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[54] **DESULFURIZATION PROCESS AND CATALYST**
6 Claims, No Drawings

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ABSTRACT: A desulfurization catalyst of an alumina-containing carrier material, a nickel component and a tin component. Nickel constitutes from 1.0 percent to about 10.0 percent by weight of the composite and tin from about 0.7 percent to 7.0 percent, and preferred catalysts also contain from 4.0 percent to about 30.0 percent by weight of a Group VI-B metal component. The catalyst is prepared in a manner which inhibits the formation of nickel aluminate.

DESULFURIZATION PROCESS AND CATALYST

APPLICABILITY OF INVENTION

Desulfurization is a process deeply rooted in petroleum refining technology. Published literature abounds with references relative to suitable catalysts, methods of catalyst manufacture and the techniques employed in the utilization thereof. Although desulfurization connotes the destructive removal of sulfurous compounds, through conversion into hydrogen sulfide and hydrocarbons, it is often included in the broad term "hydrorefining." Hydrorefining processes are effected at operating conditions which promote denitrification and desulfurization primarily, and asphaltene conversion, nondistillable conversion, hydrogenation and hydrocracking to some extent. In other words, the terms "hydrorefining" and desulfurization are generally employed synonymously to allude to a process wherein a hydrocarbonaceous feedstock is "-cleaned up," in order to prepare a charge stock suitable for utilization in a subsequent hydrocarbon conversion process, and in which some conversion to lower-boiling products is effected.

For example, it is especially advantageous to catalytically reform various straight run gasolines, natural gasolines, catalytically cracked naphtha fractions and/or thermally cracked hydrocarbon distillates for the primary purpose of improving the motor fuel and antiknock characteristics thereof. The hydrorefining process is utilized to produce a substantially saturated charge stock, for use in the catalytic reforming process, which charge stock is substantially free from sulfurous and nitrogenous compounds. Desulfurization processes are not, however, limited to improving the physical and chemical characteristics of a naphtha boiling range charge stock. The literature is replete with a multitude of processes and catalysts to be employed in the treatment of heavier charge stocks including kerosenes, light gas oils, full boiling range gas oils, heavy gas oils and even "black oils." In petroleum refining technology, a black oil is considered to be one containing excessive quantities of sulfurous and nitrogenous compounds, high molecular weight organometallic complexes principally comprising nickel and vanadium, and asphaltic material. Black oils are further characterized as containing nondistillable material—having a boiling point above a temperature of 1,050° F.

The process of the present invention is directed toward the use of a novel catalytic composite for desulfurizing hydrocarbonaceous material, and particularly the heavier material known as black oil. An illustrative example of a black oil, to which the present scheme is applicable, is a vacuum tower bottoms product having a gravity of about 7.1 ° API, and containing 4.05 percent by weight of sulfur and about 23.7 percent by weight of heptane-insoluble asphalts.

OBJECTS AND EMBODIMENTS

A principal object of the present invention is to provide a novel catalytic composite for use in the desulfurization of hydrocarbonaceous material.

Another object is to provide an improved process for desulfurizing a sulfurous hydrocarbon charge stock, which process is effected utilizing a coextruded catalytic composite of an alumina-containing carrier material, a nickel component and a tin component.

Therefore, in one embodiment, the present invention relates to a desulfurization catalyst comprising coextruded particles of an alumina-containing inorganic oxide material, a nickel component and a tin component, which catalyst contains less than 0.1 percent by weight of nickel aluminate.

In another embodiment, the desulfurization conditions include a maximum catalyst bed temperature of about 200° F. to about 900° F., a pressure of about 400 to about 5,000 p.s.i.g., an LHSV of about 0.1 to about 10.0 and a hydrogen concentration of about 1,000 to about 50,000 s.c.f./bbl.

Other objects and embodiments of my invention relate to additional details regarding the preferred catalytic ingredients, the concentration of components within the catalytic composite, the method of catalyst preparation, preferred processing techniques and similar particulars which are hereinafter given in the following, more detailed summary of my invention.

SUMMARY OF INVENTION

Catalytic composites which are tailored to be utilized in a process for hydrorefining hydrocarbonaceous material, and particularly residual stocks or black oils, have traditionally consisted of an element chosen from the Iron-group metals, particularly nickel or cobalt, combined with a metal component from the metals of Groups VI–B, particularly molybdenum or tungsten. In general, preferred metal components are nickel and molybdenum, or nickel and tungsten, and these components are generally combined with a porous carrier material comprising both alumina and silica, and which is either amorphous, or zeolitic in nature. Ample evidence may be found in the literature to indicate that the nickel component, while present in a significantly lower concentration, materially contributes to the desired activity of such catalyst.

A perusal of the published literature relative to this phase of catalysis, confirms the effect of nickel on catalytic activity. Furthermore the prior art indicates a preference for two particular methods of catalyst preparation. One method, predominantly preferred, involves impregnating a previously calcined carrier material, generally in the form of spheres or pills, with suitable soluble compounds of the nickel and molybdenum. The impregnating technique is generally followed by drying at a temperature of about 300° F. and calcination at a temperature of about 1,100° F. The second preparation scheme involves coprecipitating all the components, including those of the carrier material. For example, an aqueous solution of aluminum chloride, sodium silicate, nickel chloride and molybdenum oxide is formed and coprecipitated by the addition of ammonium hydroxide. The art, while speculatively teaching that the final catalytic composite may take the form of extrudates, quite clearly indicates an overwhelming preference for spheres and/or pills, which are impregnated with the metal components, or coprecipitated therewith. My investigations into the area of hydrorefining catalysts, containing, for example, nickel and molybdenum, have indicated that an acceptable coextruded catalyst is not readily prepared. The poor results obtained with such catalysts appear to be inherent in the catalyst manufacturing method. Extrudates are generally prepared by a scheme which involves coprecipitating the carrier material and the nickel and molybdenum components. The precipitate is filtered and dried, and then rehydrated to a proper consistency for extrusion. The extrudates are then subjected to drying and high-temperature calcination. During this calcination step, the nickel component reacts with the alumina to form a nickel aluminate which in effect destroys the desired activity of the nickel component for desulfurization.

My investigations have indicated further that a very active hydrotreating catalyst can be prepared in the form of extrudates by coextruding nickel and tin with the preformed carrier material. When the formed extrudates are dried and calcined, the nickel will preferably react with the tin rather than react with the carrier material. It is possible, therefore, to produce a coextruded hydrotreating catalyst containing the desired nickel and molybdenum, or nickel and tungsten components, and one which contains less than 0.1 percent by weight of nickel aluminate.

Other advantages include the attractive economics of a more simple and faster catalyst preparation technique. It will be immediately recognized by those possessing expertise in the art of catalyst manufacturing schemes, that the use of coextrusion eliminates several tedious steps involved, for example, in an impregnation scheme. Further, larger capacity equipment is possible, leading to greater catalyst production in a shorter period of time. One principal advantage resides in the production of catalyst particles, coextrudates, having pore diameters in the highly desired range of about 100 to about 300 Angstroms. Control of the pore diameter, or size, is readily regulated by the pressure imposed in forming the extrudates. With respect to spheres and/or pills, control of pore diameter is available only through the tedious regulation of the apparent bulk density.

Considering first the porous carrier material, it is preferred that it be an absorptive, high-surface area support. Suitable carrier materials are selected from the group of amorphous refractory inorganic oxides including alumina, titania, zirconia, chromia, magnesia, boria, and mixtures of two or more such as silica-alumina, silica-zirconia, alumina-silica-boron phosphate, etc. When of the amorphous refractory inorganic oxide type, a preferred carrier material constitutes a coprecipitated composite of alumina and silica, with silica being present in an amount of from about 10.0 percent to about 90.0 percent by weight. In many applications of the present invention, the carrier material will consist, at least in part, of a crystalline aluminosilicate. This may be naturally occurring, or synthetically prepared, and includes mordenite, faujasite, Type A or Type U molecular sieves, etc. When a crystalline aluminosilicate, or zeolitic material, is intended for use as the carrier material, it may be prepared in a number of ways known in the art. One common method is to mix solutions of sodium silicate, or colloidal silica, and sodium aluminate, and permit the solutions to react to form a solid crystalline aluminosilicate. Another method is to contact a solid inorganic oxide from the group of silica, alumina and mixtures thereof with an aqueous treating solution containing alkali metal cations (preferably sodium) and anions selected from the group of hydroxyl, silicate and aluminate, and permit the solid-liquid mixture to react until the desired crystalline aluminosilicate has been formed. In addition to the foregoing, the carrier material may comprise a combination in which the zeolitic material is dispersed within an amorphous matrix, the latter being alumina, silica, or silica-alumina. It is understood that the coextrusion scheme employed for preparing the catalyst of the present invention does not involve coprecipitation of the active metal components with the carrier material. The latter is preformed prior to any contact with the nickel and molybdenum, or tungsten.

Following the formation of the coextruded extrudates, the final composite will generally be dried at a temperature in the range of about 200° F. to about 600° F., for a period of from 2 to about 24 hours or more, and finally calcined at a temperature of about 700° F. to about 1,200° F. in an atmosphere of air, for a period of about 0.5 to about 10 hours. When the carrier material comprises a crystalline aluminosilicate, it is preferred that the calcination temperature not exceed about 1,000° F.

METHOD OF CATALYST PREPARATION

The initial step in the catalyst preparation technique involves commingling the preformed carrier material, for example, a composite of 63.0 percent by weight of alumina and 37.0 percent by weight of silica with salts of nickel and tin. Such salts include nickel nitrate hexahydrate, nickel chloride, stannic chloride, stannous chloride, nickel bromide, etc. Proportions are used which result in a final catalytic composite comprising from 1.0 percent to about 10.0 percent by weight of nickel and 0.7 percent to about 7.0 percent by weight of tin. The solid mixture is ground to a talclike powder, about 20 to 100 mesh, and preferably from 30 to 50 mesh and intimately admixed with a relatively minor quantity of a suitable acid including hydrochloric acid, nitric acid, hydrofluoric acid, etc. A preferred technique involves mulling the acidic mixture which is subsequently aged for a short period of about 15 minutes to about 20 hours. The Group VI-B metal component, where desired, in a concentration of 4.0 percent to about 30.0 percent by weight, is added at this stage of the preparation technique through the use of a suitable compound such as ammonium molybdate, tungstic acid, molybdic acid, ammonium tungstate, etc. This mixture is again subjected to mulling and a quiescent age for a period of about 15 minutes to about 2 hours. The resulting plastic-type mass is extruded under a suitable pressure in the range of about 1,000 to about 10,000 p.s.i.g., to form extrudates of the desired size—e.g. one-sixteenth inch by one-sixteenth inch. After drying and calcining in the manner hereinbefore set forth, the extrudates are found to contain less than 0.1 percent by weight of nickel aluminate.

Although not essential to successful desulfurization, it is often preferred to incorporate a halogen component into the catalytic composite. Although the precise form of the chemistry of association of the halogen component with the carrier material and metallic components is not accurately known, it is customary in the art to refer to the halogen component as being combined with the carrier material, or with the other ingredients of the catalyst. The halogen may be either fluorine, chlorine, iodine, bromine, or mixtures thereof, with fluorine and chlorine being particularly preferred. The quantity of halogen is such that the final catalytic composite contains about 0.1 percent to about 3.5 percent by weight, and preferably from about 0.5 percent to about 1.5 percent by weight, calculated on the basis of the elemental halogen.

Prior to its use in the conversion of hydrocarbons, the resultant catalytic composite may be subjected to a substantially water-free reduction technique. Substantially pure and dry hydrogen (less than about 30.0 vol. p.p.m. of water) is employed as the reducing agent. The calcined composite is contacted at a temperature of about 800° F. to about 1,200° F., and for a period of about 0.5 to about 10 hours, and effective to substantially reduce the metallic components.

Additional improvements are generally obtained when the reduced composite is subjected to a presulfiding operation for the purpose of incorporating therewith from about 0.05 percent to about 0.5 percent by weight of sulfur, on an elemental basis. The presulfiding treatment is effected in the presence of hydrogen and a suitable sulfur-containing compound such as hydrogen sulfide, lower molecular weight mercaptans, various organic sulfides, carbon disulfide, etc. The preferred technique involves treating the reduced catalyst with a sulfiding gas, such as a mixture of hydrogen and hydrogen sulfide having about 10 mols of hydrogen per mol of hydrogen sulfide, at conditions selected to effect the desired incorporation of sulfur. It is generally considered a good practice to perform the presulfiding technique under substantially water-free conditions.

In accordance with my invention, the hydrocarbon charge stock and hydrogen are contacted with a catalyst of the type described above in a hydrocarbon conversion zone. The contacting may be accomplished by using the catalyst in a fixed-bed system, a moving-bed system, in fluidized-bed system, or in a batch-type operation. In view of the risk of attrition loss of the catalyst, it is preferred to use a fixed-bed system. In this type of system, a hydrogen-rich vaporous phase and the charge stock are preheated by any suitable heating means to the desired initial reaction temperature, the mixture being passed into the conversion zone containing the fixed-bed of the catalytic composite. It is understood, of course, that the hydrocarbon conversion zone may consist of one or more separate reactors having suitable means therebetween to insure that the desired conversion temperature is maintained at the entrance to one or more catalyst beds. The reactants may be contacted with the catalyst in either upward, downward or radial flow fashion, with a downward/radial flow being preferred.

The operating conditions imposed upon the reaction zone, or zones, are primarily dependent upon the charge and the desired end result. However, these conditions will generally include a maximum catalyst bed temperature of about 200° F. to about 900° F., a pressure of about 400 to about 5,000 p.s.i.g., an LHSV of about 0.1 to about 10.0 and a hydrogen concentration of about 1,000 to about 50,000 s.c.f./bbl.

Hydrorefining processes are generally exothermic in nature, and an increasing temperature gradient will be experienced as the hydrogen and feedstock traverse the catalyst bed. It is desirable to maintain the maximum catalyst bed temperature below about 900° F., which temperature is virtually identical to that which may be conveniently measured at the outlet of the reaction zone. In order to insure that the catalyst bed temperature does not exceed the maximum allowed, the use of conventional quench streams, either normally liquid or normally gaseous, introduced at one or more intermediate loci of the catalyst bed, may be utilized. In some situations, a heavy hydrocarbonaceous material is intended for hydrorefining, accompanied by some conversion into lower-boiling hydrocarbon products. A portion of the normally liquid product effluent boiling above the end boiling point of the desired product will generally be recycled to combine with the fresh feed charge stock. In this type of process, the combined liquid feed ratio (defined as volumes of total liquid charge to the reaction zone per volume of fresh liquid to the reaction zone) will be within the range of about 1.1 to about 6.0

ILLUSTRATIVE EXAMPLE

Specific operating conditions, processing techniques, a particular catalytic composite and other individual process details will be given in the following description of a process to which my invention is applicable. In presenting this illustration, it is not intended that the present invention be limited to the specifics, nor is it intended that a given process be limited to the particular operating conditions, catalytic composite, processing techniques, charge stock, etc. Therefore, it is understood that the present invention is merely illustrated by the specifics hereinafter set forth.

A desulfurization catalyst was prepared by commingling 200 grams of a calcined alumina-silica coprecipitate, 32.6 grams of nickel nitrate hexahydrate and 12.97 grams of stannic chloride. The solid mixture was ground to a powder having a size of about 40 mesh. The powder was intimately admixed with 15 cc. of concentrated nitric acid and 55 cc. of water by mulling, and subsequently aged for a period of about one-half hour. Ammonium molybdate, in an amount of 24.24 grams, dissolved in 14.0 cc. of a 28.0 percent by weight ammonia solution, was added to the aged mixture, mulled and aged again for a period of about one-half hour. The resulting plastic-type mass was extruded at a pressure of about 4,000 p.s.i.g., to form 1/16-inch extrudates. These were dried at a temperature of 225° F. for 3 hours and calcined, in an atmosphere of air, at a temperature of 1,100° F. for a period of about 1 hour. Analyses indicated that the extrudates had an apparent bulk density of about 0.774 g./cc. and contained 3.4 percent by weight of nickel, 7.2 percent by weight of molybdenum and 2.3 percent by weight of tin.

This desulfurization catalyst is utilized in processing a blend of heavy vacuum gas oils with the intended object being the maximum production of a 350°–685° F. furnace oil having a maximum pour point of 0° F. The blended charge stock has a gravity of 23.1 ° API an initial boiling point of about 594° F., a 50.0 percent volumetric distillation temperature of 858° F. and an end boiling point of about 1,050° F. The charge stock contains 889 p.p.m. by weight of nitrogen and 2.22 percent by weight of sulfur. The desulfurization unit is designed to process about 16,500 bbl./day of the heavy vacuum gas oil blend utilizing about 7,000 cubic feet of catalyst, resulting in an LHSV of 0.56.

The charge stock is initially admixed with about 2,350 bbl./day of a recycle diluent having an initial boiling point of about 685° F., and hydrogen in an amount of 6,400 s.c.f./bbl., based only upon fresh feed; the combined liquid feed ratio is 1.14. The mixture is heated to a temperature of about 800° F., and is introduced into the reaction zone under a pressure of about 2,500 p.s.i.g. The increasing temperature gradient is maintained at a level of 50° F. through the use of a hydrogen quench in an amount of 5,100 s.c.f./bbl. (based upon the fresh gas oil charge stock).

The product yield and distribution, resulting from this desulfurization process, is indicated in the following table I.

TABLE I

Desulfurization Product Distribution

Component	Wt.%*	Vol.%
Ammonia	0.11	
Hydrogen Sulfide	2.36	
Methane	0.34	
Ethane	0.56	
Propane	1.14	
Butanes	2.27	3.61
Pentanes	1.82	2.65
Hexanes	2.28	3.02
Heptane—350° F.	14.18	17.23
350° F.—685° F.	77.45	86.44

*Inclusive of hydrogen consumption of 2.51 by weight.

Pertinent liquid product inspections are presented in the following table II.

TABLE II

Product Inspections

Stream	C_5/C_6	C_7—350°-350	350°–685°
Gravity, °API	82.6	56.3	41.0
Sulfur, wt. p.p.m.		1	5
Four Point, °F.			−25
Flash Point, ° F.			156

Significantly, these results are achieved with only 2.04 percent by weight (based upon fresh feed) loss of charge stock to light, normally gaseous hydrocarbons. Furthermore, the total volumetric yield of normally liquid hydrocarbons, including butanes, is 112.95 percent by volume. Of further significance is the fact that these results are accompanied by a catalyst service, expressed as barrels of fresh charge stock per pound of catalyst disposed in the reaction zone, greater than 100.

I claim as my invention:

1. A process for desulfurizing a sulfurous hydrocarbon charge stock which comprises reacting said charge stock and hydrogen, at desulfurization conditions, selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons, in contact with a coextruded catalytic composite of an inorganic oxide carrier material selected from the group consisting of alumina and silica-alumina, a Group VI–B metal component, a nickel component and a tin component, and containing less than 0.1 percent by weight of nickel aluminate, said catalyst having been prepared by mixing a preformed inorganic oxide carrier material as specified above with Group VI–B metal, nickel and tin components, extruding the resulting mixture, drying and calcining the resulting extrudate, said tin functioning to minimize formation of nickel aluminate during the calcination step.

2. The process of claim 1 further characterized in that said desulfurization conditions include a pressure of about 400 to about 5,000 p.s.i.g., a maximum catalyst bed temperature of about 200° F. to about 900° F., a liquid hourly space velocity of about 0.1 to about 10.0 and a hydrogen concentration of about 1,000 to about 50,000 s.c.f./bbl.

3. A desulfurization catalyst comprising coextruded particles of an inorganic oxide carrier material selected from the group consisting of alumina and alumina-silica, from 4.0 percent to about 30.0 percent by weight of a Group VI–B metal component, from about 1.0 percent to about 10.0 percent by weight of nickel, and about 0.7 percent to about 7.0 percent

by weight of tin, and containing less than about 0.1 percent by weight of nickel aluminate, said catalyst having been prepared by mixing a preformed inorganic oxide carrier material as specified above with Group VI–B metal, nickel and tin components, extruding the resulting mixture, drying and calcining the resulting extrudate, said tin functioning to minimize formation of nickel aluminate during the calcination step.

4. The catalyst of claim 3 further characterized in that said Group VI–B metal component is molybdenum, or a compound of molybdenum.

5. The catalyst of claim 3 further characterized in that said Group VI–B metal component is tungsten, or a compound of tungsten.

6. The catalyst of claim 1 further characterized in that said carrier material further includes a crystalline alumino-silicate.

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