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(54) Title: HIGH STABILITY CATALYST WITH IMPROVED SEDIMENT CONTROL

(57) Abstract: An ebullating bed catalyst used for converting a heavy hydrocarbon and controlling sediment yield at a minimum level, the catalyst includes an extrudate having a comulled mixture of an inorganic oxide, at least one metal from Group VIB of the Periodic Table of Elements, and at least one metal from Group VIII of the Periodic Table of Elements. The at least one metal from Group VIB is present in an amount greater than 7.5 wt.%, and the catalyst has a pore structure such that 8 vol.% to 18 vol.% of the total pore volume is present in pores of a diameter greater than 5,000, and 63 vol.% to 80 vol.% of the total pore volume is present in pores of a diameter less than 250.

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HIGH STABILITY CATALYST WITH IMPROVED SEDIMENT CONTROL

BACKGROUND OF THE DISCLOSURE

[0001] The present disclosure generally relates to an ebullating bed catalyst useful in hydroprocessing and hydroconversion of heavy hydrocarbon residual feedstocks. More specifically, the present disclosure relates to an ebullated bed catalyst having enhanced activity and improved catalyst stability and sediment control.

[0002] Ebullated bed (EB) residue upgrading is a process used to convert low-cost hydrocarbon residue feedstocks into better-quality crude oil products. The process includes removing components such as sulfur, nitrogen, metals, and micro-carbon residue by desulfurization, denitrogenation, and demetallization reactions, and hydrocracking heavy ends to lighter distillate fractions. In this process, heterogeneous catalysts are added to promote the catalytic reactions under conditions of elevated temperature and pressure in the presence of hydrogen. Typical catalysts used to provide for hydroprocessing and hydroconversion of heavy hydrocarbon residue feedstocks contain a Group VIB metal component, such as molybdenum or tungsten, a Group VIII metal component, such as cobalt or nickel, and phosphorus or silicon as dopant, supported on a refractory oxide support.

[0003] There is a need to find catalysts with enhanced catalytic activities and improved stability performance that are suitable for use in hydroprocessing of residue feedstocks. Due to the particular characteristic of heavy hydrocarbon residue, hydroprocessing of such feedstocks using a hydroprocessing catalyst generally results in a decline in its catalytic activity at a rapid rate. Catalysts exhibiting a lower rate of activity decline are considered to have a higher stability. It is desirable to have a catalyst with not only improved initial activity for desulfurization, denitrogenation and demetallization, but also to be highly stable (e.g., maintain improved activity for longer period of time). A catalyst with higher stability will maintain higher hydroconversion or produce less sediment than one with lower stability, even though their initial activity difference may be negligible. The catalyst stability is impacted by multiple factors, such as pore structure, metals loading, and the manner in which the catalyst is manufactured.

[0004] U.S. Patent No. 7,820,036 (Bhan) discloses a catalyst found to be useful in hydroprocessing heavy hydrocarbon feedstocks. This catalyst is especially useful in hydrodesulfurization and hydroconversion of heavy hydrocarbon feedstocks and in maintaining stability even when used at the higher process temperature conditions required for high conversion of the heavier hydrocarbon fractions. The catalyst is made by one-step comulling technology. The catalyst has up to 12 weight percent (wt. %) (as metal) molybdenum and up to 4 wt. % (as metal) nickel. Important features of the catalyst are that it has a mean pore diameter that is in a specific, narrow range and low levels of porosity with pore diameters below 350 Å (Angstroms). The mean pore diameter of the catalyst is in the range of from 85 Å to 100 Å. The catalyst has less than 4.5 volume percent (vol.%) of a total pore volume (TPV) that is contained in pores of a diameter greater than 350 Å.

[0005] U.S. Patent No. 8,969,242 (Klein) discloses a supported catalyst for processing refining hydrocarbon residual feedstocks. The carrier of the catalyst has a TPV of about 0.6 cubic centimeters/gram (cc/g) to about 1.1 cc/g, and equal to or greater than 3 vol.% to less than 12 vol.% of TPV in pores having a diameter equal to or greater than 1,000 Å. A two-step impregnation technology is applied for making the catalyst, which is different from one-step comulling.

[0006] U.S. Patent No. 9,879,187 (Bhan) discloses another heavy hydrocarbon hydroprocessing catalyst that has excellent catalytic performance properties. This catalyst yields a treated product having enhanced product stability as reflected by its P-value (e.g., catalyst stability of a constant). The catalyst further has enhanced micro-carbon residue (MCR) removal activity and enhanced vanadium removal capability and stability. The patent indicates that the unique physical characteristics of the catalyst provide for its excellent catalytic properties. An important feature of the catalyst is that at least 20 vol. % of its total pore volume is contained in pores having diameters greater than 5,000 Å and less than 70 vol. % of the total pore volume is contained in pore diameters in the range of 70 Å to 250 Å.

[0007] U.S. Patent No. 20220062871A1 (Bhan) discloses a heavy carbon hydroprocessing catalyst that has high macroporosity (e.g., >18 vol.% of the total pore volume is in pores with diameters > 5000 Å). It has 18 vol.% of the total pore volume present in pores of a diameter greater than 5,000 Å and at least 25 vol.% of the total pore volume present in pores of a diameter greater than 1,000 Å. This catalyst provides desirable conversion of the pitch portion of heavy hydrocarbon feedstocks while controlling sediment at extremely low amounts (e.g., <0.1 wt.% in the product). However, due to the large macroporous structure (e.g., 18 vol.% of the total pores volume is in pores having diameters > 5000 Å) of this catalyst, the microporosity (e.g., pores having diameters below 250 Å) is impacted, as is the surface area, which may affect the catalytic performance of this catalyst, particularly hydrodesulfurization and hydrogenation activity. Therefore, it may be advantageous to develop a catalyst having both improved sediment control and catalyst activity for hydrodesulfurization and hydroconversion of heavy hydrocarbon feedstock.

SUMMARY

[0008] In an embodiment, an ebullating bed catalyst used for converting a heavy hydrocarbon and controlling sediment yield at a minimum level, the catalyst includes an extrudate having a comulled mixture of an inorganic oxide, at least one metal from Group VIB of the Periodic Table of Elements, and at least one metal from Group VIII of the Periodic Table of Elements. The at least one metal from Group VIB is present in an amount greater than 7.5 wt.%, and the catalyst has a pore structure such that at least 12 vol.% of the total pore volume is present in pores of a diameter greater than 1,000 angstroms (Å), 8 vol.% to 18 vol.% of the total pore volume is present in pores of a diameter greater than 5,000 Å, and 63 vol.% to 80 vol.% of the total pore volume is present in pores of a diameter less than 250 Å.

[0009] Additional features and advantages of exemplary implementations of the disclosure will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by the practice of such exemplary implementations. The features and advantages of such implementations may be realized and obtained by means of the instruments and combinations particularly pointed out in the appended claims. These and other features will become more fully apparent from the following description and appended claims or may be learned by the practice of such exemplary implementations as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Advantages of the disclosure may become apparent upon reading the following detailed description and upon reference to the drawings in which:

[0011] FIG. 1 is a schematic of an ebullated bed reactor system that includes a high stability ebullated bed catalyst, in accordance with an embodiment of the present disclosure;

[0012] FIG. 2 is a comparative plot of hydrodesulfurization (HDS) conversion as a function of catalyst age for the high stability ebullated bed catalyst and reference catalysts;

[0013] FIG. 3 is a comparative plot of pitch conversion as a function of catalyst age for the high stability ebullated bed catalyst of and reference catalysts; and

[0014] FIG. 4 is a comparative plot of the amount of sedimentation as a function of catalyst age for the high stability ebullated bed catalyst and reference catalysts.

DETAILED DESCRIPTION

[0015] One or more specific embodiments of the present disclosure will be described below. These described embodiments are examples of the presently disclosed techniques. Additionally, in an effort to provide a concise description of these embodiments, not all features of an actual implementation may be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions will be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[0016] When introducing elements of various embodiments of the present disclosure, the articles "a," "an," and "the" are intended to mean that there are one or more of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements. Additionally, it should be understood that references to "one embodiment" or "an embodiment" of the present disclosure are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features.

[0017] The terms "approximately," "about," and "substantially" as used herein represent an amount close to the stated amount that still performs a desired function or achieves a desired result. For example, the terms "approximately," "about," and "substantially" may refer to an amount that is within less than 10% of, within less than 5% of, within less than 1% of, within less than 0.1% of, and within less than 0.01% of a stated amount.

[0018] The surface area of the alumina based material is measured by nitrogen adsorption, using the well-known B.E.T. method. The B.E.T. method of measuring surface area has been described in *J. Am. Chem. Soc. 60 (1938) 309-316*, which is the method used to measure nitrogen adsorption in the present application.

[0019] The pore size distribution and pore volume of the alumina based material refers to those properties determined by mercury penetration porosimetry. The measurement of the pore size distribution of the alumina based material is by any mercury porosimeter suitable for pressure ranges between atmospheric pressure and approximately 60,000 pounds per square inch (psi) (4137 bar), using a contact angle of 130° with a mercury surface tension of 474 dyne/cm at 25 °C.

[0020] As used herein, the term "pore volume" is defined as the total volume of the catalyst measured using the mercury intrusion method measured at pressures between atmospheric pressure and a pressure of about 60,000 psi (4137 bar). The reference herein to median pore diameter (MPD) corresponds to the median pore diameter by area. The term "micropore" as used herein denotes pores having a pore diameter of less than 250 Å. The term "mesopore" as used herein denotes pores having a pore diameter of between 250 Å to 1,000 Å. The term "macropore" as used herein denotes pores having a pore diameter equal or greater than 1,000 Å.

[0021] Catalytic hydroconversion of heavy hydrocarbon feedstocks (e.g., feedstock boiling above about 538 °C (1,000 °F)) in ebullated bed processes may result in undesirable sedimentation within reactors, which may also decrease catalyst activity. Sedimentation results in the deposit of solid particulates of inorganic solids (e.g., clay fines, iron sulfide), catalyst fines, coke, and/or asphaltene, among others, on surfaces of the process equipment and hydroprocessing catalysts. Deposits of sediment on process equipment and the catalyst may result in fouling of equipment and defluidization/deactivation of the catalyst, respectively. Moreover, the formed sediment may contaminate products formed in the process. Therefore, it is desirable to control sedimentation in the catalytic hydroconversion of heavy hydrocarbon feedstocks in ebullated bed processes while also maintaining the desired performance and activity of the catalyst.

[0022] It is well known that a catalyst's pore structure affects catalyst performance. For example, catalyst activity, stability, selectivity, and physical strength are all impacted by the overall pore structure of the catalyst. The pore structure of the catalyst is determined by the respective volume of micropores, mesopores, and macropores that make up the total pore volume of the catalyst. The respective volume of each of the micropores, mesopores, and macropores that make up the total pore volume of the catalyst directly or indirectly impact the overall performance of the catalyst. For example, the micropore volume affects the surface area and catalytic performance, such as, for example, hydrodesulfurization, hydrodenitrogenation, and hydrogenation, the mesopore volume provides diffusion channels for a flow of heavy hydrocarbon feedstock through the catalyst pore structure, and the macropore volume affects sediment control and provides space for adsorbing contaminant metals from the feedstock as well as the generated insoluble coke materials. Therefore, to improve the overall performance of the catalyst and sediment control, a balanced ratio of micropores, mesopores, and macropores is particularly important.

[0023] The ratio (i.e., the pore distribution) between the micropores, mesopores, and macropores of the catalyst may be tailored based on properties of the heavy hydrocarbon feedstock. For example, catalysts having a pore distribution in which less than 50 vol.% of the total pore volume is in pores having a diameter less than 250 Å and greater than 45 vol.% of the total pore volume is in pores having pore diameters greater than 1,000 Å may have better performance when used for controlling sediment or demetallization. However, such catalyst may have an undesirable performance with respect to hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation. In contrast, catalysts having a pore distribution in which more than 80 vol.% of the total pore volume has a diameter less than 250 Å is desirable for deeper HDS and HDN. That is, these catalysts remove greater than 95 wt.% of sulfur and nitrogen in the feedstock. Therefore, the balance of pore diameters in the catalyst pore structure is important for a residue catalyst.

[0024] In addition to the pore structure, metal content of the catalyst also affects catalyst activity, stability, and selectivity. Indeed, the amount of sedimentation during hydroprocessing of heavy hydrocarbon feedstocks depends on catalyst activity, in particular, the level of hydrogenation achieved which is impacted by the metal content. For example, organic sediment increases as the level of conversion of heavy hydrocarbons increases. However, if a catalyst is able to provide adequate hydrogenation, precursors of the organic sediments may be stabilized in the hydrocarbon product. Therefore, it is also important to have a balance for the metal content to provide enough hydrocracking as well as hydrogenation.

[0025] The inventive catalyst of the present disclosure has a bimodal catalyst composition that is useful in hydroprocessing (e.g., HDS, HDN, hydrogenation, and hydrodemetalization) and hydroconversion of heavy hydrocarbon feedstocks and uniquely balances the metal content and pore structure to provide improved performance, stability and sediment control compared to typical catalysts. The disclosed catalyst has particular application as an ebullating bed catalyst used in ebullated bed hydroconversion processes and provides desirable conversion of the pitch portion of heavy hydrocarbon feedstocks into lower boiling hydrocarbons (e.g., boiling point less than 370 °C) while also yielding low amounts (e.g., <0.1 wt.%) of undesirable sediment. As discussed in further detail below, the inventive catalyst disclosed herein combines an optimized active metal ratio, surface area, and meso- and macroporosity that result in improved HDS stability (e.g., slow catalyst decay and maintains high activity after aging), sediment control, and performance, along with maximized metal removal capacity compared to typical catalysts.

[0026] U.S. Patent No. 7,169,294 (Abe) discloses that catalysts having above 2 vol. % of their pore volume in pores greater than 4000 Å have decreased catalyst strength and result in undesirable desulfurization activity. Therefore, catalysts used for ebullated bed hydroconversion processes have less than 2 vol. % of their pores present in pores greater than 4000 Å. However, it has been surprising found that ebullated bed catalyst having more than 8 vol.% of pores present in pore having greater than 4000 Å have improved properties. For example, the stability of the inventive catalyst disclosed herein is impacted by the macropores being present in pores having a pore diameter of greater than 5000 Å. An important aspect is that it is desirable for the catalyst to include macropores having pore diameters exceeding 5000 Å; such pores provide porosity for metal complexes in the feedstock to enter the pores, thereby facilitating demetallization of the feedstock and sediment control. It is, therefore, desirable that from approximately 8 vol.% to 18 vol.% of the total pore volume is present in pores having a diameter greater than 5000 Å.

[0027] The inventive catalyst disclosed herein is a co-mulled mixture of an inorganic component and a metal component. The inorganic component includes an inorganic oxide material such as, for example, alumina, silica, aluminosilcates, or the like and combinations thereof. The amount of the inorganic oxide material in the co-mulled mixture is such to provide in the range of from approximately 70 wt.% to approximately 92.5 wt.% inorganic oxide material in a final calcined mixture/particle or hydroprocessing catalyst with the weight percent being based on the total weight of the calcined mixture or hydroprocessing catalyst. Preferably, the amount of the inorganic oxide material in the calcined mixture is in the range of from 72 to 91 wt.%, and, most preferably, from 74 to 90 wt.%.

[0028] As discussed above, the co-mulled mixture includes a metal component. The metal component includes one or more metals that facilitate hydroconversion of the heavy hydrocarbon feedstock. For example, the metal component may include a Group VIB metal, such as molybdenum, and a Group VIII metal, such as nickel. The concentrations of these metals in the final catalyst composition are important to the performance of the catalyst as well as its unique physical properties (e.g., surface area, mesoporosity, and macroporosity). For example, the nickel content of the calcined particle, thus, the hydroprocessing catalyst, is in a range of from 1.0 to 5.0 wt.% of the total weight of the calcined particle, calculated as metal, regardless of its actual form. In particular, the nickel content of the calcined particle is greater than 1.5 wt.% of the total weight of the calcined particle and less than 4.5 wt.%. It is more desirable for the nickel to be present in the calcined particle in an amount in the range from 1.5 wt.% to 4.0 wt.%. The molybdenum content of the calcined particle is present in an amount of greater than 7.5 wt.% of the total weight of the calcined particles, calculated as metal, regardless of its actual form. For example, the molybdenum content of the calcined particle may be 8 wt.%, 8.5 wt.%, 9 wt.%, 10 wt.%, 11 wt.%, 12 wt.% or more, calculated as metal, regardless of its actual form. The atomic ratio of nickel (Ni) to molybdenum (Mo) of the calcined particle is between approximately 0.40 to approximately 0.65. This atomic ratio is calculated and presented on an elemental basis. For example, in a preferred embodiment, the atomic ratio of Ni:Mo is in a range of approximately 0.50 to approximately 0.60.

[0029] As discussed above, the inventive catalyst includes a co-mulled mixture of an inorganic component and a metal component. The metal and inorganic components, along with other starting materials (e.g., binders, fillers, etc.) are mixed to form the co-mulled mixture. The co-mulled mixture is extruded into a desired geometric shape (e.g., sphere, cylinder, lobed, etc.), thereby forming a particle that is calcined to generate a calcined catalyst (e.g., the hydroprocessing catalyst).

[0030] An important physical feature of the catalyst disclosed herein is the ratio of microporosity and macroporosity. Unlike typical ebullated bed residue catalysts, the catalyst disclosed herein has a portion of the total pore volume of the catalyst contained in pores having a diameter greater than 5,000 Å. For example, the inventive catalyst has in a range of between 8 vol.% and 18 vol.% of the total pore volume contained in pores having a diameter greater than 5,000 Å. This macroporosity, in combination with the active metal ratio and surface area provided by the micropore structure, provides advantageous catalytic activity (e.g., hydrogenation), while also improving sediment control of the catalyst compared to typical catalysts.

[0031] The disclosed catalyst has a bimodal pore structure with a portion of the pores being micropores and another portion of the pores being macropores. For example, the catalysts include pore diameters within the range of from 40 Å to 250 Å, and pore diameters that are equal to or greater than 1,000 Å. In one embodiment, the bimodal pore structure of the inventive catalyst preferably has a first portion of pores having pore diameters within the range of from 50 Å to 150 Å and a second portion of pores having pore diameters within the range of from 1,000 Å to 20,000 Å. More preferably, the first portion of pores have pore diameters within the range of from 50 Å to 120 Å and the second portion of pores have pore diameters within the range of from 1,000 Å to 10,000 Å.

[0032] The catalyst of the present disclosure also has a total pore volume of equal to or greater than 0.80 cubic centimeters (cc)/gram (g), cc/g. Preferably, the total pore volume of the disclosed catalyst is larger than 0.85 cc/g. The percentage of the total pore volume of the catalyst contained in pores of diameters less than 250 Å is in the range of from 63 vol.% to 80 vol.% of the total pore volume of the catalyst. Preferably, in the range of from 64 vol.% to 75 vol.% of the total pore volume of the catalyst is present in pores having diameters less than 250 Å. As discussed above, the micropore structure (i.e., microporosity) of the catalyst impacts the surface area of the catalyst. Therefore, the volume of pores having diameters less than 250 Å that make up the total pore volume of the catalyst is such that the catalyst has a surface area of in the range of approximately 240 to 300 square meters (m^2)/gram (g), m^2/g. The total pore volume of typical catalysts is less than 0.8 cc/g, but the catalyst of this invention has total pore volume higher than 0.88 cc/g, due to a significant portion of the total pore volume being present in pores having diameters greater than 1000 Å. By boosting the total pore volume from approximately 0.80 cc/g to greater than approximately 0.88 cc/g while also maintaining the same microporosity as in the catalyst of the present disclosure, macroporosity is gained without losing surface area and catalyst activity.

[0033] In addition, the percentage of the total pore volume of the catalyst that is contained in pores having a diameter in the range of from 250 Å and 1,000 Å is greater than 0.04 vol.%. This range of the pores are the diffusion channels for the feedstock to enter into the catalytic sites of the catalyst.

[0034] As discussed above, the macroporosity of the inventive catalyst provides sediment control and affects the capacity of the catalyst for removing certain metal contaminants (e.g., vanadium, nickel, iron, etc.). Therefore, it is desirable for the catalyst to have a macroporosity that decreases sedimentation and maximizes removal of metal contaminants. Accordingly, in preferred embodiments of the catalyst, at least 12 vol.% of the total pore volume is contained within macropores having a diameter greater than 1,000 Å. In addition, the catalyst disclosed herein has more than 8 vol.% of its total pore volume contained in pores of diameters greater than 5,000 Å. Preferably, in a range of from 8 vol.% to 18 vol.% of the total pore volume of the catalyst is in its pores having diameters greater than 5,000 Å.

[0035] By having at least 12 vol.% of the total pore volume of the catalyst within the macropores having a diameter greater than 1000 Å, sedimentation is improved compared to catalysts having macropores outside of this range. For example, the macropores provide space to hold (e.g., trap) sediment generated during hydroprocessing of heavy hydrocarbon feedstock, thereby decreasing the overall sedimentation. As should be appreciated, it is important to have the proper balance between the volume of micropores and macropores in the total pore volume such that the micropores provide a surface area that facilitates deposition of the Group VIII metal and the Group VIB metal on surfaces of the catalyst and the macropores trap the sediment generated during hydroprocessing of the heavy hydrocarbon feedstock. For example, the more macropores that make up the total pore volume of the catalyst, the less volume of micropores the catalyst will have. As such, because the catalyst does not have a sufficient volume of micropores contained in its total pore volume, the surface area of the catalyst will be low (e.g., less than 200 square meters (m^2)/gram (g)). Therefore, the Group VIII and Group VIB metals, which affect catalytic activity, selectivity, and stability, may not be exposed to the heavy hydrocarbon feedstock to allow catalytic reactions to occur. Accordingly, conversion of the hydrocarbon feedstock into lighter distillate fractions may be undesirably low.

[0036] The catalyst disclosed herein may be prepared via a one-step co-mulling process. For example, the starting materials are mixed by co-mulling the components to form a co-mulled mixture. The starting materials in the preparation of the co-mulled mixture, in one embodiment, include at least one Group VIB metal compound, such as molybdenum, at least one Group VIII metal compound, such as nickel, alumina material, and, optionally, a poly-organic (e.g., polyacrylamides such as Superfloc® and the like). The Group VIB metal compound is preferably a molybdenum oxide (e.g., molybdenum trioxide), a molybdenum salt (e.g., ammonium dimolybdate (ADM)), or any other suitable molybdenum compound in the form of finely divided particles that may be as a dry powder or as particles in a suspension or slurry. The Group VIII metal compound is selected from a group of suitable nickel compounds such as, but not limited to, nickel oxide, a nickel salt (e.g., nickel nitrates, nickel hydroxides, nickel chlorides, and nickel acetates), any other nickel compound that is capable of being mixed with the other components of the co-mulled mixture that is shaped into a particle. In a preferred embodiment, the nickel component is nickel nitrate.

[0037] The co-mulled mixture may also include other components such as, but not limited to, organic additives, acid, and a solvent (e.g., water). By way of non-limiting example, the organic additives include flocs and the acid may include solutions of nitric acid. The co-mulled mixture is extruded into a shaped particle, followed by drying and calcination to form the calcined particle of the invention.

[0038] The formation of the co-mulled mixture may be done by any method or means known to those skilled in the art. These include the use of such suitable types of solids-mixing machines as tumblers, stationary shells or troughs, muller mixers, which are either batch type or continuous type, and impact mixers, and the use of such suitable types of either batch-wise or continuous mixers for mixing solids and liquids or for the formation of paste-like mixtures that are extrudable. Suitable types of batch mixers include, but are not limited to, change-can mixers, stationary-tank mixers, double-arm kneading mixers that are equipped with any suitable type of mixing blade. Suitable types of continuous mixers include single or double screw extruders, and trough-and-screw mixers .

[0039] The mixing of starting materials of the calcined particle may be conducted for any suitable time-period necessary to properly homogenize the co-mulled mixture. Generally, the blending time may be in the range of upwardly to 2 or more than 3 hours. Typically, the blending time is in the range of from 0.1 hours to 3 hours.

[0040] The term “co-mulling” as used herein is intended to mean that at least the starting materials are mixed together to form a mixture of the individual components of the co-mulled mixture that is preferably a substantially uniform or homogeneous mixture of the individual components of such co-mulled mixture. This term is intended to be broad enough in scope to include the mixing of the starting materials to yield a paste that exhibits properties making it capable of being extruded or formed into extrudate particles by any of the known extrusion methods. But, also, the term is intended to encompass the mixing of the starting materials to yield a mixture that is preferably substantially homogeneous and capable of being agglomerated into formed particles. Examples of the formed particles include spheroids, pills or tablets, cylinders, irregular extrusions or merely loosely bound aggregates or clusters, by any of the methods known to those skilled in the art, including, but not limited to, molding, tableting, pressing, pelletizing, extruding, and tumbling.

[0041] Once the starting materials of the calcined particle are properly mixed and formed into the shaped or formed particles, a drying step may advantageously be used for removing certain quantities of water or volatiles that are included within the co-mulled mixture or formed particles. The drying of the formed particles may be conducted at any suitable temperature for removing excess water or volatiles, but, preferably, the drying temperature will be in the range of from about 75 °C to 250 °C (167 °F to 482 °F). The time period for drying the particles is any suitable period of time necessary to provide for the desired amount of reduction in the volatile content of the particles prior to the calcination step.

[0042] The dried or undried particles are calcined in the presence of an oxygen-containing fluid, such as air, at a calcination temperature that provides a final calcined particle having the required pore structure and enhanced catalytic properties that are described herein. The dried particle of the invention is calcined at a temperature is in the range of from 677 °C (1250 °F) to 843 °C (1550 °F). The preferred calcination temperature is in the range of from 704°C (1300 °F) to 815 °C (1500 °F), and, more preferred, from 718°C (1325°F) to 774°C (1425 °F).

[0043] The calcined particle is particularly useful as a hydroprocessing catalyst for use in the hydroprocessing of a heavy hydrocarbon feedstock stream that has high contents of pitch (e.g., >90 wt.%), organic metals such as nickel and vanadium compounds, and sulfur. Prior to its use, the calcined particle may, but is not required to, be sulfided or activated by any of the methods known to those skilled in the art. Generally, in its use in the hydroprocessing of a heavy hydrocarbon feedstock, the calcined particle is contained within a reaction zone, such as that which is defined by a reactor vessel, wherein the heavy hydrocarbon feedstock is contacted with the calcined particle under suitable hydroprocessing reaction conditions and from which a treated hydrocarbon or heavy hydrocarbon conversion product is yielded. The heavy hydrocarbon feedstock used in the process disclosed herein may be derived from any of the high boiling temperature petroleum cuts such as atmospheric tower gas oils, atmospheric tower bottoms, vacuum tower gas oils, and vacuum tower bottoms or resid.

[0044] It is a particularly useful aspect of the present disclosure to provide a catalyst that may be used in a process for the hydroprocessing of a heavy hydrocarbon feedstock that is generally defined as having a boiling temperature at its 5 wt.% distillation point, i.e. T(5), that exceeds 300 °C (572 °F) as determined by using the testing procedure set forth in ASTM D-1160. The disclosed catalyst is more particularly directed for use in the hydroprocessing of a heavy hydrocarbon feedstock having a T(5) that exceeds 315 °C (599 °F) and, even, one that exceeds 340 °C (644 °F). The heavy hydrocarbon feedstock further may include heavier hydrocarbons that have boiling temperatures above 538 °C (1,000 °F). These heavier hydrocarbons are referred to herein as pitch, and, as discussed above, it is recognized that one of the special features of the catalyst of the present disclosure is that it is particularly effective in the hydroconversion of the pitch content of a heavy hydrocarbon feedstock into low density distillate fractions (e.g., distillate fractions having a boiling point less than 370 °C (698 °F)).

[0045] The heavy hydrocarbon feedstock may include as little as 10 vol.% pitch or as much as 99 vol.% pitch, but, generally, the amount of pitch included in the heavy hydrocarbon feedstock is in the range of from 20 to 95 vol.%. And, more typically, the pitch content in the heavy hydrocarbon feedstock is in the range of from 30 to 90 volume percent.

[0046] The heavy hydrocarbon feedstock further may include a significantly high sulfur content. One of the special features of the disclosed catalyst is that it also provides for the desulfurization of the heavy hydrocarbon feedstock. In particular, the disclosed catalyst provides for the desulfurization of the heavy feedstock having a significantly high sulfur content. Such a sulfur content is typically much greater than 1 weight percent. For example, in certain embodiments, the sulfur content of the heavy hydrocarbon feedstock may exceed 2 weight percent, and with such a heavy hydrocarbon feedstock, the sulfur content may be in the range of from approximately 2 to 8 wt.%. In one embodiment, the heavy hydrocarbon feedstock has an especially high sulfur content exceeding approximately 3 or even 4 wt.% and being in the range of from approximately 3 to 7 wt.% or even from approximately 4 to 6.5 wt.%. The sulfur content of the heavy hydrocarbon feedstock is primarily in the form of organic sulfur-containing compounds, which may include, for example, mercaptans, substituted or unsubstituted thiophenes, heterocyclic compounds, or any other type of sulfur-containing compound. When referring herein to the sulfur content of either the heavy hydrocarbon feedstock or the treated hydrocarbon or heavy hydrocarbon conversion product, the weight percents are determined by the use of testing method ASTM D-4294. The catalyst disclosed herein facilitates desulfurization so as to provide for a treated hydrocarbon product or a heavy hydrocarbon conversion product having a reduced sulfur content, such as a sulfur content of less than 1 weight percent, preferably, less than 0.75 wt.%, and, more preferably, less than 0.5 wt.%.

[0047] The disclosed catalyst having improved stability may be used in hydroprocessing heavy hydrocarbon feedstocks to provide for simultaneous desulfurization, denitrogenation, and pitch conversion with a reduced or low sediment yield. In this process, the heavy hydrocarbon feedstock is contacted with the catalyst disclosed herein under suitable hydrodesulfurization and hydroconversion process conditions to yield the heavy hydrocarbon conversion product.

[0048] As discussed above, the macroporosity of the catalyst disclosed facilitates removal of undesirable metals contained in the heavy hydrocarbon feedstock. The heavy hydrocarbon feedstock may contain undesirable metals such as nickel and vanadium. The nickel content of the heavy hydrocarbon feedstock is typically in the form of organic nickel compounds. The nickel concentration of the heavy hydrocarbon feedstock may be in the range of from 2 ppmw to 250 ppmw. More typically, the heavy hydrocarbon feedstock has a concentration of nickel that is in the range of from 5 ppmw to 225 ppmw, and, most typically, the nickel concentration is in the range of from 7 ppmw to 200 ppmw. The vanadium concentration in the heavy hydrocarbon feedstock is generally in the range of from 5 ppmw to 350 ppmw. More typically, the vanadium concentration of the heavy hydrocarbon feedstock is in the range of from 10 ppmw to 300 ppmw. The macropore structure of the catalyst disclosed herein provides for demetallization, and, thus, the removal of nickel and vanadium from the heavy hydrocarbon feedstock.

[0049] The sediment typically yielded with the heavy hydrocarbon conversion product (e.g., the hydroprocessed product) is less than approximately 0.1 wt.%, and, preferably, it is less than approximately 0.05 wt.% as determined by testing method ASTM-4870. The use of the catalyst disclosed herein provides a heavy hydrocarbon conversion product having significantly lower sediment content than provided by comparative catalysts. The sediment content of the heavy hydrocarbon conversion product can even be less than 0.03 wt.% of the heavy hydrocarbon conversion product.

[0050] The calcined particle (high stability catalyst) of the present disclosure may be employed as a part of any suitable reactor system that provides for the contacting of the catalyst with the heavy hydrocarbon feedstock under suitable hydroprocessing conditions that may include the presence of hydrogen and an elevated total pressure and temperature. Such suitable reaction systems can include fixed catalyst bed systems, ebullating catalyst bed systems, slurried catalyst systems, and fluidized catalyst bed systems. The catalyst disclosed herein is particularly useful as an ebullating bed catalyst used in ebullated bed reactor systems. The ebullated bed reactor system is described in greater detail below with respect to the **FIG. 1**.

[0051] The catalyst disclosed herein may be used in a process that generally operates at a hydroprocessing (hydroconversion and hydrodesulfurization) reaction pressure in the range of from 2298 kPa (300 psig) to 20,684 kPa (3000 psig), preferably from 10,342 kPa (1500 psig) to 17,237 kPa (2500 psig), and, more preferably, from 12,411 kPa (1800 psig) to 15,513 kPa (2250 psig). The hydroprocessing reaction temperature is generally in the range of from 340 °C (644 °F) to 480 °C (896 °F), preferably, from 360 °C (680 °F) to 455 °C (851 °F), and, most preferably, from 380 °C (716 °F) to 425 °C (797 °F).

[0052] The flow rate at which the heavy hydrocarbon feedstock is charged to a reaction zone of the reactor system is generally such as to provide a liquid hourly space velocity (LHSV) in the range of from 0.01 hr^{-1} to 3 hr^{-1}. The term "liquid hourly space velocity", as used herein, means the numerical ratio of the rate at which the heavy hydrocarbon feedstock is charged to the reaction zone in volume per hour divided by the volume of the reaction zone to which the heavy hydrocarbon feedstock is charged. The preferred LHSV is in the range of from 0.05 hr^{-1} to 2 hr^{-1}, more preferably, from 0.1 $hr^{-}1$ to 1.5 hr^{-1} and, most preferably, from 0.2 hr^{-1} to 0.7 hr^{-1}.

[0053] It is preferred to charge hydrogen along with the heavy hydrocarbon feedstock to the reaction zone. In this instance, the hydrogen is sometime referred to as hydrogen treat gas. The hydrogen treat gas rate is the amount of hydrogen relative to the amount of heavy hydrocarbon feedstock charged to the reaction zone and generally is in the range upwardly to 1781 m^3/m^3 (10,000 SCF/bbl). It is preferred for the treat gas rate to be in the range of from 89 m^3/m^3 (500

SCF/bbl) to 1781 m^3/m^3 (10,000 SCF/bbl), more preferably, from 178 m^3/m^3 (1,000 SCF/bbl) to 1602 m^3/m^3 (9,000 SCF/bbl), and, most preferably, from 356 m^3/m^3 (2,000 SCF/bbl) to 1425 m^3/m^3 (8,000 SCF/bbl).

[0054] **FIG. 1** is a schematic representation of an ebullated bed reactor system **20** in which the catalyst of the present disclosure may be used. The ebullated bed reactor system includes elongated vessel **24** that defines several zones such as a contacting zone for contacting a heavy hydrocarbon feedstock under suitable hydroconversion reaction conditions with the high stability catalyst and a separation zone for the separation of a hydrotreated heavy hydrocarbon product from the high stability catalyst.

[0055] Within the elongated vessel **24** is a settled/static high stability catalyst bed **26** having a settled high stability catalyst bed level **28**. A reactor feed comprising heavy hydrocarbon feedstock and hydrogen is introduced into lower zone **30** located below the ebullated catalyst bed within the elongated vessel **24** by way of conduit **32**.

[0056] The reactor feed passes through horizontal distributor plate **34** that provides means for directing the reactor feed upwardly and through the settled high stability catalyst bed **26**. The passing of the reactor feed through the settled high stability catalyst bed **26** serves to lift and to expand the bed of high stability catalyst to thereby provide an expanded high stability catalyst bed **36** (ebullated catalyst bed) having an expanded high stability catalyst bed level **38**.

[0057] In separation zone **40** of the elongated vessel **24**, high stability catalyst is separated from liquid hydrocarbon **42**, having a liquid level **46**, and the heavy hydrocarbon conversion product, which passes from the elongated vessel **24** by way of conduit **48**. Downcomer **50** within the elongated vessel **24** provides a conduit for recycling the liquid hydrocarbon **42** to the bottom of the expanded high stability catalyst bed **36**. Conduit **52** is operatively connected in fluid flow communication between the downcomer **50** and ebullating pump **58**. The ebullating pump **58** provides means for recycling and circulating the liquid hydrocarbon **42** through the expanded hydroconversion catalyst bed **36**. The ebullating pump **58** may be positioned either outside or inside the reaction vessel **24**. However, in certain embodiments, the ebullating pump **58** may not be used or omitted.

[0058] The upper end of the elongated vessel **24** includes catalyst inlet conduit **60**, which provides for the introduction of fresh high stability catalyst while the ebullated bed reactor system **20** is in operation. High stability catalyst can be introduced into the elongated vessel **24** through the inlet conduit **60** by way of conduit **62**. The lower end of the elongated vessel **24** includes catalyst outlet conduit **64**, which provides for the removal of spent high stability catalyst while the ebullated bed reactor system **20** is in operation. The spent high stability catalyst passes from the elongated vessel **24** by way of conduit **68**.

[0059] Set forth below is an illustrative example of the manner in which the catalyst disclosed herein is prepared and its composition. Performance of the catalyst and a comparative reference catalyst is also provided. As should be appreciated, the illustrative example is not to be construed as limiting the scope of the present disclosure.

Inventive Catalyst Composition

[0060] An embodiment of a catalyst composition in accordance with the present disclosure was prepared by combining 796.74 parts by weight of alumina powder, having loss on ignition (LOI) of 23.6 wt.%, 93.69 parts by weight nickel nitrate ($Ni(NO_3)_2$) dissolved in 100.00 parts by weight deionized water, 87.57 parts by weight molybdenum trioxide (MoO_3) powder, and 188.78 parts by weight finely ground alumina, molybdenum oxide and nickel oxide powder within a Muller mixer along with 32.14 parts by weight 69.7 wt.% concentrated nitric acid and 1102 parts by weight deionized water. After 15 minutes of mulling, 9.00 parts by weight of ammonia and 9.00 parts by weight of superfloc were added followed by another 20 minutes of mulling. The mixture was then extruded using 1.0 mm cylinder dies to form 1.0 mm cylinder extrudate particles. The extrudate particles were dried in air for a period of one hour at a temperature of 125 °C (257 °F). The dried extrudate particles were calcined in air for one hour with a maximum temperature of 752 °C (1385 °F). The final calcined mixture contained 2.92 weight percent nickel metal (3.71 wt.% as NiO) and 9.15 wt.% molybdenum metal (13.73 wt.% as MoO_3) and 75.84 wt.% of alumina (Al_2O_3).

Comparison Catalyst Composition

[0061] The comparison catalyst composition A (Reference Catalyst A) was prepared by combining 853.95 parts by weight of alumina powder, having LOI of 22.65 wt.%, 75.45 parts by weight nickel nitrate ($Ni(NO_3)_2$) and 48.05 parts by weight ammonium dimolybdate (ADM) dissolved in 100.00 parts by weight deionized water, and 188.78 parts by weight finely ground alumina, molybdenum oxide and nickel oxide powder within a Muller mixer along with 75.45 parts by weight 69.7 wt.% concentrated nitric acid and 894.18 parts by weight deionized water. After 15 minutes of mulling, 9.00 parts by weight of superfloc were added followed by another 20 minutes of mulling. The mixture was then extruded using 1.0 mm cylinder dies to form 1.0-cylinder extrudate particles. The extrudate particles were dried in air for a period of one hour at a temperature of 125 °C (257 °F). The dried extrudate particles were calcined in air for one hour with a maximum temperature of 788 °C (1450 °F). The final calcined mixture contained 2.44 weight percent nickel metal (3.11 wt.% as NiO) and 6.11 wt.% molybdenum metal (9.17 wt.% as MoO_3) and 80.91 wt.% of alumina (Al_2O_3).

[0062] The comparison catalyst composition B (Reference Catalyst B, example one in US20220062871A1) was prepared by combining 932.2 parts of alumina powder, having an LOI of 23.9 wt.%, with 20 parts of a high molecular weight polyacrylamide component (Tramfloc® 133 M nonionic flocculant), 210.7 parts of catalyst fines (finely ground alumina, molybdenum oxide and nickel oxide powder), 75.2 parts of molybdenum trioxide, and 78.8 parts of nickel nitrate in a muller. The muller was operated for about a minute before adding a mixture of 1354.5 parts of water and 29.4 parts of 68 wt.% nitric acid. The mix was mulled for 10 minutes and then 20 parts of lower molecular weight cationic dispersant were added, and the mixture mulled for 15 additional minutes. The mixed material was extruded using a screw extruder to make cylindrical pellets. The extruded material was dried in an oven for 1 hour at 121.1 °C (250 °F). This material was calcined in a muffle furnace at 754.4 °C to 768.3 °C (1390 °F to 1415 °F) temperature for one hour. The metal loadings of the final catalyst included 2.9 wt.% nickel and 12.1 wt.% molybdenum, both of these values are on an oxide basis.

[0063] The following Table 1 presents the pore structure properties of the catalyst of the present disclosure and comparison catalysts.

TABLE 1 – Catalyst Pore Structure Properties

	Inventive Catalyst	**Reference Catalyst A**	**Reference Catalyst B**
Median pore diameter (MPD)	<110 A	<110 A	<110A

% PV, Pore Dia >5000A	9.4	5.3	18.0
% PV, Pore Dia <250A	67.1	72.4	61.7
Surface Area, m^2/g	270	260	260
Atomic Ni:Mo ratio	0.54	0.65	0.47
Mo, wt.% (as Mo metal)	9	6	7.5 - 8.5

Catalyst Performance Testing

[0064] The catalysts described above were evaluated in a pilot scale reactor using heavy feedstock and conditions as in Tables 2 and 3. 200 cc of catalyst were loaded to the reactor for each testing. The properties of the feed are summarized in Table 2, and the process conditions are presented in Table 3.

TABLE 2 - Properties of the feed used to evaluate the catalysts

PROPERTY	VALUE
524 °C+ (975 °F+), wt.%	8.6
SULFUR, wt.%	5.793
MCR, wt.%	20.71
NICKEL, wppm	110
VANDIUM, wppm	274
FEED DENSITY, g/ml	1.0471
n-C7 Insolubles, wt.%	11.1
n-C5 Insolubles, wt.%	20.0

TABLE 3 - Process conditions used to evaluate the catalysts

Catalyst LHSV, hr^{-1}	0.46
Total pressure, psia	2000
H2/Oil Ratio, scft/bbl	3600
Temperature, °F (°C)	790

[0065] **FIGS. 2-4** demonstrate performance results of the disclosed catalyst and the comparative reference catalyst. **FIG. 2** is a comparative plot **100** of sulfur conversion in wt.% as a function of catalyst age in bbl/lb (barrels of liquid feed/pound of catalyst). As shown in **FIG. 2**, the inventive catalyst **102** has increased activity for desulfurization (e.g., HDS) of the heavy hydrocarbon feedstock compared to reference A catalyst **104** and reference B catalyst **106**. Specifically, the inventive catalyst **102** has approximately 4 wt.% higher activity compared to the reference catalysts **104**, **106**.

[0066] Moreover, not only did the inventive catalyst of the present disclosure improve HDS, the inventive catalyst also had improved stability compared to the reference B catalyst. For example, **FIG. 3** is a comparative plot **110** of the conversion at 975 °F + as a function of the catalyst age. As shown in the comparative plot **110**,the inventive catalyst **102** maintained a stable conversion with age. In contrast, the conversion activity of the reference catalysts **104** decreased with age. Without being bound by theory, the improved stability of the inventive catalyst is believed to be attributed, in part, to the optimized macroporosity and metal ratio compared to the reference catalysts.

[0067] As discussed above, the pore structure of the catalyst impacts sedimentation that occurs during hydroconversion of the heavy hydrocarbon feedstock. As shown in comparative plot **112** illustrated in **FIG. 4**, the inventive catalyst **102** of the present disclosure has better sediment control compared to the reference catalyst **104**. The reference catalyst **104** has less than 8 vol.% of its respective pore volume contained in pores having a diameter greater than 5,000 Å. In contrast, the inventive catalyst **102** has in the range of 8 vol.% to 18 vol.% of its total pore volume contained in pores having a diameter of greater than 5,000 Å. The inventive catalyst **102** provides for better sediment control due, in part, to the increased amount of pores having a diameter greater than 5,000 Å in the total pore volume, which provide a space for the sediment to be trapped rather than settling at the bottom of the reactor and contaminating the lighter hydrocarbon products generated in the hydroconversion process.

[0068] A review of the performance results for the inventive catalyst and the reference catalyst **A**, **B** are presented in Table 4 below. As shown in Table 4, desulfurization performance (**FIG. 2**) and product density reduction of the inventive catalyst is better than those of the reference catalysts **A**, **B**. The inventive catalyst also provides an improvement on sediment control and pitch conversion (**FIG. 3**) as compared to the comparison reference catalyst A (**FIG. 4**). All listed results show that the inventive catalyst with improved pore distribution and nickel-to-molybdenum ratio, as discussed above, provides for controlling sediment while advancing the catalytic conversions.

TABLE 4 – Relative performance of the catalysts

	Reference Catalyst A	Reference Catalyst B	Inventive Catalyst
Sulfur Conversion, wt.%	100	102	105
797F+ Fraction Sediment (IP-375), wt.%	100	65	75
Pitch Conversion	100	102	102
797F+ Density, kg/m^3	1000	1000	988

[0069] The technical effects of the catalyst disclosed herein is that the combination of balanced and optimized active metal ratio, surface area, and macroporosity, the stability, strength, hydrogenation activity, metal removal capacity, and sediment control is improved compared to catalysts typically used for the hydrogenation of heavy hydrocarbon feedstocks. For example, Reference Catalysts A does not have desirable sulfur conversion, sediment control, or hydrogenation activity. While Reference Catalyst B has desirable pitch conversion and sediment control, the hydrogenation activity is not as good as the inventive catalyst. However, the catalyst of the present disclosure has all of those - desirable hydrogenation activity, sulfur conversion, and sediment control. The catalyst of the present disclosure reduces the density of the resultant hydroconversion products by 5 kg/m^3 and the density of bottom product cut by more than 10 kg/m^3 compared to the reference catalysts, which is another desirable outcome.

[0070] The present disclosure may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the disclosure is, therefore, indicated by the appended claims rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

1. An ebullating bed catalyst used for converting a heavy hydrocarbon and controlling sediment yield, wherein the catalyst comprises:

   an extrudate comprising a comulled mixture of an inorganic oxide, at least one metal from Group VIB of the Periodic Table of Elements, and at least one metal from Group VIII of the Periodic Table of Elements, wherein the at least one metal from Group VIB is present in an amount greater than 7.5 wt.%, and wherein the catalyst has a pore structure such that 8 vol.% to 18 vol.% of the total pore volume is present in pores of a diameter greater than 5,000Å, and 63 vol.% to 80 vol.% of the total pore volume is present in pores of a diameter less than 250 Å.

2. The ebullating bed catalyst of claim 1, wherein the total pore volume is greater than 0.88 cubic centimeters per gram (cc/g).

3. The ebullating bed catalyst of claims 1 and 2, wherein greater than 12 vol.% of the pores have a pore diameter greater than 1,000 Å.

4. The ebullating bed catalyst of any of the preceding claims, wherein the total pore volume of pores having a pore diameter greater than 5,000 Å is between 8 vol.% and 14 vol.%.

5. The ebullating bed catalyst of any of the preceding claims, wherein the total pore volume of pores having a diameter of less than 250 Å is in the range of 64 vol.% and 70 vol.%.

6. The ebullating bed catalyst of any of the preceding claims, comprising a bimodal pore size distribution.

7. The ebullating bed catalyst of any of the preceding claims, wherein the bimodal pore size distribution is defined as having a first portion of pores having a first pore diameter of equal to or less than 250 Å and a second portion of pores having a second pore diameter equal to or greater than 1000 Å.

8. The ebullating bed catalyst of claim 7, wherein the first pore diameter is within a range of from 40 Å to 250 Å and the second pore diameter is within a range of from 1000 Å to 20,000 Å.

9. The ebullating bed catalyst of claim 7, wherein less than 5 vol.% of the total pore volume is present in pores having a pore diameter greater than 20,000 Å.

10. The ebullating bed catalyst of any of the preceding claims, wherein the atomic ratio of Group VIII metal to Group VIB metal is in the range of from 0.40 to 0.65.

11. The ebullating bed catalyst of any of the preceding claims, wherein the Group VIII metal is metal from the group consisting of cobalt, nickel and mixture thereof and the Group VIB metal is molybdenum.

12. The ebullating bed catalyst of any of the preceding claims, wherein greater than 4 vol.% of the total pore volume of the catalyst is contained in pores having a diameter in the range of from 250 Å and 1,000 Å.

13. The ebullating bed catalyst any of the preceding claims, wherein the catalyst is used in a single stage or a multi-stage system.

14. A process for hydroprocessing and hydroconversion of heavy hydrocarbon residual feedstocks, comprising:

contacting the heavy hydrocarbon residual feedstock with the catalyst according to any of the preceding claims.

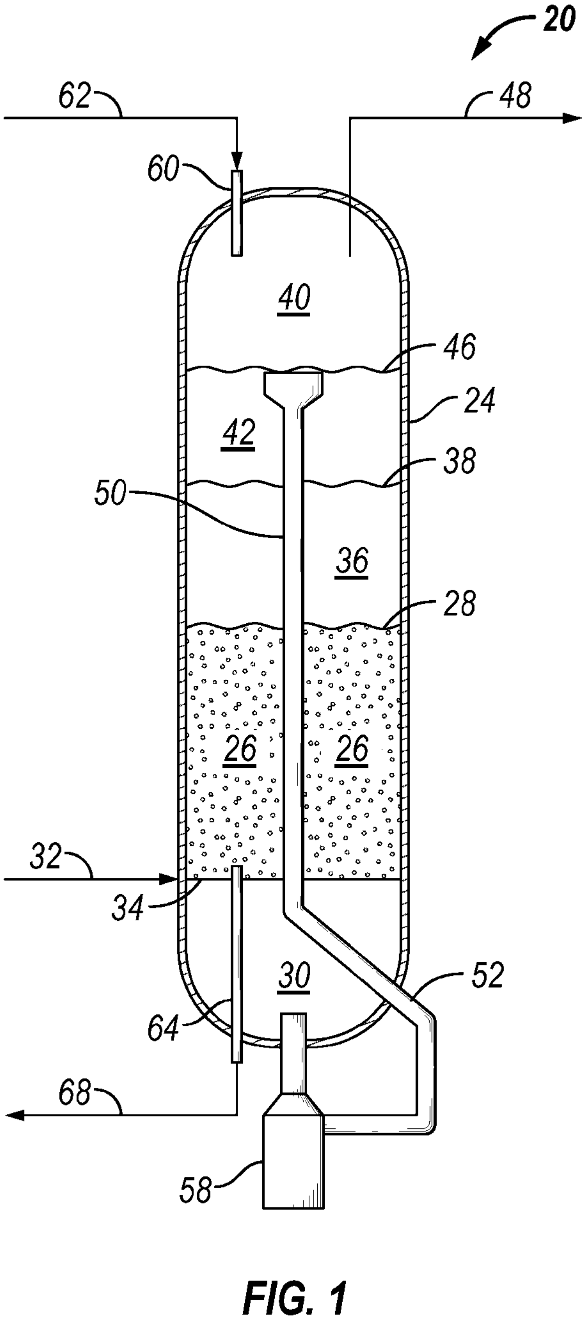

FIG. 1

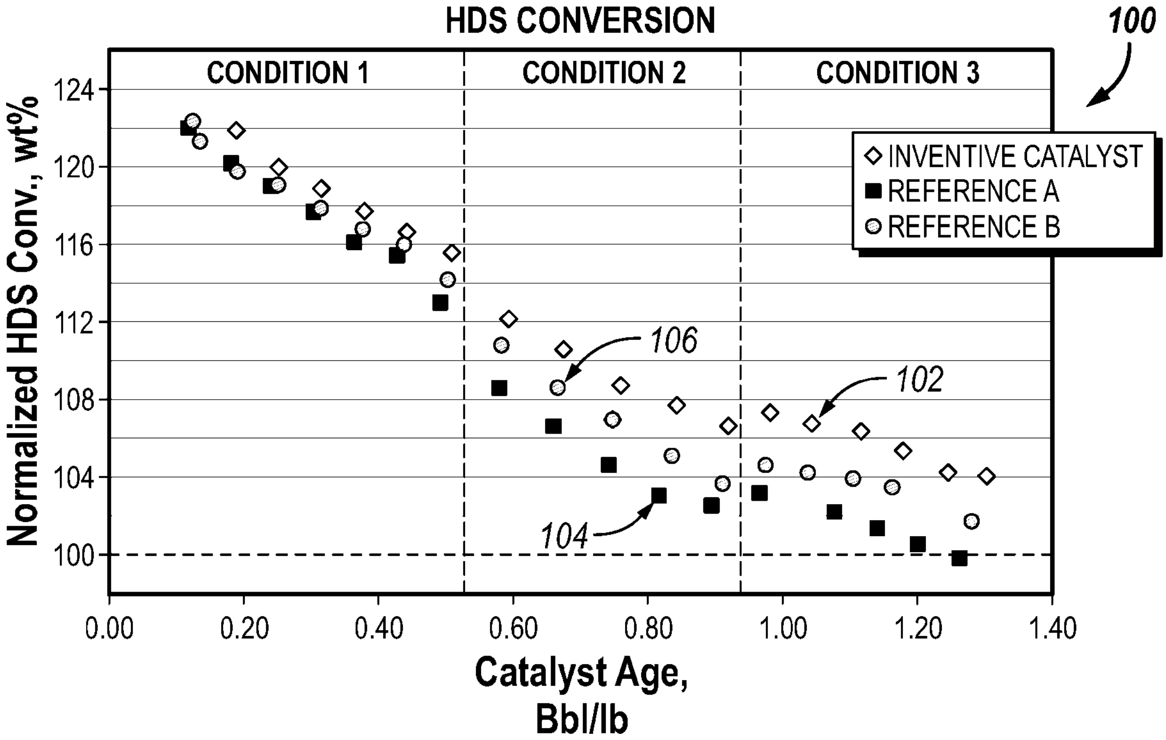
HDS CONVERSION
100
CONDITION 1
CONDITION 2
CONDITION 3
◇ INVENTIVE CATALYST
■ REFERENCE A
○ REFERENCE B
Normalized HDS Conv., wt%
124
120
116
112
108
104
100
106
102
104
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
Catalyst Age, Bbl/lb

FIG. 2

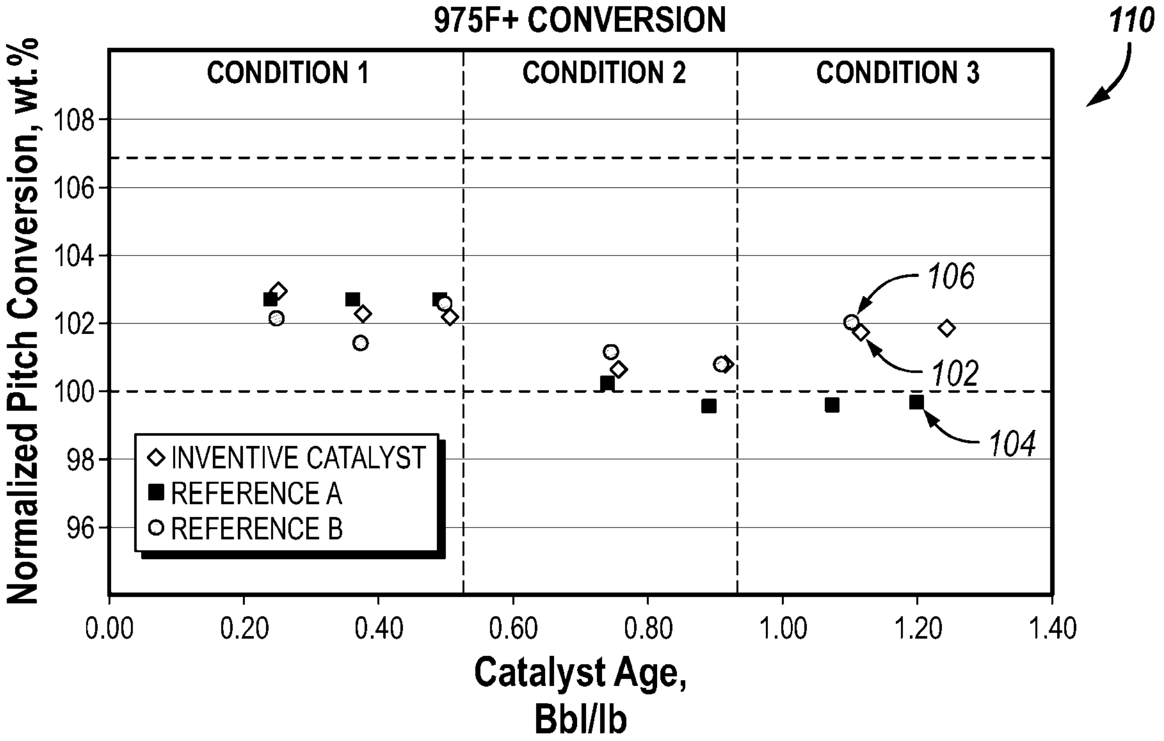
975F+ CONVERSION
110
CONDITION 1
CONDITION 2
CONDITION 3
Normalized Pitch Conversion, wt.%
108
106
104
102
100
98
96
106
102
104
◇ INVENTIVE CATALYST
■ REFERENCE A
○ REFERENCE B
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
Catalyst Age, Bbl/lb

FIG. 3

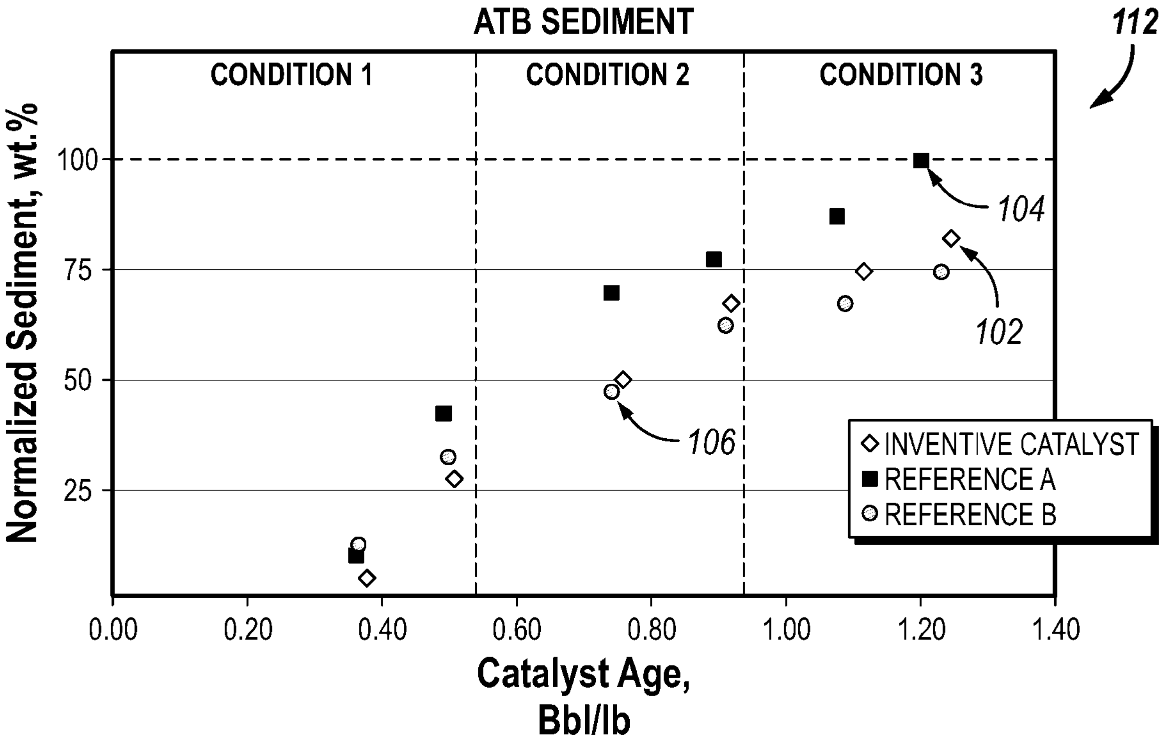
ATB SEDIMENT
112
CONDITION 1
CONDITION 2
CONDITION 3
Normalized Sediment, wt.%
100
75
50
25
104
102
106
◇ INVENTIVE CATALYST
■ REFERENCE A
◎ REFERENCE B
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
Catalyst Age, Bbl/lb

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/032521

A. CLASSIFICATION OF SUBJECT MATTER

INV.	B01J23/85	B01J23/883	B01J35/63	B01J35/64	B01J35/66
	B01J35/69	B01J37/00	C10G45/08	C10G45/16	C10G49/12
ADD.					

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/062871 A1 (BHAN OPINDER KISHAN [US]) 3 March 2022 (2022-03-03) cited in the application	1-3,5-14
A	examples I,II claims 1-20 paragraphs [0024], [0030], [0031], [0032], [0034] table 1 -----	4
A	US 9 879 187 B2 (SHELL OIL CO [US]) 30 January 2018 (2018-01-30) cited in the application examples claims 1-18 table 1 -----	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 4 September 2024	Date of mailing of the international search report 13/09/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Zuurdeeg, Boudewijn

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/032521

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