United States Patent Office 3,598,725
Patented Aug. 10, 1971

3,598,725

HYDROCARBON DESULFURIZATION WITH A RHENIUM CATALYST ON SILICEOUS CARRIER MATERIAL

Lee Hilfman, Prospect Heights, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill.

No Drawing. Filed Mar. 20, 1969, Ser. No. 809,050
Int. Cl. C10g 23/02
U.S. Cl. 208—216 5 Claims

ABSTRACT OF THE DISCLOSURE

A catalyst for effecting the desulfurization of sulfurous, hydrocarbonaceous charge stocks. The catalyst comprises a composite of a siliceous carrier material combined with rhenium sulfide. The rhenium sulfide is present in an amount of from 0.01% to about 2.0% by weight, calculated as the elemental metal, and is combined with one or more sulfided metallic components from Groups VI–B and the Iron-group. The use of the rhenium component imparts additional hydrogenation activity to the catalyst.

APPLICABILITY OF INVENTION

The present invention primarily involves a novel catalytic composite for utilization in effecting the desulfurization of sulfur-containing, hydrocarbon charge stocks. More specifically, the present invention involves the purification of hydrocarbon mixtures containing olefinic hydrocarbons and further contaminated with sulfurous compounds. In essence, the catalytic composite employed comprises a siliceous carrier material combined with rhenium sulfide. Other catalytically active components, those from Groups VI–B and particularly the Iron-group are combined therewith, the selection being principally dependent upon the character of the charge stock, especially with respect to contaminant level and boiling range, and the desired end result. However, it is necessary that the catalytically active metallic components exist in a sulfided state prior to contact with the particular hydrocarbon, or hydrocarbon mixture.

Although directed principally toward the destructive removal of sulfurous compounds contained within a hydrocarbon charge stock, the catalytic composites of my invention may be utilized to great advantage, as a direct result of inherent increased hydrogenation activity, in the preparation of substantially saturated charge stocks. The charge stocks suitable for processing in accordance with the present invention will be readily recognized by those possessing expertise in the field of petroleum processing; however, a brief discussion of applicable charge stocks is believed warranted. In general, hydrocarbonaceous fractions and/or distillates are divided into various categories determined by the overall boiling range. Depending upon various refinery demands, as well as the particular locale in which the final product is to be utilized, the boiling ranges of the various distillates will vary individually, and may even overlap in some instances. For example, the gasoline, or naphtha boiling range is generally considered to include pentanes and heavier hydrocarbons boiling up to an end boiling point of about 400° F. to about 425° F., with intermediate fractions being designated as "light naphtha," or "heavy naphtha." The kerosene boiling range commonly has an initial boiling point of from 300° F. to 425° F., and an end boiling point of from 500° F. to about 600° F. Light gas oils, therefore, generally have an initial boiling point of from 500° F. to about 600° F. and an end boiling point of about 750° F. to about 800° F., while heavy gas oils boil from about 750° F. to an end boiling point of about 1050° F. In recent years, interest has been generated with respect to the desulfurization of still higher-boiling hydrocarbonaceous material commonly referred to as "black oils." These are generally characterized as containing a considerable quantity of non-distillable material which would normally boil above a temperature of about 1050° F. In general, the degree of contamination, particularly with respect to sulfurous compounds, increases as the content of higher-boiling material increases. Thus, a heavy vacuum gas oil contains greater quantities of the contaminating influences than does a naphtha fraction. The particular catalytic composite utilized in the desulfurization of the foregoing hydrocarbon fractions will, in most instances, be modified to a certain extent as determined by the physical and/or chemical characteristics of the charge stock.

OBJECTS AND EMBODIMENTS

A principal object of my invention is to provide a desulfurization catalytic composite of a siliceous carrier material combined with rhenium sulfide. A corollary objective resides in a desulfurization catalyst which comprises a sulfided composite of a siliceous carrier material combined with rhenium and Iron-group metallic component.

In particular, an object of the present invention is to effect the desulfurization of a sulfurous, hydrocarbonaceous charge stock, utilizing the novel catalyst of the present invention. Therefore, in one embodiment, the present invention is directed toward a desulfurization catalytic composite of a siliceous carrier material combined with rhenium sulfide and the sulfide of at least one metal component from Group VI–B and the Iron-group.

In another embodiment, the present invention provides a process for the desulfurization of a sulfur-containing hydrocarbonaceous charge stock, which process comprises reacting said charge stock with hydrogen, at desulfurization conditions, in contact with a desulfurization catalyst comprising a siliceous carrier material combined with rhenium sulfide, and the sulfide of at least one metal selected from the group consisting of the metals from Group VI–B and the Iron-group, separating the resulting product effluent to provide a hydrogen-rich vaporous phase and to recover a desulfurized normally liquid hydrocarbon product.

Other embodiments of my invention involve the utilization of various particular modifications to the sulfided siliceous catalyst, and the operating conditions employed to effect desulfurization of the hydrocarbonaceous feed stock. For example, the siliceous carrier material may be an amorphous composite of alumina and silica, or a zeolitic composite of alumina and silica, the latter commonly referred to in the art as a "crystalline aluminosilicate," or a "molecular sieve." Among the various process variables, or operating conditions, are a pressure of from about 300 to about 5000 p.s.i.g. and a catalyst bed inlet temperature in the range of from about 200° F. to about 800° F. Other objects and embodiments of my invention will become evident from the following, more detailed description thereof.

SUMMARY OF INVENTION

As hereinbefore stated, my invention is principally concerned with a novel catalytic composite capable of effecting the desulfurization of a wide variety of hydrocarbonaceous charge stock. Essentially, the catalytic composite is formulated from two principal categories of ingredients; one ingredient constitutes one or more catalytically active metallic components, selected from the group consisting of the metals hereinafter specifically set forth, while the second ingredient is a carrier material therefor, being selected from one or more refractory inorganic oxides.

An essential feature of my invention is that the carrier material be siliceous in nature, and that the catalytically active metallic component be sulfided rhenium, and/or technetium, in combination with at least one metallic component selected from Group VI–B and the Iron-group of the Periodic Table. Thus, in accordance with the Periodic Table of The Elements, E. H. Sargent & Co., 1964, suitable metallic components are selected from the group consisting of rhenium, technetium, chromium, molybdenum, tungsten, iron, cobalt, nickel and mixtures thereof. The rhenium, or technetium component will be present within the catalytic composite, in a sulfided form, in concentrations within the range of from about 0.01% to about 2.0% by weight, and preferably from about 0.05% to about 1.0% by weight, calculated as the element. When the catalytic composite contains a metallic component from Group VI–B, for example molybdenum, it is present in an amount of from about 4.0% to about 40.0% by weight, and preferably from about 10.0% to about 30.0% by weight, calculated as the element. With respect to the Iron-group metals, these are employed in amounts of from about 1.0% to about 6.0% by weight.

Although the overall method for preparing the catalytic composite is not considered an essential feature of my invention, it is necessary that the metallic components be sulfided prior to being placed in service for the desulfurization of hydrocarbonaceous feed stocks. It must be acknowledged that a wide variety of sulfiding techniques are well-known and well-described in the literature; however, one sulfiding technique is particularly preferred in order to obtain all the beneficial results of the rhenium component in admixture with the other components. Following the incorporation of the catalytically active metallic components in the carrier material, the composite is dried at a temperature in the range of from about 200° F. to about 400° F. for a period of from about 2 to about 24 hours. The dried composite is then subjected to a calcination technique, in an atmosphere of air or other free oxygen containing gaseous mixture, at an elevated temperature of about 500° F. to about 1200° F., and for a period ranging from about 0.5 to about 10 hours. The sulfiding technique is effected when the composite is in a substantially reduced state; therefore, following the calcination treatment, an inert gas is utilized to sweep the composite free from excess oxygen, and the composite reduced in an atmosphere of substantially dry hydrogen. Substantially dry hydrogen is intended to connote a hydrogen stream containing less than about 5.0 p.p.m. of water, by volume. Although the reduction operation may be effected at the same temperature level as the calcination technique, it is preferred to reduce the catalytic composite while cooling the same to a lower temperature within the range of from about 400° F. to about 700° F. The time for the reduction technique is generally short, ranging from about 0.5 to about 5.0 hours. The substantially reduced composite is initially contacted at the lower temperature level with a stream of hydrogen and hydrogen sulfide in which the hydrogen/hydrogen sulfide mol ratio is at least about 1.5:1, with an upper limit of about 4:1. The temperature of the composite, during the sulfiding procedure is increased to a level in the range of from about 750° F. to about 850° F., and the sulfiding continued at this temperature for a period of about one hour. In order to assure substantially complete sulfidation of the composite, the overall sulfiding technique should be effected for a period of at least about 2 hours. Following the sulfidation of the composite, hydrogen sulfide is introduced intermittently, as is necessary to maintain a positive pressure of at least about 15.0 p.s.i.g., on the sulfided catalyst, while the latter is being cooled to a temperature below about 400° F. At this stage of the manufacturing procedure, a stream of suitable inert gaseous material, such as nitrogen, may be employed to cool the sulfided catalyst further in order to facilitate handling and ultimate storage.

The catalytically active components are combined with a siliceous carrier material. Regardless of the use of other refractory inorganic oxides, whether alumina, zirconia, magnesia, titania, boria, hafnia, etc., or mixtures thereof, it is preferred that the carrier material have a silica content of from about 10.0% by weight to about 90.0% by weight. To illustrate, where the catalytic composite is intended for the purpose of desulfurizing a kerosene fraction for the purpose of improving its jet fuel characteristics, a relatively low-silica carrier material is preferred. On the other hand, when desulfurizing a heavy vacuum gas oil in order to produce an ultimate product suitable for hydrocracking into lower-boiling gasoline components, a relatively high-silica composite is preferred. When existing in an amorphous state, the carrier material may be prepared by any of the co-precipitative, or successive precipitation methods known to the art. Similarly, where the carrier material is zeolitic in nature, the crystalline aluminosilicate, including Type X, Type Y, mordenite, or mordenite dispersed in an alumina, silica, or alumina-silica matrix, may also be prepared by any method known to the art. The incorporation of the catalytically active metallic components may be effected by co-precipitation with the siliceous material, impregnation of a dried and/or calcined carrier material, or ion-exchange as is the case with zeolitic material.

In some instances, generally dependent upon the ultimately desired result, the catalytic composite may contain a halogen component, the precise form of the association thereof with the carrier material not being accurately known. However, the prior art indicates that it is customary to refer to the halogen component as being combined therewith, or with the other ingredients of the composite, and it is, therefore, commonly referred to as combined halogen or combined halide. The halogen may be either fluorine, chlorine, iodine, bromine or mixtures thereof, with fluorine being particularly preferred. The halogen component may be added to the carrier material in any suitable manner, either during the preparation thereof, or before or after the addition of the other catalytically active components. When utilized, halogen component will be composited in such a manner as results in a final composite containing about 0.1% to about 1.5% by weight, and preferably from about 0.4% to about 0.9% by weight, calculated on an elemental basis.

Suitable desulfurization conditions of operation include a quantity of catalyst, preferably disposed in one or more fixed-bed reaction zones, such that the liquid hourly space velocity (defined as volumes of fresh feed charge per hour per volume of catalyst disposed within the zone) is within the range of from about 0.4 to about 10.0. In general, lower space velocities are utilized with the higher-boiling, more severely contaminated feed stocks, while the higher space velocities are utilized where the charge stocks are not severely contaminated. Hydrogen circulation, through the catalyst bed, during processing is a preferred technique from the standpoint of maintaining a "clean" catalytic composite, or one in which the deactivation rate due to the deposition of carbonaceous material is inhibited. Hydrogen circulation rates ranging from about 500 to about 15,000 standard cubic feet per barrel are utilized, again depending primarily on the character of the charge and the desired result. Operating pressures will generally range from about 500 to about 5000 p.s.i.g., while the catalyst bed inlet temperature is generally maintained in the range of from about 200° F. to about 800° F. Since the reactions being effected are exothermic in nature, a temperature increase will be experienced as the charge stock flows through the catalyst bed, resulting in a higher catalyst bed outlet temperature. A preferred technique limits the temperature increase to 100° F., and duced at intermediate loci of the catalyst bed, may be very often to 50° F.; conventional quench streams, intro-

CATALYST PREPARATION METHOD

As hereinbefore stated, the entire method of manufacturing the catalytic composite is not essential to my invention. However, for the sake of being complete, one such preferred method is herein set forth.

Water glass, containing 28.0% by weight of silica and having a specific gravity of 1.38, is commingled with water to make a 50/50 diluted solution. Similarly, hydrochloric acid (32.0% HCl by weight), having a specific gravity of about 1.16 is commingled with water to provide a 50/50 by weight, diluted solution. The hydrochloric acid and water glass solutions are intimately commingled. An aqueous solution of 7.65% by weight of aluminum oxide and 26.0% of aluminum sulfate, having a specific gravity of 1.31, is added to the previously prepared water glass-hydrochloric acid mixture.

Approximately 1275 pounds of the resulting mixture are simultaneously commingled with about 260 pounds of an aqueous solution of 28.0% by weight ammonium hydroxide. The rates of addition are such that the pH of the mixture is maintained in the range of 5.5 to about 6.5. Additional ammonium hydroxide, 600 pounds, is then added, followed by an additional 1275 pounds of the hydrochloric acid-water glass, aluminum sulfate mixture.

The resulting finely-divided slurry is filtered and water-washed to remove excessive ammonium hydroxide, sodium and sulfate ions. The final filter cake is dried to a volatile matter content of about 17.0% by weight, and subsequently ground to a talc-like powder. A suitable lubricating and binding agent, polyvinyl alcohol, is added thereto, and the powder is formed into 1/8" x 1/8" cylindical pills having a nominal crushing strength of about 12.0 pounds. The pills are calcined in an atmosphere of air for 2 hours at a temperature of about 1150° F. Molybdic acid, 85.0% by weight of molybdenum oxide, and hydrated nickel nitrate are separately commingled with the 28.0% solution of ammonium hydroxide, the individual solutions being commingled and utilized as an impregnating solution for the previously prepared alumina-silica pills. The impregnated pills are dried for three hours at 300° F., and calcined in air for one hour at 1100° F. The unimpregnated carrier material is 88.0% by weight of alumina and 12.0% by weight of silica. The impregnating solution is utilized in an amount to yield a final catalyst containing 2.0% by weight of nickel and 6.0% by weight of molybdenum, calculated on the basis of the elements.

These particles are then contacted with still another impregnating solution of hydrochloric acid and, for example, perrhenic acid in amounts to incorporate 0.2% by weight of rhenium and about 0.7% by weight of combined chloride, again on an elemental basis. The impregnated pills are dried for one hour at 300° F. and calcined in air at about 955° F. for about one hour.

The calcined alumina/silica composite is swept with nitrogen at the elevated temperature for about one-half hour, and the temperature is reduced to 500° F. in a flowing hydrogen stream. A gaseous stream of hydrogen sulfide and hydrogen in which the H_2/H_2S mol ratio is 3:1 is introduced into contact with the catalyst. The temperature is raised to 700° F., and the component concentration changed to 2:1 H_2/H_2S. After a period of about two hours, the sulfiding stream is discontinued and the catalyst cooled to 300° F., during which time 100.0% hydrogen sulfide is intermittently introduced to maintain a positive pressure of about 15.0 p.s.i.g. The introduction of hydrogen sulfide is ceased at a temperature of 300° F., and a stream of nitrogen employed to cool the catalyst to a temperature suitable for handling.

EXAMPLES

The following examples are presented for the purpose of illustrating the variety of uses of the catalysts encompassed by my invention, and to indicate the benefits attendant the utilization thereof. It is understood that the invention is not to be unduly limited to the particular charge stock, operating conditions, various processing techniques, and/or the specific catalyst utilized in these illustrative examples.

Example I

The charge stock utilized in this example is a blend of straight-run and coker distillates boiling within the gasoline boiling range. The charge stock has a gravity of about 55.9° API, an initial boiling point of about 194° F., an end boiling point of about 409° F., a bromine number of 7.2, and contains about 10.0 p.p.m. of nitrogen and about 0.052% by weight of sulfur (520 p.p.m.). The standard hydrodesulfurization catalyst, with which the catalyst of the present invention is compared, is a composite of an alumina carrier material combined with about 6.0% by weight of molybdenum and about 2.2% by weight of cobalt. The catalytic components are combined by way of impregnation, and this technique is followed by drying and calcination in an atmosphere of air. The composite is reduced in a stream of hydrogen, after which it is placed in a bench-scale reaction zone fabricated from 1-inch, Schedule 80, Type 316 stainless steel. The catalyst bed is in an amount of about 50.0 cubic centimeters, and is maintained at an operating pressure of about 800 p.s.i.g. The hydrogen circulation rate is 3000 standard cubic feet per barrel of liquid charge, and the inlet temperature to the catalyst bed is 700° F. Sulfiding of the catalyst is effected in situ during the processing of the sulfurous charge stock. At the foregoing conditions of operation, and a liquid hourly space velocity of about 6.0, the normally liquid product effluent indicates a gravity of 56.2° API, an initial boiling point of about 207° F., an end boiling point of about 411° F., a nitrogen content of about 0.5 p.p.m., a bromine number of about 0.4 and a sulfur concentration of about 19 p.p.m. by weight.

A sulfided catalytic composite encompassed by the present invention is prepared in the manner hereinbefore set forth. The carrier material is an amorphous composite of 90.0% by weight of alumina and 10.0% by weight of silica. Since the intended object is to prepare a charge stock suitable for use in a catalytic reforming unit, an excessive degree of hydrocracking to lower-boiling components is not desired. The catalytic composite is substantially halogen-free, containing 6.0% by weight of molybdenum and 1.0% by weight of rhenium, calculated as the elements, notwithstanding a presulfiding technique in an atmosphere of hydrogen and hydrogen sulfide, with hydrogen in a molar excess of about 2:1. The operating conditions are maintained at a pressure of 800 p.s.i.g., a catalyst bed inlet temperature of 700° F., a hydrogen circulation rate of 3000 standard cubic feet per barrel and a liquid hourly space velocity of about 6.0. Inspection of the normally liquid product effluent indicates a gravity of 56.2° API, an initial boiling point of about 190° F., an end boiling point of about 410° F., a bromine number of about 0.1, the presence of nitrogen in an amount of about 0.10 p.p.m. and a sulfur concentration less than about 1.0 p.p.m.

Example II

In this example, the charge stock is a light cycle oil having a gravity of about 25.9° API, an initial boiling point of 324° F., an end boiling point of about 670° F., a bromine number of 15.6, and contains 322 p.p.m. of nitrogen and 3400 p.p.m. of sulfur. A single change is effected in the composition of the catalytic composite. In this instance, the catalytic composite considered as the standard hydro-desulfurization catalyst, is also sulfided prior to contact with the charge stock. Operating conditions are changed slightly in view of the higher-boiling charge stock; the pressure is about 1000 p.s.i.g., the catalyst bed inlet temperature is about 720° F., the hydrogen circulation rate is about 2500 standard cubic feet per barrel and the liquid hourly space velocity is 3.0. The catalytic composite without the rhenium com-

ponent produces a normally liquid product having a nitrogen concentration of about 60.0 p.p.m., a bromine number of about 6.6 and a sulfur concentration of about 200 p.p.m. The product effluent emanating from the reaction zone containing the sulfided rhenium-molybdenum catalyst indicates a lower sulfur concentration of about 100 p.p.m., a lower nitrogen content of about 11.2 p.p.m. and a lower bromine number of the order of about 2.0.

Example III

This example is presented to illustrate the benefits of the desulfurization catalyst of my invention when processing a kerosene boiling range feed stock for the purpose of improving its jet fuel characteristics. The kerosene fraction has a gravity of about 40.9° API, an initial boiling point of about 361° F., an end boiling point of about 518° F., and is further characterized by an IPT Smoke Point of about 20.8 mm., a sulfur concentration of about 1480 p.p.m. and an aromatic hydrocarbon content of about 19.0 vol. percent.

The kerosene fraction is initially processed with about 650 standard cubic feet per barrel of hydrogen, in contact with a catalytic composite of about 0.75% by weight of rhenium and 5.7% by weight of molybdenum, combined with a carrier material of 90.0% by weight of alumina and 10.0% by weight of silica. Prior to contacting the kerosene fraction, as the last step in the manufacturing procedure, the catalytic composite is subjected to the presulfiding technique hereinbefore set forth. The pressure imposed upon the reaction zone is about 550 p.s.i.g., and the catalyst bed inlet temperature is at a level necessary to control the outlet temperature at about 725° F. The liquid hourly space velocity through the reaction zone is 4.8, and the operation is effected for a period of about 50 hours. Analyses of the product effluent indicate a gravity of 41.1° API, an initial boiling point of 340° F. and an end boiling point of 512° F. The IPT Smoke Point is slightly increased to a level of about 21.9 mm., the aromatic concentration is about 17.0 vol. percent and the sulfur concentration is reduced to about 30 p.p.m.

The normally liquid product effluent from the first catalytic reaction zone, following the removal of hydrogen sulfide, is processed in contact with a catalytic composite of 1.0% by weight of nickel and 0.75% by weight of rhenium, combined with a carrier material of 90.0% by weight of alumina and 10.0% by weight of silica. The catalytic composite is presulfided in accordance with the previously-described procedure, and utilized in an amount such that the liquid hourly space velocity therethrough is about 1.0. The reaction zone is maintained under an imposed pressure of 810 p.s.i.g., and the hydrogen circulation rate is about 4000 standard cubic feet per barrel.

Following separation and distillation to concentrate the kerosene fraction, analysis indicate that the product has a gravity of about 44.2° API, an initial boiling point of 325° F. and an end boiling point of about 512° F. The aromatic concentration is decreased to a level of 1.7% by volume, the IPT Smoke Point is increased to 33.7 mm., and the sulfur concentration is essentially "nil."

The foregoing specification and examples indicate the method by which my invention is effected, and the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the desulfurization of a sulfurous, hydrocarbonaceous charge stock which comprises reacting the sulfur content of said charge stock with hydrogen in contact with a desulfurization catalyst comprising an alumina-silica carrier material containing at least 10% by weight of silica combined with rhenium sulfide and the sulfide of at least one metal selected from the group consisting of the metals from Group VI–B and the Iron-group, and separating the resulting effluent to recover a desulfurized normally liquid hydrocarbon product.

2. The process of claim 1 further characterized in that said desulfurization conditions include a pressure of about 300 to about 5,000 p.s.i.g. and a catalyst bed inlet temperature of from about 200° F. to about 800° F.

3. The process of claim 1 in which the alumina/silica weight ratio in said carrier material is in the range of from 10/90 to about 90/10.

4. A proces for the desulfurization of a sulfurous, hydrocarbonaceous charge stock which comprises reacting the sulfur content of said charge stock with hydrogen in contact with a sulfided catalytic composite of an alumina-silica carrier material containing at least 10% by weight of silica combined with 0.01% to 2.0% by weight of a rhenium component and 4.0% to about 40.0% by weight of a Group VI–B metal component, and separating the resulting product effluent to recover a desulfurized normally liquid hydrocarbon product.

5. The process of claim 4 further characterized in that said catalytic composite contains 1.0% to about 6.0% by weight of an Iron-group metal component.

References Cited

UNITED STATES PATENTS

3,394,077	7/1968	Kovach et al.	208—217
3,449,078	6/1969	Quik et al.	252—459

DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner

U.S. Cl. X.R.

208—217