, such as, for example, a hydrogen donatability greater than about 1.0 wt %, as determined, for example, by NMR.

[0036] In one embodiment, the hydrocarbonaceous liquid comprises a coal-derived solvent, or a distillate fraction thereof. In another embodiment, the hydrocarbonaceous liquid comprises a hydrogenated aromatic, a naphthenic hydrocarbon, a phenolic material, or a similar compound, or a combination or mixture thereof. In another embodiment, the hydrocarbonaceous liquid comprises one or more aromatics, such as one or more alkyl substituted aromatics. Solvents known to donate hydrogen during liquefaction include, for example, the dihydronaphthalenes, the C₁₀-C₁₂ tetrahydronaphthalenes, the hexahydrofluorenes, the dihydro-, tetrahydro-, hexahydro- and octahydrophenanthrenes, the C₁₂-C₁₃ acenaphthenes, the tetrahydro-, hexahydro- and decahydropyrenes, the di-, tetra- and octahydroanthracenes, and other derivatives of partially saturated aromatic compounds. They can be prepared by subjecting a distillate stream

from atmospheric distillation to a conventional hydrogenation reactor. Particularly effective mixed solvents include heavy gas oil fractions (often called vacuum gas oils, or VGO) with an initial boiling point of about 343° C. (650° F.) and a final boiling point of about 538° C. (1000° F.). This stream comprises aromatics, hydrogenated aromatics, naphthenic hydrocarbons, phenolic materials, and similar compounds. If a solvent is used which does not have donatable hydrogen, hydrogen may be added from another source.

[0037] The solvent generally boils at a temperature greater than 300° C., such as, for example a temperature in the range of 450-900 or 650-850° F. In one embodiment, the hydrocarbonaceous liquid is a fluid catalytic cracking (FCC) type process oil cut that boils at a temperature of about 500° F. or higher (FCC-type process oil (500° F.+cut)). In another embodiment, the hydrocarbonaceous liquid is an FCC-type process oil boiling at a temperature of about 500° F. or less ("FCC-type process oil (500° F.-cut)"). In another embodiment, the hydrocarbonaceous liquid is a hydrotreated FCC oil. In another embodiment, the hydrocarbonaceous liquid is tetralin (1,2,3,4 tetrahydronaphthalene). In another embodiment, the hydrocarbonaceous liquid comprises one or more compounds that have an atmospheric boiling point ranging from about 350-850° F.

[0038] Any suitable ratio of hydrocarbonaceous liquid to carbonaceous material (such as carbonaceous particles, or even coal particles) can be used in the context of the present invention, such as, for example, a ratio in a range of about 1:10 to about 10:1, such as 1:6 to about 6:1, or a range of about 1:2 to about 2:1, by weight of the mixture. In one embodiment, the ratio of hydrocarbonaceous liquid to carbonaceous material used in the pretreatment process is about 0.75:1 to about 1:1.

Catalyst Precursor

[0039] The process for converting a solid carbonaceous material comprises heating the carbonaceous material in the presence of a catalyst composition. In embodiments, the process for converting a solid carbonaceous material comprises heating a solid carbonaceous material in the presence of at least one active source of cobalt for a time sufficient to form a liquid product from the solid carbonaceous material. In embodiments, the active source of cobalt is provided to the carbonaceous material in the form of a catalyst precursor that is transformable into a catalyst via chemical reaction with one or more reagents and/or via any other suitable treatment. The catalyst precursor may be oil soluble, oil dispersible, water soluble and/or water dispersible. In embodiments, the process comprises pretreating the solid carbonaceous material at a pretreatment temperature and in the presence of at least one active source of cobalt; heating the pretreated material in the presence of hydrogen to a conversion temperature which is greater than the pretreatment temperature; and reacting the heated material for a time sufficient to form a liquid product from the solid carbonaceous material.

[0040] Suitable catalyst precursors include:

[0041] a) cobalt metal;

[0042] b) cobalt containing inorganic compounds, such as the sulfates, nitrates, carbonates, sulfides, oxysulfides, oxides and hydrated oxides, ammonium salts and heteropoly acids of cobalt;

[0043] c) salts of organic acids, such as acyclic and alicyclic aliphatic, carboxylic acids containing two or more carbon atoms (non-limiting examples include acetates, oxylates, citrates);

[0044] d) cobalt-containing organometallic compounds including chelates such as 1,3-diketones, ethylene diamine, ethylene diamine tetraacetic acid, phthalocyanines, thiocarbamates, phosphorothioates, and combinations or mixtures thereof (non-limiting examples include cobalt alkyl dithiocarbamate, cobalt alkyl phosphorodithioate); and/or,

[0045] e) cobalt salts of organic amines such as aliphatic amines, aromatic amines, quaternary ammonium compounds, or combinations or mixtures thereof, and

[0046] f) cobalt-containing minerals.

[0047] In embodiments, the process for converting a solid carbonaceous material further comprises heating the solid carbonaceous material in the presence of at least one active source of a second metal. In embodiments, the second metal is selected from the group consisting of iron, molybdenum, tungsten, nickel, cobalt, titanium and tin. In some such embodiments, the active source of the metal is provided to the carbonaceous material in the form of a catalyst precursor that is transformable into a catalyst via chemical reaction with one or more reagents and/or via any other suitable treatment. The catalyst precursor may be oil soluble, oil dispersible, water soluble and/or water dispersible.

[0048] In embodiments, the catalyst composition comprises for converting the solid carbonaceous material further comprises at least one active source of iron. Suitable catalyst precursors which provide the active iron source include:

[0049] a) iron metal;

[0050] b) iron containing inorganic compounds, such as the sulfates, nitrates, carbonates, sulfides, oxysulfides, oxides and hydrated oxides, ammonium salts and heteropoly acids of iron;

[0051] c) salts of organic acids, such as acyclic and alicyclic aliphatic, carboxylic acids containing two or more carbon atoms (non-limiting examples include acetates, oxylates, citrates);

[0052] d) iron-containing organometallic compounds including ferrocene, chelates such as 1,3-diketones, ethylene diamine, ethylene diamine tetraacetic acid, phthalocyanines, thiocarbamates, phosphorothioates, and combinations or mixtures thereof (non-limiting examples include iron alkyl dithiocarbamate, iron alkyl phosphorodithioate); and/or,

[0053] e) iron salts of organic amines such as aliphatic amines, aromatic amines, quaternary ammonium compounds, or combinations or mixtures thereof, and

[0054] f) iron-containing minerals.

[0055] The catalyst precursor can be formed in any suitable manner prior to the hydroconversion process. In one embodiment, for example, one or more catalyst precursors are formed by:

[0056] a) mixing a hydrocarbonaceous liquid (such as a liquefaction solvent) with an active source of at least one metal (such as a metal oxide, e.g., iron oxide, or other compound containing any suitable metal as discussed herein) to form a catalyst precursor,

[0057] b) combining the catalyst precursor with a carbonaceous material;

[0058] c) optionally subjecting the mixture to pretreatment conditions (such as under hydrogen pressure) in a

- manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0059] d) heating the mixture for a time sufficient to form a liquid product.
- [0060] In embodiments, the catalyst precursors are formed by:
- [0061] a) mixing a hydrocarbonaceous liquid (such as a liquefaction solvent) with at least one active source of cobalt and with at least one active source of a second metal to form a catalyst precursor;
- [0062] b) combining the catalyst precursor with a carbonaceous material;
- [0063] c) optionally subjecting the mixture to pretreatment conditions in a manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0064] d) heating the mixture for a time sufficient to form a liquid product.
- [0065] In embodiments, the catalyst precursors are formed by
- [0066] a) mixing a hydrocarbonaceous liquid with an active source of at least one metal,
- [0067] b) combining the mixture with a sulfiding agent (such as by passing hydrogen sulfide through the mixture or adding elemental sulfur to the mixture) in a manner such that the sulfided metal-containing compound is dispersible,
- [0068] c) combining the sulfided mixture with a carbonaceous material,
- [0069] d) optionally subjecting the mixture to pretreatment conditions in a manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0070] e) heating the mixture for a time sufficient to form a liquid product.
- [0071] In embodiments, the catalyst precursors are formed by
- [0072] a) mixing a hydrocarbonaceous liquid with an active source of at least one metal;
- [0073] b) combining the catalyst precursor with a carbonaceous material;
- [0074] c) combining the mixture with a sulfiding agent;
- [0075] d) optionally subjecting the mixture to pretreatment conditions in a manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0076] e) heating the mixture for a time sufficient to form a liquid product.
- [0077] In another embodiment, one or more catalyst precursors are formed by
- [0078] a) mixing one or more metal containing compounds, a sulfiding agent, and water, to form a colloidal suspension,
- [0079] b) combining the colloidal suspension with a hydrocarbonaceous liquid (such as a liquefaction solvent) to drive water out of the suspension,
- [0080] c) combining the suspension with a carbonaceous material,
- [0081] d) optionally subjecting the suspension to pretreatment conditions (such as under hydrogen pressure), in a manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0082] e) heating the mixture for a time sufficient to form a liquid product.
- [0083] In another embodiment, one or more catalyst precursors are by
- [0084] a) sulfiding an ammonium containing Group VIB metal compound in an aqueous phase with hydrogen sulfide, in a substantial absence of hydrocarbon oil, at a temperature less than about 177° C., to form a pre-sulfided product; and
- [0085] b) separating ammonia from said presulfided product to form a sulfided product, in a manner such that one or more catalyst precursors form in or on the carbonaceous material.
- [0086] In another embodiment, one or more catalyst precursors are formed by a process comprising:
- [0087] a) mixing an active source of cobalt and an active source of the second metal and water, to form a colloidal suspension or solution;
- [0088] b) combining the colloidal suspension or solution with a solid carbonaceous material at conditions sufficient to deposit at least a portion of the cobalt and a portion of the second metal onto [wherein depositing onto includes depositing onto the surface of any fractures, pores, or other openings into the internal volume of the solid carbonaceous material] the solid carbonaceous material;
- [0089] c) combining the solid carbonaceous material having the active sources of the metals deposited thereon with a hydrocarbonaceous liquid (such as a liquefaction solvent); and
- [0090] d) optionally subjecting the suspension to pretreatment conditions (such as under hydrogen pressure), in a manner such that one or more catalyst precursors form in or on the carbonaceous material; and
- [0091] e) heating the mixture for a time sufficient to form a liquid product.
- [0092] In some such embodiments, the process further comprises combining the colloidal suspension or solution and an active source of sulfur with the solid carbonaceous material.
- [0093] Any suitable amount of the catalytic materials can be used to hydroconvert the carbonaceous material in the context of the present invention. In one embodiment, the mixture of catalyst precursor, carbonaceous material, and hydrocarbonaceous liquid comprises about 25-10000 ppm (such as about 50-9000 ppm, about 100-8000 ppm, about 250-5000, about 500-3000 ppm, or even about 1000-2000 ppm) of one or more catalyst or catalyst precursor by weight, based on the total weight of the mixture. In embodiments, the metal content of the catalyst or catalyst precursor refers to added metal, and does not include metal which is native to the carbonaceous material or metal which is eroded from processing equipment.
- [0094] The catalytic materials can be used in the context of the present invention in any suitable form, such as, but not limited to, particulate form, impregnated within a carbonaceous material, dispersed in the hydrogen donor solvent, and/or soluble in the hydrogen donor solvent. Additionally, the catalytic materials may be used in processes employing fixed, moving, and ebullated beds as well as slurry reactors.
- [0095] The catalyst precursor(s) can be transformed into a catalyst by thermal decomposition, such as prior to or during liquefaction, without the addition of additional reactants. In other embodiments, following pretreatment, one or more additional reactants can be added to the pretreated carbonaceous material mixture (such as prior to or during the lique-

faction process), to transform the dispersed catalyst precursor into a catalyst. Any suitable reactants can be used in this regard, such as for example any suitable sulfiding or reducing agents.

Sulfiding Agent Component

[0096] In embodiments, the catalyst composition further comprises at least one active source of sulfur. In those embodiments in which catalyst precursors are utilized, one or more sulfur compounds can be added subsequent to the pre-treating step to activate the catalyst precursor to its corresponding sulfided active catalyst. The one or more sulfur compounds can be introduced at any point of the system, following pretreatment. In one embodiment, one or more sulfur compounds are introduced into the pretreatment zone following the performance of the pretreatment process and before the pretreatment composition is delivered to the liquefaction zone. In another embodiment, one or more sulfur compounds are introduced into the liquefaction zone.

[0097] In one embodiment, the catalyst is prepared using a sulfiding agent in the form of a solution which, under prevailing conditions, is decomposable into hydrogen sulfide. Such a sulfiding agent can be used in any suitable amount in preparing the catalyst, such as in an amount in excess of the stoichiometric amount required to form the catalyst. In one embodiment, the sulfiding agent is present in a sulfur to cobalt mole ratio of at least 3 to 1. Additionally, any suitable sulfiding agent (such as described above with respect to the catalyst precursor) can be used.

[0098] In one embodiment, the sulfiding agent is an aqueous ammonium sulfide. Such a sulfiding agent can be prepared in any suitable manner, such as from hydrogen sulfide and ammonia. This synthesized ammonium sulfide is readily soluble in water and can easily be stored in aqueous solution in tanks prior to use.

[0099] Suitable sulfiding agents include, for example, any sulfur compound that is in a readily releasable form, such as, for example, hydrogen sulfide, ammonium sulfide, dimethylsulfide, ammonium sulfate, carbon disulfide, elemental sulfur, and sulfur-containing hydrocarbons. Elemental sulfur is preferred in some embodiments, because of its low toxicity, low cost, and ease of handling. Additional sulfiding agents include, for example, ammonium sulfide, ammonium polysulfide, ammonium thiosulfate, sodium thiosulfate, thiourea, dimethyl sulfide, tertiary butyl polysulfide, tertiary nonyl polysulfide, and mixtures thereof. In another embodiment, the sulfiding agent is selected from the group consisting of alkali- and/or alkaline earth metal sulfides, alkali- and/or alkaline earth metal hydrogen sulfides, and mixtures thereof.

[0100] The sulfiding agent can be added in any suitable form. In one embodiment, elemental sulfur is added to the carbonaceous material mixture in the form of a sublimed powder or as a concentrated dispersion (such as a commercial flower of sulfur). Allotropic forms of elemental sulfur, such as orthorhombic and monoclinic sulfur, are also suitable for use herein. In one embodiment, the one or more sulfur compounds are in the form of a sublimed powder (flowers of sulfur), a molten sulfur, a sulfur vapor, or a combination or mixture thereof.

[0101] The sulfiding agent can be used in any suitable concentration. In one embodiment, a concentration of sulfur is introduced such that the atomic ratio of sulfur to metal in the catalyst precursor is in the range of from about 1:1 to about 10:1, such as from about 2:1 to about 8:1, about 2:1 to about

7:1, about 2:1 to about 6:1, about 2:1 to about 9:1, about 2:1 to about 8:1, about 2:1 to 7:1, about 3:1 to about 9:1, about 3:1 to about 8:1, about 3:1 to about 7:1 or even about 3:1 to about 6:1.

Catalyst

[0102] The catalyst contains an active catalytic component in elemental or compound form. Examples include finely divided particles, salts, or compounds of the transition elements, particularly Groups IV-B, V-B, VI-B or Group VIII of the Periodic Table of the Elements, as shown in Handbook of Chemistry and Physics, 45th Edition, Chemical Rubber Company, 1964. In embodiments, alkaline earth elements, such as magnesium, may be included. In embodiments, lanthanoid (or lanthanide, or sometimes referred to as rare earths) elements refer to the fifteen elements in the Periodic Table with atomic numbers 57 through 71, may be included.

[0103] The catalyst includes any cobalt-containing material that is suitable for use in a hydroconversion process for a carbonaceous material (such as coal) when subjected to and/or when experiencing suitable catalyzing reaction conditions. The catalyst further comprises any suitable metal, such as, for example, a metal selected from the group consisting of Group IIB metals, Group IIIB metals, Group IVA metals, Group IVB metals, Group VB metals, Group VIB metals, Group VIIB metals, Group VIII metals, or a combination or mixture thereof, such as in combination with one or more of oxygen, sulfur, nitrogen, and phosphorous. In embodiments, a second metal is selected from the group consisting of Fe, Mo, W, Co, Ni, Cu, Ti and Sn.

[0104] In embodiments, the sulfided cobalt-containing catalyst can be CoS—FeS, CoS—MoS₂, CoS—WS₂, CoS—NiS, CoS—CuS, CoS—TiS₂, CoS—SnS and any of their combinations and mixtures, for example CoS—MoS₂—TiS₂. In the catalyst system, Co can be the rich phase or serve as dopant.

[0105] The amount of cobalt that is provided as a catalyst component of the catalyst is sufficient to catalyze the conversion of the solid carbonaceous material to liquid hydrocarbons; likewise, the amount of the second metal that is provided as a catalyst component is sufficient to catalyze the conversion of the solid carbonaceous material. In embodiments, cobalt is present in the catalyst in an amount of 10 ppm to 10 wt %, based on dry, ash free coal. In some such embodiments, cobalt is present in the catalyst in the amount of 0.1 wt % to 5 wt %. An exemplary quantity of cobalt, as metal, present in the catalyst is in the amount of 0.5 wt % to 2.5 wt %.

[0106] In embodiments, the second metal in the catalyst is present in an amount of 10 ppm to 10 wt %, based on dry, ash free coal. In some such embodiments, the second metal is present in the catalyst in the amount of 0.1 wt % to 5 wt %. An exemplary quantity of the second metal, expressed as a metal, is in the amount of 0.5 wt % to 2.5 wt %. In some such embodiments, the second metal in the catalyst is iron. As such, iron is present in the catalyst in an amount of 10 ppm to 10 wt %, based on dry, ash free coal. In some such embodiments, iron is present in the catalyst in the amount of 0.1 wt % to 5 wt %. An exemplary quantity of iron, as metal, present in the catalyst is in the amount of 0.5 wt % to 2.5 wt %. In embodiments, the molecular ratio between Co and other metals in combination can be between 0.1 to 1 and 10 to 1.

[0107] In embodiments, the catalytic materials are added as finely divided particulate metal solids, their oxides, sulfides,

etc., e.g., FeS_x ; waste fines from metal refining processes, e.g., iron, molybdenum, and nickel; crushed spent catalysts, e.g., spent fluid catalytic cracking fines, hydroprocessing fines, recovered coal ash, and solid coal liquefaction residues. In embodiments, the cobalt and the second metal are added as separate particulate solids. In other embodiments, the catalyst composition comprises particles that are richer in cobalt and leaner in the amount of the second metal, or particles that are richer in the second metal and leaner in the amount of cobalt. In another embodiment, cobalt and other metals can form bi-metallic compounds as a catalyst precursor rather than being added to the feed separately. As an example, $\text{Co}_x\text{Fe}_{(1-x)}\text{OOH}$ is prepared by titrating a FeSO_4 and CoSO_4 mixture solution with $\text{NH}_3\text{H}_2\text{O}$, followed by oxidizing in flowing air at elevated temperatures. $\text{Co}_x\text{Fe}_{(1-x)}\text{OOH}$ can be pre-sulfided to $\text{Co}_x\text{Fe}_{(1-x)}\text{S}$ before mixing with the feed.

[0108] In embodiments, at least a portion of the catalyst particles are attached to, adsorbed onto, absorbed by, supported on or intimately associated with at least a portion of the solid carbonaceous material during conversion of the carbonaceous material. In embodiments, at least a portion of the catalyst, or catalyst precursor, is deposited on the solid carbonaceous material before or during pretreatment, using an aqueous or an organic liquid to carry the catalyst or catalyst precursor to the carbonaceous material. In embodiments, at least a portion of the catalyst, or catalyst precursor, is deposited on the solid carbonaceous material during the step of heating the material to conversion temperature, or during the conversion process.

[0109] In an embodiment, the catalyst is prepared using a catalyst precursor comprising a metal that comprises a water-soluble cobalt component, such as cobalt nitrate, cobalt sulfate, cobalt acetate, cobalt chloride, or a mixture thereof. In another embodiment, the catalyst is prepared using a catalyst precursor comprising a metal that comprises a cobalt compound which is at least partly in the solid state, e.g., a water-insoluble cobalt compound such as cobalt carbonate, cobalt hydroxide, cobalt phosphate, cobalt phosphite, cobalt formate, cobalt sulfide, cobalt molybdate, cobalt tungstate, cobalt oxide, cobalt alloys such as cobalt-molybdenum or cobalt-iron alloys, or a mixture thereof. In another embodiment, the catalyst is prepared using a catalyst precursor comprising a metal that comprises a water-soluble cobalt sulfate solution which optionally also includes a second promoter metal compound, such as an iron component in the solute state selected from iron acetate, chloride, formate, nitrate, sulfate, or a mixture thereof. In one embodiment, the catalyst is prepared using a catalyst precursor that comprises a metal comprising a cobalt sulfate aqueous solution.

[0110] In embodiments, at least a portion of the catalyst particles is dispersed as particles separate from the carbonaceous material during the pretreatment step, during the step of heating the carbonaceous material to a conversion temperature, or during the conversion process.

[0111] In embodiments, the catalyst is dissolved or otherwise suspended in the liquid phase, e.g., as fine particles, emulsified droplets, etc. The dispersed catalyst can be added to the coal before contact with the hydrocarbonaceous liquid, it can be added to the hydrocarbonaceous liquid before contact with the coal, or it can be added to the coal-liquid slurry. In some such embodiments, the dispersed catalyst is added in the form of an oil/aqueous solution emulsion of a water-soluble compound of the catalyst hydrogenation component. The water soluble salt of the catalytic metal can be essentially

any water soluble salt of metal catalysts. The nitrate or acetate may be the most convenient form of some metals. Non-limiting active sources of cobalt include cobalt nitrate and cobalt acetate. Non-limiting sources of iron are iron nitrate or iron acetate. In embodiments, organometallic complexes such as ferrocene are also employed as sources of iron. For molybdenum, tungsten or vanadium, a complex salt such as an alkali metal or ammonium molybdate, tungstate, or vanadate may be preferable. Mixtures of two or more metal salts can also be used. Particular salts are ammonium heptamolybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, nickel dinitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$, and sodium tungstate dihydrate $[\text{NaWO}_4\cdot 2\text{H}_2\text{O}]$. Any convenient process can be used to emulsify the salt solution in the hydrocarbon medium. The dispersed dissolution catalyst can also be an oil-soluble compound containing a catalytic metal, for example, ferrocene, phosphomolybdic acid, naphthenates of molybdenum, chromium, and vanadium, etc. Suitable oil-soluble compounds can be converted to dissolution catalysts in situ.

[0112] In embodiments, the particulate catalyst comprises cobalt and a second metal as an unsupported catalyst, meaning that the components of the catalyst are not associated with or supported on inorganic carriers such as silica, alumina, magnesia, carbon, etc. In other embodiments, at least a portion of the metal components of the catalyst composition are associated with or supported on at least one inorganic carrier or binder. The binder material can comprise any materials that are conventionally utilized as binders in hydroprocessing catalysts. Suitable binder material includes, for example, silica, alumina such as (pseudo) boehmite, silica-alumina compounds, gibbsite, titania, zirconia, cationic clays or anionic clays such as saponite, bentonite, kaoline, sepiolite or hydrocalcite, or combinations or mixtures thereof. In one embodiment, one or more binder materials are selected from silica, colloidal silica doped with aluminum, silica-alumina, alumina, titanium, zirconia, or a mixture thereof. In another embodiment, the binder material comprises a refractory oxide material having at least 50 wt. % of titania, on an oxide basis. Any suitable alumina binder can be used in the catalyst preparation process. In one embodiment, the alumina binder has a surface area ranging from 100 to 400 m^2/g , with a pore volume ranging from 0.5 to 1.5 m^3/g measured by nitrogen adsorption. Similarly, any suitable titania binder can be used in the catalyst preparation process. In one embodiment, the titania of the binder has an average particle size of less than 50 microns (such as less than about 5 microns) and/or greater than 0.005 microns. In another embodiment, the titania of the binder has a BET surface area of 10 to 700 m^2/g .

[0113] In some embodiments, the binder material is a binder that has undergone peptization. In another embodiment, precursors of the binder materials are used in the preparation of the catalyst, wherein the precursor is converted into an effective or functional binder during the catalyst preparation process. Suitable binder material precursors, in this regard, include alkali metal aluminates (to obtain an alumina binder), water glass (to obtain a silica binder), a mixture of alkali metal aluminates and water glass (to obtain a silica alumina binder), 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 silicon (to prepare a cationic clay and/or anionic clay), chlorohydril, aluminum sulfate, or a combination or mixture thereof. In the case of supported

catalysts, the weight ratio of metal components (ie. cobalt and the second metal components) to support components is in the range of 10:1 to 1:10.

[0114] In embodiments, at least a portion of the catalyst particles comprises additional components, such as catalyst promoters. Such promoters are selected from the group consisting of a non-noble Group VIII metal (such as Ni, Co, Fe), a Group VIB metal (such as Cr), a Group IVB metal (such as Ti), a Group IIB metal (such as Zn), a Group IB metal (such as Cu) and combinations and mixtures thereof.

[0115] During the conversion process, during which time the solid carbonaceous material contacted with the active sources of the catalyst composition and optionally pretreated at a temperature in the range of 100-350° C. and then heated to conversion temperature for conversion of the carbonaceous material to liquid materials, the active sources of the catalyst are converted to their active forms. The conversion process is facilitated by the addition of sulfur to the catalyst.

[0116] Properly sulfided cobalt species such as CoS and cobalt alkyl dithiocarbamate, cobalt alkyl phosphorodithioate and sulfided metallic species such as MoS₂, ammonium tetrathiomolybdate, NiS, ZnS, WS₂, SnS, TiS₂, CuS, FeS, Fe₂S₃, moly alkyl dithiocarbamate, iron alkyl dithiocarbamate, titanium alkyl dithiocarbamate, iron alkyl phosphorodithioate, can be used directly as catalyst precursors without pre-sulfiding. For a non-sulfided metal precursor, including cobalt-based cobalt metal, cobalt oxide, cobalt acetate, cobalt nitrate, cobalt sulfate and other cobalt salts, cobalt minerals and cobalt organo compounds; iron-based iron metal, iron oxide, ferrous sulfate, ferric nitrate and other iron salts, red mud and other iron minerals, ferrocene and other iron organo compounds, molybdenum-based, tungsten-based, nickel-based, cobalt-based, titanium-based, copper-based or tin-based metal, oxide, salts, minerals and organo compounds, etc., elemental sulfur or other sulfiding agent such as DMDS, H₂S, CS₂, and (NH₄)₂S can be used to pre-sulfide the catalyst precursor to form metal sulfides or the sulfiding agent is added directly during the hydroconversion run to properly sulfide the catalyst at the atomic ration of (S/(Co+other metal))=1/1 to 10/1. Alternatively, one or more sulfur compounds can be added during, or subsequent to the pretreating step to activate the catalyst or catalyst precursor to its corresponding sulfided active catalyst. The one or more sulfur compounds can be introduced at any point of the system. Any suitable amount of the one or more sulfur compounds can be used in the context of the present invention. In one embodiment, one or more sulfur compounds are introduced into the pretreatment zone following the performance of the pretreatment process and before the pretreatment composition is delivered to the conversion zone. In another embodiment, one or more sulfur compounds are introduced into the conversion (i.e. liquefaction) zone. In one embodiment, a concentration of sulfur is introduced such that the atomic ration of sulfur to metal in the catalyst is from about 2:1 to about 10:1.

[0117] Any suitable sulfur compound may be used in this regard. In one embodiment, the sulfiding agent is hydrogen sulfide (H₂S). In one embodiment, the sulfiding agent is in the form of a solution that under prevailing conditions is decomposable into hydrogen sulfide, present in an amount in excess of the stoichiometric amount required to form the catalyst. In another embodiment, the sulfiding agent is selected from the group of ammonium sulfide, ammonium polysulfide ((NH₄)₂S_x), ammonium thiosulfate ((NH₄)₂S₂O₃), sodium thiosul-

fate (Na₂S₂O₃), thiourea (CSN₂H₄), carbon disulfide (CS₂), dimethyl disulfide (DMDS), dimethyl sulfide (DMS), tertiarybutyl polysulfide (PSTB), tertiarynonyl polysulfide (PSTN), and mixtures thereof. In another embodiment, the sulfiding agent is selected from elemental sulfur and sulfur containing hydrocarbons. 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 may require an additional separation process step to remove the alkali- and/or alkaline earth metals from the spent catalyst.

[0118] Elemental sulfur may be added to the pretreatment composition in the form of a sublimed powder or as a concentrated dispersion (such as a commercial flower of sulfur). Allotropic forms of elemental sulfur, such as orthorhombic and monoclinic sulfur, as also suitable for use herein. In one embodiment, the one or more sulfur compounds are in the form of a sublimed power (flowers of sulfur), a molten sulfur, a sulfur vapor, or a combination or mixture thereof.

Other Additives

[0119] Any additional additives can be utilized during or subsequent to the pretreating step, such as, to enhance or facilitate the pretreatment process (such as by enhancing, facilitating, and/or enhancing dispersion of the catalyst or catalyst precursor into the carbonaceous material) and/or to enhance or facilitate hydroconversion of the pretreated carbonaceous material.

[0120] Any suitable surfactant can be utilized in the context of the invention, such as to improve dispersion, metal surface area, morphology, and/or other characteristics of the catalyst or catalyst precursor. Suitable surfactants include, for example, any anionic surfactant, zwitterionic surfactant, amphoteric surfactant, nonionic surfactant, cationic surfactant, or combination or mixture thereof. Suitable non-ionic surfactants include, for example, polyoxyethylenesorbitan monolaurate, polyoxyethylenated alkyphenols, polyoxyethylenated alkyphenol ethoxylates, and the like. Suitable cationic surfactants include, for example, quarternary long-chain organic amine salts, quarternary polyethoxylated long-chain organic amine salts, and the like, such as water-soluble cationic amines (e.g., cetyl trimethyl ammonium bromide, cetyl trimethyl ammonium chloride, dodecyl trimethyl ammonium amine, nonyl trimethyl ammonium chloride, dodecyl phenol quaternary amine soaps, or combinations or mixtures thereof). Suitable anionic surfactants such as sodium succinate compounds, include, for example, dioctyl sodium sulfosuccinate or sodium bis(2-ethylhexyl)sulfosuccinate). Suitable surfactants can also comprise solvent materials having a high surface tension property, such as ethylene carbonate; benzophenone; benzyl cyanide; nitrobenzene; 2-phenylethanol; 1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; diethyleneglycol; triethyleneglycol; glycerol; dimethyl sulfoxide; N-methyl formamide; N-methylpyrrolidone; and combinations and mixtures thereof. Suitable surfactants also include those surfactants having a high surface tension, such as N-methyl pyrrolidone. Other examples of surfactants include acetonitrile, acetone, ethyl acetate, hexane, diethyl ether, methanol, ethanol, acetyl acetone, diethylcarbonate, chloroform, methylene chloride, diethyl ketone, and combination and mixtures thereof. In another embodiment, the surfactant comprises a nitrogen- or phosphorous-containing organic additive having a carbosulfide phase with enhanced

catalytic activities. The amount of the N-containing/P-containing organic additive to be added generally depends on the desired activity of the final catalyst composition.

[0121] In another embodiment, the surfactant is an ammonium or phosphonium of the formula $R_1R_2R_3R_4Q^+$, wherein Q is nitrogen or phosphorous, wherein at least one of R_1, R_2, R_3, R_4 is an aryl or alkyl group having 8-36 carbon atoms (e.g., $C_{10}H_{21}, C_{16}H_{33}, C_{18}H_{37}$, or a combination thereof), and wherein the remainder of R_1, R_2, R_3, R_4 is selected from the group consisting of hydrogen, an alkyl group having 1-5 carbon atoms, or a combination thereof. Suitable such examples of surfactants include: cetyltrimethylammonium, cetyltrimethylphosphonium, octadecyltrimethylphosphonium, cetylpyridinium, myristyltrimethylammonium, decyltrimethylammonium, dodecyltrimethylammonium, dimethyldidodecylammonium, or a combination or mixture thereof. The compound from which the above ammonium or phosphonium ion is derived may be, for example, a hydroxide, halide, silicate, or combination or mixture thereof.

[0122] In one embodiment, the surfactant comprises a nitrogen-containing organic additive, such as aromatic amines, a cyclic aliphatic amines, a polycyclic aliphatic amines, or a combination or mixture thereof. In another embodiment, the surfactant comprises a nitrogen-containing organic additive is selected from compounds containing at least one primary, secondary, and/or tertiary amine group (such as hexamethylenediamine, monoethanolamine, diethanolamine, triethanolamine, N,N-dimethyl-N'-ethylethylenediamine, or a combination or mixture thereof); amino alcohols (such as, for example, 2 (2-amino ethyl amino)ethanol, 2 (2-aminoethoxy, or a combination or mixture thereof) ethanol, 2-amino-1-butanol, 4-amino-1-butanol, 2,2-diethoxyethylamine, 4,4-diethoxybutylamine, 6-amino-1-hexanol, 2-amino-1,3-propanediol, 3-amino-1,2-propanediol, 3-amino-1-propanol, or a combination or mixture thereof); and amino alkoxy-silanes (such as, for example, 3-glycidoxypopyl) trimethoxysilane, 3-(2-aminoethylamino) propyltrimethoxysilane, 3-aminopropyl)trimethoxy-silane, or a combination or mixture thereof).

[0123] In another embodiment, the surfactant is an organic carboxylic acid surfactant or stabilizer. In one embodiment, for example, the surfactant is citric acid. In another embodiment, the surfactant is pentadecanoic acid, decanoic acid, or other similar long chain acids. In yet another embodiment, the surfactant is alginate acid.

[0124] The optional additives can be utilized at any suitable point prior to or after the pretreatment process and/or hydroconversion process. In one embodiment, one or more additives are combined with one or more of the carbonaceous material, hydrocarbonaceous liquid, and one or more catalysts or catalyst precursors prior to pretreatment. In another embodiment, the additive(s) are combined with the carbonaceous material, hydrocarbonaceous liquid, and catalysts or catalyst precursors during the pretreatment process. In another embodiment, the additive(s) are combined with the pretreated carbonaceous material following pretreatment and before hydroconversion. In yet another embodiment, the additive(s) are combined with the pretreated carbonaceous material following during hydroconversion.

[0125] The additive(s) can be utilized in any suitable concentration. In one embodiment, for example, the additive(s) are utilized in a concentration of about 0.001 to 5 wt. % of the total pretreatment mixture. In another embodiment, the additive(s) are utilized in a concentration of about 0.005 to 3 wt. %

of the total pretreatment mixture. In another embodiment, the additive(s) are utilized in a concentration of about 0.01 to 2 wt. % of the total pretreatment mixture. If the additive(s) are solely added to the hydroconversion feedstock, the amount to be added ranges from 0.001 to 0.05 wt. % (such as about 0.005-0.01 wt. %) of the feed, or in any suitable concentration, such as described, for example, in *Acta Petrolei Sinica*, Vol. 19, Issue 4, pp. 36-44, ISSN 10018719 and in *Khimiya I Tekhnologiya Topilv I Masel*, Issue 3, Year 1997, pp. 20-21, ISSN 00231169, the contents of which are incorporated herein by reference in their entirety.

Mixing

[0126] Any suitable process or system can be used to combine and/or mix the carbonaceous material with the hydrocarbonaceous liquid and the catalysts or catalyst precursors. In some embodiments, any suitable mixer is used to simultaneously, successively, and/or sequentially mix the carbonaceous material, hydrocarbonaceous liquid, and the catalyst or catalyst precursors in a manner suitable to form a homogeneous or heterogeneous mixture (or slurry), as desired. In other embodiments, a mixer is utilized in conjunction with any suitable grinder (such as a hammer mill, a ball mill, a rod mill, or a combination thereof, or the like), such that at least a portion of the carbonaceous material is ground, optionally in the presence of the hydrocarbonaceous liquid and/or the one or more catalysts or catalyst precursors and mixed to form a homogeneous or heterogeneous slurry, as desired. In some embodiments, the mixer and/or grinder comprises a gas delivery system for providing an inert or a reducing atmosphere (such as, for example, hydrogen, nitrogen, helium, argon, syn-gas, or any combination or mixture thereof) during mixing and/or grinding of the carbonaceous material, the hydrocarbonaceous liquid, and/or the catalyst or catalyst precursors. In some embodiments, the mixer and/or grinder are situated upstream of the pretreatment system. In other embodiments, the mixer and/or grinder form a portion of the pretreatment system. In embodiments, the catalyst precursor used in this process can be mixed directly to ground coal or other carbonaceous materials before feeding into the reactor, or added into coal during coal solvent grinding. The catalyst can be dissolved and sprayed onto coal or impregnated onto coal by incipient wetness using methanol/ethanol or water as dissolving/wetting agent. The catalyst can also be dispersed or soluble in the solvent that is then mixed with coal.

[0127] An embodiment of the invention is illustrated in FIG. 1. Coal feed **3**, with at least 50 wt % of the coal particles having a mean particle diameter of less than 0.5 inches, is combined with catalytic material **5**, comprising an active source of cobalt and an active source of iron in a molar ratio of cobalt to iron within the range of between 0.1/1 to 10/1, and the combination **1** is passed to preheat furnace **20** for heating to a reaction temperature in the range of between 350° C. and 500° C. The heated combination of coal and the catalytic material **23** leaving the preheat furnace is then passed to reaction zone **30** for conversion of at least a portion of the coal to liquid product **33**.

[0128] Considering an exemplary process of the invention illustrated in FIG. 2, coal feed **103**, with at least 50 wt % of the coal particles having a mean particle diameter of less than 0.5 inches, is combined with catalytic material **105**, comprising an active source of cobalt and an active source of iron in the molar ratio of cobalt to iron within the range of between 0.1/1 to 10/1, and the combination **101** is passed to pretreatment

zone **110** for maintaining the combination at a pretreatment temperature within the range of 100-350° C. and for a time of between 5 and 600 minutes. Following pretreatment, the combination **113** is passed to preheat furnace **120** for heating to a reaction temperature in the range of between 350° C. and 500° C. The heated combination of coal and the catalytic material **123** leaving the preheat furnace is then passed to reaction zone **130** for conversion of at least a portion of the coal to liquid product **133**.

[0129] Considering an exemplary process of the invention illustrated in FIG. 3, coal feed **203**, with at least 80 wt % of the coal particles having a mean particle diameter in the range of 50 microns to 500 microns, is passed to pretreatment zone **210**. In a particular exemplary process, coal is supplied to pretreatment zone as a powder. In another exemplary process, coal is supplied as a slurry in a hydrocarbonaceous liquid, such as a coal derived distillate fraction.

[0130] A catalytic material **205**, comprising an active source of cobalt and an active source of iron in the molar ratio of cobalt to iron within the range of between 3/1 and 1/3, is combined with the coal particles in the pretreatment zone. In an embodiment, the cobalt is supplied to the pretreatment zone as an aqueous solution or slurry of a cobalt salt such as cobalt nitrate, cobalt chloride, cobalt sulfate, cobalt acetate, cobalt sulfide, cobalt oxide or cobalt carbonate. Iron is supplied to the pretreatment zone as an aqueous solution or slurry of an iron salt such as iron nitrate, iron chloride, iron sulfate, iron acetate, iron sulfide, iron oxide or iron carbonate. In another embodiment, cobalt and iron are added as organometallic compounds contained in a liquid such as a coal derived distillate fraction. Exemplary organometallic compounds include cobalt alkyl dithiocarbamate and ferrocene. An active source of sulfur **207** is added to the pretreatment zone to supply a sulfur to catalytic metal atomic ratio within the range of between 2/1 and 6/1. Hydrogen or a hydrogen containing gas **209** is further supplied to the pretreatment zone to maintain a pressure within the pretreatment zone within a range of between atmospheric pressure and 500 psig. In another embodiment, hydrogen or a hydrogen containing gas is supplied to the pretreatment zone to maintain a pressure within the pretreatment zone within a range of between 500 psig and 3500 psig. The materials in the pretreatment zone are maintained at a pretreatment temperature within the range of 180-220° C. and for a time of between 5 and 600 minutes. Following pretreatment, the combination **213** is passed to preheat furnace **220** for heating to a reaction temperature in the range of between 350° C. and 500° C. The heated combination of coal and the catalytic material **223** leaving the preheat furnace is then passed to reaction zone **230** for conversion of at least a portion of the coal to liquid product **233**.

[0131] Considering an exemplary process of the invention illustrated in FIG. 4, coal feed **303**, with at least 50 wt % of the coal particles having a mean particle diameter of less than 0.5 inches is passed to pretreatment zone **310**. A catalytic material **307**, comprising an active source of cobalt and a catalytic material comprising an active source of iron **309** in the molar ratio of cobalt to iron within the range of between 0.1/1 to 10/1, are combined with the coal particles in the pretreatment zone, and the combination is maintained at a pretreatment temperature within the range of 100-350° C. and for a time of between 5 and 600 minutes. Following pretreatment, the combination **313** is passed to preheat furnace **320** for heating to a reaction temperature in the range of between 350° C. and 500° C. The heated combination of coal and the catalytic

material **323** leaving the preheat furnace is then passed to reaction zone **330** for conversion of at least a portion of the coal to liquid product **333**.

Hydroconversion

[0132] The carbonaceous material is subjected to any suitable hydroconversion and/or liquefaction conditions to produce a product-enriched hydrocarbonaceous material comprising any desired liquid and/or gaseous products. The carbonaceous material (such as coal) is introduced into at least one hydroconversion zone wherein the pretreated carbonaceous material encounters suitable temperature, pressure, and additives (such as sulfur-containing compounds) to at least partially or substantially activate the catalyst or catalyst precursor of the pretreated carbonaceous material, and generate liquid and/or gaseous products. In one embodiment, for example, greater than about 50 wt. %, such as about 55 wt. %, about 60 wt. %, about 65 wt. %, about 70 wt. %, about 75 wt. %, about 80 wt. %, about 85 wt. %, about 90 wt. %, about 95 wt. %, about 96 wt. %, about 97 wt. %, about 98 wt. %, or even about 99 wt. % of the catalyst or catalyst precursor of the pretreated carbonaceous material becomes active catalyst, such that it possesses and/or exhibits hydroconverting activity.

[0133] Suitable hydroconverting temperatures include, but are not limited to, temperatures greater than about 350° C., such as greater than about 375° C., about 400° C., about 425° C., about 450° C., about 475° C., about 500° C. In some such embodiments, the step of hydroconverting the heated material is conducted at a temperature in the range of between 350° C. and 500° C. In some such embodiments, the heated material is reacted in the hydroconversion step for a time of at least 10 minutes.

[0134] Suitable hydroconverting pressures include, but are not limited to, within the range of 300-5000 psig (such as within the range of about 300-4800 psig, about 300-4600 psig, about 300-4400 psig, about 300-4200 psig, about 400-4000 psig, about 500-3500 psig, 1000-3000 psig, 1200-2800 psig, 1400-2600 psig, or even about 1500-2600 psig) of any suitable gas such as a hydrogen containing gas (such as a hydrogen/methane mixture, or a hydrogen/carbon dioxide/water mixture) atmosphere and/or a syn-gas atmosphere. In one embodiment, in this regard, the pretreated carbonaceous material is suitable for low or lower pressure hydroconversion (such as a hydroconversion pressure less than about 2000 psig, such as less than about 1800 psig, or even less than about 1600 psig). Specifically, for example, hydroconversion of the pretreated carbonaceous material can yield at least about 10% higher (such as at least about 20%, about 40%, about 60%, about 80%, about 100%, about 150%, about 200%, about 300%, or even at least about 400% higher liquid product yield at a hydroconversion pressure less than about 2000 psig (such as less than about 1800 psig, or even less than about 1600 psig) than the same carbonaceous material that has not been pretreated. In another embodiment, hydroconversion of the pretreated carbonaceous material consumes about 10% less (such as about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, or even about 100% less) hydrogen, as compared to the same carbonaceous material that has not been pretreated.

[0135] In embodiments, the hydroconversion of the solid carbonaceous material is accomplished by heating the solid carbonaceous material for a time sufficient to form a liquid product. In some such embodiments, the solid carbonaceous

material is heating in the presence of at least one active source of cobalt and at least one active source of a second metal. In some such embodiments, the solid carbonaceous material is heated at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig. In some such embodiments, the solid carbonaceous material is heated at a reaction temperature in the range of between 350° C. and 500° C. In some embodiments, the solid carbonaceous material is heated for a time within the range of 5 minutes to 600 minutes.

[0136] In one embodiment, hydroconversion and/or liquefaction of the carbonaceous material occurs in a single reactor. In another embodiment, hydroconversion and/or liquefaction of the carbonaceous material occurs in two or more (such as a plurality) of zones or reactors for hydroconversion which may be arranged in any suitable manner (such as in parallel, or in series such that, for example, the temperature in each reactor in series is progressively higher and/or there is a commensurate increase in the hydrogen partial pressure in each downstream reactor). Preferably, hydroconversion and/or liquefaction of the pretreated carbonaceous material occurs in a reactor or zone that is separate and/or distinct from the pretreatment reactor or zone.

[0137] In one embodiment, hydroconversion and/or liquefaction of the carbonaceous material produces a liquid yield greater than about 50%, about 55%, about 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 87%, about 90%, about 95%, or even greater than about 99%. In an embodiment, pretreatment of the carbonaceous material results in a liquid yield that is at least about 10% higher (such as at least about 15%, about 20%, about 25%, about 30%, about 35%, or even at least about 40% higher) than the liquid product yield of a similar carbonaceous material that is not pretreated prior to hydroconversion. In another embodiment, hydroconversion and/or liquefaction of the pretreated carbonaceous material produces a total conversion (such as of coal) greater than about 80%, about 85%, about 90%, about 95%, or even 99%.

[0138] In some embodiments, pretreatment of the carbonaceous material results in a total conversion (such as of coal) that is at least about 5% higher (such as at least about 10%, about 12%, about 14%, about 16%, about 18%, or even at least about 20% higher) than the conversion of a similar carbonaceous material that is not pretreated prior to hydroconversion. In other embodiments, hydroconversion and/or liquefaction of the pretreated carbonaceous material produces less than about 10% (such as less than about 8%, about 6%, about 4%, about 3%, about 2%, or even less than about 1%) of C₁-C₃ gases.

Separation of Hydroconversion Products

[0139] The effluent from the hydroconversion zone can be fed into any suitable one or more separation zones. In one embodiment, the effluent is fed into a first separation zone wherein lighter products such as gases, naptha, and distillate are removed via overhead lines. Such a first separation zone can be run at a substantially atmospheric pressure. A bottoms, or high boiling, fraction of the effluent from the first separation zone can optionally be recycled to the hydroconversion reaction zone. All or some of the remaining effluent of the first separation zone can be passed to a second separation zone wherein it is fractionated into a gas oil fraction and a bottoms fraction. The bottoms fraction of the second separation zone can be passed to a third separation zone. A portion of the gas

oil can be recycled to the hydroconversion zone. In this regard, any suitable high pressure, medium pressure, and low pressure separators can be used in the context of the present invention.

Recovery of Catalyst or Catalyst Precursor

[0140] The one or more separation systems or zones can be followed by one or more catalyst and/or metal recovery systems or zones in which at least a portion (such as one or more metals) of the catalyst and/or catalyst precursor is recovered from one or more portions or fractions of the hydroconverted carbonaceous material. In one embodiment, metal from a metal-containing catalyst and/or metal-containing catalyst precursor is recovered in the recovery system from a solids fraction (such as a residual solids fraction) of the hydroconverted carbonaceous material that was separated and/or collected in the separation system (and which may include ash).

[0141] The recovery system can be operated at any suitable temperature, such as at a temperature of about 1200-1900° C., such as about 1300-1800° C., or even 1400-1700° C. In one embodiment, the recovery system provides an atmosphere of air that is suitable to cause spent catalysts (such as molybdenum sulfides) to be oxidized and sublimated to MoO₃, in the case where the metal is molybdenum, such as described in U.S. Pat. App. Ser. No. 60/015,096, filed Dec. 19, 2007, the contents of which are incorporated by reference in their entirety. The treated spent catalyst, catalyst precursor, and/or recovered metal can be collected and passed from the catalyst recovery zone to a catalyst or catalyst precursor preparation zone.

Catalyst or Catalyst Precursor Preparation

[0142] The one or more recovery systems can be followed by one or more catalyst or catalyst precursor preparation systems, in which at least a portion of the catalyst or catalyst precursor (such as metal of the catalyst precursor) recovered in the recovery system is reacted to form a catalyst or catalyst precursor (such as the same catalyst or catalyst precursor that was originally used to pretreat the carbonaceous material).

[0143] In one embodiment, for example, a recovered metal of the catalyst or catalyst precursor (such as MoO₃) is reacted with a sulfur compound (such as ammonium sulfide) to form ammonium tetrathiomolybdate catalyst precursor. The resulting formed catalyst or catalyst precursor can then be delivered, optionally in combination with new or fresh catalyst precursor, into the pretreatment system and/or the hydroconversion system.

Characterization of the Catalyst

[0144] In embodiments, a catalyst which is active for converting at least a portion of the solid carbonaceous material to a liquid product, having the formula (R¹)_a(M¹)_b(L¹)_c(S¹)_d(C¹)_e(H¹)_f(O¹)_g(N¹)_h, and having improved morphology and dispersion characteristics, can be characterized using techniques known in the art, including elemental analysis, Surface Area analysis (BET), Particle Size analysis (PSA), Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDS), and other methods. In one method, electron microscopy is used to complement the x-ray diffraction study. In another method, the surface area of the catalyst is determined using the BET

method. In yet another method, scanning tunneling microscopy (STM) and density functional theory (DFT) can be used to characterize the catalyst.

[0145] The catalyst of the formula $(R^p)_i(M^f)_a(L^u)_b(S^v)_d(C^w)_e(H^x)_f(O^y)_g(N^z)_h$ is characterized as giving excellent conversion rates in the upgrades of coal depending on the configuration of the upgrade process and the concentration of the catalyst used. In one embodiment, the slurry catalyst provides conversion rates of at least 70% in one embodiment, at least 75% in a second embodiment, at least 80% in a third embodiment, and at least 90% in a fourth embodiment. In one embodiment of a coal upgrade system employing the catalyst of the formula $(R^p)_i(M^f)_a(L^u)_b(S^v)_d(C^w)_e(H^x)_f(O^y)_g(N^z)_h$ at least 98 wt. % of coal feed is converted to lighter products. In a second embodiment, at least 98.5% of coal feed is converted to lighter products. In a third embodiment, the conversion rate is at least 99%. In a fourth embodiment, the conversion rate is at least 95%. In a fifth embodiment, the conversion rate is at least 80%. As used herein, conversion rate refers to the conversion of coal feedstock to less than 1200° F. (650° C.) boiling point materials.

[0146] In one embodiment, the catalyst has a pore volume in the range of from 0.05 to 5.0 ml/g as determined by nitrogen adsorption. In a second embodiment, the pore volume is in the range of from 0.1 to 4.0 ml/g, such as from 0.1 to 3.0 ml/g or from 0.1 to 2.0 ml/g.

[0147] In embodiments, the catalyst has a surface area of at least 5 m²/g, or at least 10 m²/g, or at least 50 m²/g, or greater than 100 m²/g, or greater than 200 m²/g, as determined via the B.E.T. method. In embodiments, the catalyst is characterized by aggregates of crystallites of 10 to 20 angstrom, for an overall surface area greater than 100 m²/g.

[0148] In embodiments, the catalyst has a particle size ranging from nanometer to micrometer (μm) size dimensions. Exemplary suspended catalyst particles have a median particle size of 0.0005 to 1000 microns, or a median particle size of 0.001 to 500 microns, or a median particle size of 0.005 to 100 microns, or a median particle size of 0.05 to 50 microns. In embodiments, the catalyst in the form of a suspension that is characterized by a median particle size of 30 nm to 6000 nm. In embodiments, the catalyst has an average particle size in the range of 0.3 to 20 μm.

[0149] In embodiments, the catalyst comprises catalyst particles of molecular dimensions and/or extremely small particles that are colloidal in size (i.e., less than 1 micrometer or less than 0.1 micrometer or in the range of 0.1 to 0.001 micrometer). In some embodiments, the catalyst is dispersed on the coal surface in 1 to 100 nanometer particles by impregnation of the catalyst precursor on the coal. In some embodiments, the catalyst forms a slurry catalyst, in a hydrocarbon diluent, having "clusters" of the colloidal particles, with the clusters having an average particle size in the range of 1-100 micrometers.

[0150] As is further illustrated in the following examples, the systems and processes described herein can be used to achieve optimization and efficiency in the production of any desired proportions (or yield percentages) of liquid and/or gas products having a variety of desired properties. Specifically, a full range of hydroconversion products can be accomplished under a variety of hydroconversion conditions (such as at low hydrogen pressure and/or with short duration) through selection of any of a variety of combinations of hydrocarbonaceous liquid, catalysts and/or catalyst precursors, as well as pretreatment and hydroconversion conditions. In this manner, the systems and process offers tremendous flexibility to a user in being able to achieve desired hydroconversion products from any solid carbonaceous material using any of a variety of

different combinations of hydrocarbonaceous liquid, catalyst, and/or catalyst precursor, as well as pretreatment and hydroconversion conditions.

EXAMPLES

Example 1 (Fe/Zn)

[0151] Run 1—A solution of a mixed catalyst precursor iron nitrate (Fe(NO₃)₃·9H₂O) and zinc nitrate (Zn(NO₃)₂·6H₂O) dissolved in methanol was prepared. A sample of moisture-free coal feed (i.e. less than 1% by weight water) having a particle size of less than 100 mesh was impregnated to incipient wetness with the solution, at a solution to coal weight ratio of 1 to 1, to yield an iron to coal loading on a dry, ash-free (daf) basis of 1% iron and a zinc to coal loading on a dry, ash free basis of 1 wt % zinc. The catalyst impregnated coal was then dried under nitrogen at 105° C. for up to 24 hours to remove the methanol. The dried catalyst impregnated coal was mixed with an FCC-type process oil (500° F.-cut) as solvent, at a solvent to coal ratio of 1.6 to 1. Elemental sulfur was added to sulfide the iron and zinc, at a sulfur to iron molar ratio of 2 to 1 and a sulfur to zinc ratio of 2 to 1. The mixture was then heated quickly in a vessel to 200° C., and held at 200° C. for 2 hours, while the hydrogen partial pressure within the vessel increased from about 100 psia to about 1000 psia. The mixture was then further heated to 430° C., and then held at 430° C. for 3 hours under a hydrogen partial pressure of 2500 psia. After 3 hours the reaction vessel containing the sulfided solvent and coal mixture, hydrogen and any reaction products was quenched to room temperature. Product gases (CO, CO₂, C₁, C₂ and C₃) were vented through a wet test meter to determine the gas yield. Solids, primarily unconverted coal, ash and catalyst sulfide were separated from liquid products (C₄⁺) by filtration. Coal conversion was determined as follows:

$$\text{Coal conversion} = (\text{solids recovered} - (\text{ash in coal} + \text{recovered catalyst})) / \text{coal feed}$$

By subtracting the solvent added at the beginning of the run, oil yield was determined based on dry, ash-free basis coal. Product yields are tabulated in Table I.

[0152] Run 2—Run 1 was repeated using zinc nitrate as the catalyst precursor at a zinc to coal loading on a dry, ash free basis of 2 wt % zinc. Elemental sulfur was added to sulfide the zinc, at a sulfur to zinc ratio of 2 to 1. Product yields are tabulated in Table I.

[0153] Run 3—Run 1 was repeated using iron nitrate as the catalyst precursor at an iron to coal loading on a dry, ash free basis of 2 wt % iron. Elemental sulfur was added to sulfide the iron, at a sulfur to iron ratio of 2 to 1. Product yields tabulated in Table I show that the catalyst combination containing iron and zinc produces much higher liquid yields and coal conversion than do catalysts containing either iron or zinc alone.

TABLE I

Run	Reaction Condition	Liquid Yield (%)	Coal Conversion (%)	Gas Yield (%)
1	430° C., 3 hr, 1% Zn, 1% Fe, S	73.8	97.8	16.4
2	430° C., 3 hr, 2% Zn, S	50.4	80.6	25.3
3	430° C., 3 hr, 2% Fe, S	68.7	94.8	15.5

Example 2 (Fe/Co)

[0154] Run 4—Run 1 was repeated using iron nitrate (Fe(NO₃)₃·9H₂O) and cobalt nitrate (Co(NO₃)₂·6H₂O) mixed

catalyst precursor at an iron to coal loading on a dry, ash free basis of 1 wt % iron, and a cobalt to coal loading on a dry, ash free basis of 1 wt % cobalt. Elemental sulfur was added to sulfide the iron and cobalt, at a sulfur to iron molar ratio of 2 to 1 and a sulfur to cobalt ratio of 2 to 1. Product yields are compared with an iron catalyst precursor in Table II.

TABLE II

Run	Reaction Condition	Liquid Yield (%)	Coal Conversion (%)	Gas Yield (%)
4	430° C., 3 hr, 1% Co, 1% Fe, S	72.8	97.6	16.8
3	430° C., 3 hr, 2% Fe, S	68.7	94.8	15.5

What is claimed is:

1. A process for converting solid carbonaceous material to a liquid product, comprising maintaining a solid carbonaceous material in the presence of at least one active source of cobalt and at least one active source of a second metal at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig for a time sufficient to form a liquid product.

2. The process of claim 1, the process comprising:

a) preparing a combination of the solid carbonaceous material, at least one hydrocarbonaceous liquid, at least one active source of cobalt and at least one active source of the second metal; and

b) passing the combination to a hydroconversion reaction zone and maintaining the solid carbonaceous material at a reaction temperature of greater than 350° C. and at a pressure in the range of 300 to 5000 psig for a time sufficient to convert at least a portion of the solid carbonaceous material to a liquid product boiling in the temperature range of C₅ to 650° C.

3. The process of claim 2, wherein the step of preparing the combination comprises:

a) preparing a mixture comprising at least one active source of cobalt and at least one active source of a second metal;

b) combining the mixture with coal to form catalyst-containing coal particles; and

c) providing a hydrocarbonaceous liquid to the catalyst-containing coal particles to prepare the combination.

4. The process of claim 3, further comprising drying the catalyst-containing coal particles prior to the step of passing the combination to the hydroconversion reaction zone.

5. The process of claim 3, wherein the mixture further comprises a surfactant.

6. The process of claim 2, further supplying an active source of sulfur to the combination.

7. The process of claim 6, wherein the active source of sulfur is supplied at an atomic ratio of sulfur to metal within the range of between 0.1 to 1 and 10 to 1.

8. The process of claim 2, further comprising supplying hydrogen or hydrogen-containing gas to the hydroconversion reaction zone.

9. The process of claim 2, further comprising pretreating the combination at a pretreatment temperature within the range of 100-350° C. and for a time of between 5 and 600 minutes prior to passing the combination to the hydroconversion reaction zone.

10. The process of claim 9, further comprising pretreating the combination in the presence of an active source of sulfur.

11. The process of claim 9, further comprising pretreating the combination in the presence of hydrogen or a hydrogen-containing gas.

12. The process of claim 1, wherein the second metal is selected from the group consisting of iron, molybdenum, nickel, manganese, vanadium, tungsten, copper, titanium, chromium and tin.

13. The process of claim 1, wherein the second metal is iron.

14. The process of claim 1, wherein the cobalt is present in an amount of 10 ppm to 10 wt %, based on dry, ash free coal.

15. The process of claim 1, wherein the second metal is present in an amount of 10 ppm to 10 wt %, based on dry, ash free coal.

16. The process of claim 1, wherein cobalt and the second metal are present in a molar ratio within the range of between 0.1 to 1 and 10 to 1.

17. The process of claim 1 further comprising maintaining the solid carbonaceous material in the presence of at least one active source of sulfur.

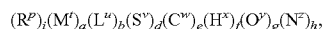
18. The process of claim 1, further comprising maintaining the solid carbonaceous material in the presence of hydrogen or a hydrogen containing gas.

19. The process of claim 2, further comprising converting at least 25% by weight of the solid carbonaceous material to a liquid product boiling in the temperature range of C₅ to 650° C.

20. The process of claim 19, further comprising converting in the range 30% to 99% by weight of the solid carbonaceous material to the liquid product.

21. The process of claim 2, further comprising maintaining the solid carbonaceous material at a reaction temperature in the range of between 350° C. and 800° C.

22. The process of claim 2, wherein the active source of cobalt and the active source of the second metal form a catalyst composition having a formula:



wherein

R is optional, R is at least a lanthanoid element metal or an alkaline earth metal;

M is cobalt;

L is at least a "d" block element metal different from the "d" block element metal M;

0<=i<=1;

0<b/a<=5,

0.5 (a+b)<=d<=5(a+b),

0<e<=11(a+b),

0<f<=7(a+b),

0<g<=5(a+b),

0<h<=2(a+b),

p, t, u, v, w, x, y, z, each representing total charge for each of: M, L, S, C, H, O and N, respectively, wherein pi+ta+ub+vd+we+xf+yg+zh=0, S=sulfur, C=carbon, H=hydrogen, O=oxygen and N=nitrogen.

23. The process of claim 22, wherein L is selected from the group consisting of iron, molybdenum, manganese, vanadium, tungsten, nickel, copper, titanium, chromium, platinum, palladium, cerium, zirconium, zinc and tin.

24. The process of claim 23, wherein L is iron.

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