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# RESIDUE DESULFURIZATION WITH CATALYST WHOSE PORE VOLUME IS DISTRIBUTED OVER WIDE RANGE OF PORE SIZES

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## ABSTRACT OF THE DISCLOSURE

The disclosure relates to the hydrodesulfurization of sulfur-containing petroleum oils containing residual components and metallic contaminants employing catalyst comprising a hydrogenating component composited on an alumina base whose pore volume is distributed over a wide range of pore sizes.

This invention relates to desulfurization of petroleum oils containing residual components and having high sulfur contents and more particularly to a catalytic hydrodesulfurization process for reducing high sulfur content petroleum oils containing residual components by the use of catalytic compositions that are especially effective for such purpose.

Residual petroleum oil fractions containing relatively high proportions of sulfur as well as high sulfur crude oils are relatively less salable than the corresponding oils of low sulfur content. In fact, high sulfur residual fuels may be entirely unsalable in some localities, since they cannot be used as low grade fuel in municipalities that have adopted maximum sulfur specifications for fuels burned in their jurisdictions. Such residual fuels may be still more difficultly disposable when their viscosities and/or heavy metals content are so great as to require dilution with the relatively large proportions of cutter stocks of relatively greater value.

It has been proposed to improve the salability of high sulfur content, residual-containing petroleum oils by a variety of hydrodesulfurization processes. However, difficulty has been experienced in achieving an economically feasible catalytic hydrodesulfurization process, because notwithstanding that the desulfurized products may have a wider marketability, the manufacturer may be able to charge little or no additional premium for the low sulfur desulfurized products, and since hydrodesulfurization operating costs have tended to be relatively high in view of the previously experienced, relatively short life for catalysts used in the hydrodesulfurization of residual-containing stocks. Short catalyst life is manifested by inability of a catalyst to maintain a relatively high capability for desulfurizing charge stock with increasing quantites of coke and/or metallic contaminants which act as catalyst poisons. Satisfactory catalyst life can be obtained relatively easily with distillate oils but is especially difficult to obtain in desulfurizing petroleum oils containing residual components, since the asphaltene or asphaltic components of an oil, which tend to form disproportionate amounts of coke, are concentrated in the residual fractions of a petroleum oil, and since a relatively high proportion of the metallic contaminants that normally tend to poison catalysts are commonly found in the asphaltene components of the oil.

The present invention relates to a process for the catalytic hydrodesulfurization of sulfur-containing petroleum oils containing residual components and containing metallic contaminants in the presence of a catalyst having an unusual tolerance for the coke and metallic contaminants that accompany processing of residual-containing stocks, as evidenced by a continued high level of desulfurization activity, notwithstanding a relatively heavy deposition of coke and metal contaminants. In accordance with the process of this invention a sulfur-containing petroleum oil that contains residual components and metallic contaminants normally tending to act as catalyst poisons, is contacted with hydrogen at hydrodesulfurization conditions in the presence of a catalyst comprising at least one hydrogenating component composited with an alumina base, said composite catalyst having not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units. Catalysts of the class indicated that also have a surface area of at least 100 square meters per gram are preferred. The hydrodesulfurization reactions of the present process can be effected at a hydrogen partial pressure in the range of about 500 to 4000 p.s.i.g., preferably about 1000 to 2000 p.s.i.g., a temperature, after startup, in the range of about 600° to 850° F., preferably about 650° to 800° F., at a space velocity in the range of 0.1 to 10, preferably about 0.5 to 5, volumes of liquid per volume of catalyst per hour, using a hydrogen:oil ratio in the range of about 1000 to 15,000, preferably about 5000 to 10,000 s.c.f. of hydrogen per barrel of oil. Especially advantageous results are obtained by the present invention in the desulfurization of petroleum oil stocks containing at least 2 percent sulfur and at least 10 p.p.m. vanadium, and when the operating conditions of the process are so selected and maintained as to produce a constant reduction in sulfur content of about 40 to 80 percent, preferably 50 to 75 percent.

The feed stock to the desulfurization reaction zone of the present process can be any sulfur-containing petroleum stock containing residual materials. Since the catalysts of the class disclosed herein have an especially high tolerance for feed stocks containing metallic contaminants normally tending to act as catalyst poisons, the present process is especially advantageous in connection with crude oils containing at least 10 p.p.m. vanadium and with residues containing at least 20 p.p.m. vanadium. Since an important advantage achieved by the present invention is the maintenance of a relatively high level of desulfurization, notwithstanding a relatively large accumulation of coke deposits and metallic contaminants, the invention is especially useful in connection with crude oils containing at least 1.5 percent sulfur and with residues containing at least 2 percent sulfur. From what has been said, it will be clear that the feed stock can be a whole crude. However, since the high sulfur content components of a crude oil tend to be concentrated in the higher boiling fractions, the present process more commonly will be applied to a bottoms fraction of a petroleum oil, i.e., one which is obtained by atmospheric distillation of a crude petroleum oil to remove lower boiling materials such as naphtha and furnace oil, or by vacuum distillation of an atmospheric residue to remove gas oil. Typical residues to which the present invention is applicable will normally be substantially composed of residual hydrocarbons boiling above 900° F. and containing a substantial quantity of asphaltic materials. Thus, the charge stock can be one having an initial or 5 percent boiling point somewhat below 900° F., provided that a substantial proportion, for example, about 40 or 50 percent by volume, of its hydrocarbon components boil above 900° F. A hydrocarbon stock having a 50 percent boiling point of about 900° F. and which contains asphaltic materials, 3 percent by weight sulfur and 15 p.p.m. vanadium is illustrative of such charge stock.

The hydrodesulfurization reactions effected pursuant to the process of this invention are carried out at a temperature that is maintained, after the relatively rapid elevation of temperature employed during startup, in the range of about 600° to 850° F. Hydrodesulfurization at temperatures in the range of about 650° to 800° F. are preferred, since notwithstanding that the same given degree of desulfurization can be maintained at higher temperatures, relatively larger proportions of gaseous products are produced, which products involve a disproportionate consumption of hydrogen.

The desulfurization reactions are effected in the presence of uncombined hydrogen partial pressures in the range of about 750 to 4000 p.s.i.g. The process of this invention is especially useful in connection with desulfurizations in which the degree of desulfurization is maintained at a relatively high level, i.e., 40 to 80 percent, preferably 50 to 75 percent, and in which hydrogen consumption is minimized. To this end we prefer to carry out the process of this invention at hydrogen partial pressures in the range of 1000 to 2500 p.s.i.g.

The desulfurization reactions of the subject process are carried out at a liquid hourly space velocity in the range of 0.1 to 10, preferably about 0.5 to 5 liquid volumes of oil per volume of catalyst per hour.

The hydrogen gas which is used during the hydrodesulfurization is circulated at a rate between about 1000 and 15,000 s.c.f./bbl. of feed and preferably between about 5000 and 10,000 s.c.f./bbl. The hydrogen purity may vary from about 60 to 100 percent. If the hydrogen is recycled, which is customary, it is desirable to provide for bleeding off a portion of the recycle gas and to add makeup hydrogen in order to maintain the hydrogen purity within the range specified. Satisfactory removal of hydrogen sulfide from the recycled gas will ordinarily be accomplished by such bleed-off procedures. However, if desired, the recycled gas can be washed with a chemical absorbent for hydrogen sulfide or otherwise treated in known manner to reduce the hydrogen sulfide content thereof prior to recycling.

As indicated, the invention is especially beneficial where hydrodesulfurization is effected without concomitant cracking of the hydrocarbons present in the feed stock. To achieve this objective, the temperature and space velocity are selected within the ranges specified that will result in the reduction in the sulfur content of the feed stock of about 40 to 80 percent, preferably 50 to 75 percent, and so that no more than about 1 to 5 gram moles of hydrogen will be consumed per gram atomic weight of sulfur removed from the feed stock.

As indicated, it has been found that the nature of the catalyst employed in the process is very important with respect to the results achieved. The class of catalysts useful for purposes of the present invention comprises those containing at least one hydrogenating component composited with an alumina carrier, which composite catalyst has not more than 15 percent of the volume of the pores having a radius of 0 to 300 Angstrom units in any 10 Angstrom unit increment of pore radius in the range of pores having a 0 to 120 Angstrom unit radius. Furthermore, the pore volume should be more or less uniformly distributed over this range so that at least about 10 percent of the above pore volume of the pores having a radius in the range of 0 to 300 Angstrom units is in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume is in pores having a radius of greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume is in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units.

It will be appreciated that for most porous catalyst supports, the major portion of the pore volume will be in pores of less than 300 Angstrom units radius and that by far the major portion of the total pore volume in these relatively small pores will be found in pores having a radius from 0 to 120 Angstrom units. Since the chief portion of the total pore volume of a given porous catalyst support material is normally made up of pores in the 0 to 120 Angstrom unit radius range, it is these pores that are considered to be chiefly responsible for the behavior of a given catalyst. Although the present invention is based on the discovery of a correlation between the hydrodesulfurization of petroleum residues and the distribution of the pore volume in the 0 to 120 Angstrom unit radius range, the pore volume fractions set forth herein have been stated in terms of the volume of the pores having a radius in the 0 to 300 Angstrom unit radius range, since pore volume distribution, as measured by conventional nitrogen adsorption-desorption techniques, is normally reported in these terms.

For most porous catalytic supports, particularly those considered to be especially effective in the hydrodesulfurization of distillate stocks, it has been observed that a very high concentration of the pore volume will be concentrated in pores of about the same size, and it has been postulated that there is a correlation between the catalytic effect of a catalyst, the diameter or radius of the most frequently occurring pore size, and the average molecular diameter of the feed stock. While this theory may hold true for the desulfurizing activity of catalysts with respect to distillate feed stocks, it has now been found that contrary to supposition, what is needed for greater effectiveness in the desulfurization of residual stocks is not a catalyst having a large concentration of pores of any particular size range, but rather a catalyst having a relatively uniform, wide distribution of pores over the entire 0 to 120 Angstrom radius range.

While the mechanism by which the catalysts of this invention function has not been conclusively established, it is considered that their unusual effectiveness may be due to the fact that there are sufficient large pores present to accommodate the preferentially adsorbed large molecules without blocking, so that the pores in other size ranges, which would normally tend to become blocked by the coked residue of large molecules, remain relatively free to effect desulfurization of small and intermediate sized molecules. This hypothesis is supported by the fact that catalysts of the class disclosed herein show superior aging characteristics as compared to catalysts having a disproportionate pore volume distribution, even though the latter catalysts show higher initial desulfurizing activity.

Thus, the class of catalysts included by the present invention comprises those containing at least one hydrogenating component composited with a porous alumina support, which composite catalyst has not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units. Such catalysts also should have a surface area of at least 100 square meters per gram.

Catalysts of the class indicated can be obtained in any convenient way, for example by impregnation of a suitable alumina support with solutions containing the desired hydrogenating component or components, drying and calcining. Suitable alumina supports, like the finished catalysts, are those having not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units. Such supports can be obtained as articles of commerce or they can be prepared in any convenient manner. An example of a suitable commercial support are selected batches of Filtrol Grade 86 alumina having the indicated pore volume distribution.

Alternatively, a support having the desired pore volume distribution can be prepared by precipitation, at a pH in the range of about 4.5 to 6.0 of aluminum hydroxide from an aqueous solution of aluminum sulfate, at a temperature in the range of about 160° to 210° F., preferably 180° to 200° F., by addition of ammonia gas or ammonium hydroxide. The pH of the mixture can be raised as high as 8 to minimize peptization or colloid formation. The mixture is preferably allowed to age for a period of at least 4 to 6 hours or longer, preferably with stirring, in order to complete the reaction as far as possible. The elevated temperature is maintained throughout the aging period. After aging, the precipitate is filtered and washed free of sulfate ions and dried. The thus-obtained mixture will comprise a crystalline alumina mixture containing principally boehmite and bayerite aluminas. This material is then calcined with a suitable hot gas, such as flue gas, at a temperature in the range of about 1000° to 1250° F. and sufficient to obtain a temperature in the solids such as to effect substantial dehydration of the water of constitution. The calcined product will have the pore size distribution characteristic of the class of supports useful for the purposes of the present invention.

It is emphasized that the hydrogenating components need not be deposited on the support after calcination, and, if desired, can be deposited on the dried uncalcined support, prior to calcination.

The hydrogenating component of the class of catalysts disclosed herein can be any material or combination thereof that is effective to hydrogenate and desulfurize the charge stock under the reaction conditions utilized. For example, the hydrogenating component can be at least one member of the group consisting of Group VI–B and Group VIII metals in a form capable of promoting hydrogenation reactions, especially effective catalysts for the purposes of this invention are those comprising molybdenum and at least two members of the iron group metals. Preferred catalysts of this class are those containing nickel, cobalt and molybdenum, but other combinations of iron group metals and molybdenum such as iron, nickel and molybdenum and iron, nickel and molybdenum and iron, cobalt and molybdenum, as well as combinations of nickel and molybdenum, cobalt and molybdenum, nickel and tungsten or other Group VI–B or Group VIII metals taken singly or in combination. The hydrogenating components of the catalysts of this invention can be employed in sulfided or unsulfided form; however, the use of catalysts whose hydrogenating component is in sulfided form is preferred.

Although the hydrogenating components indicated above can be employed in any proportions with respect to each other, especially effective catalysts for the purposes of this invention are those in which the hydrogenating component is selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent, preferably 4 to 16 percent, by weight molybdenum and at least 2 iron group metals where the iron group metals are present in such proportions that the atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4, and (b) a combination of about 5 to 40 percent, preferably 10 to 25 percent, by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:0.1 to 5, preferably 1:0.3 to 4.

When the use of a catalyst in sulfided form is desired, the catalyst can be presulfided, after calcination, or calcination and reduction, prior to contact with the charge stock, by contact with a sulfiding mixture of hydrogen and hydrogen sulfide, at a temperature in the range of about 550° to 650° F., at atmospheric or elevated pressures. Presulfiding can be conveniently effected at the beginning of an onstream period at the same conditions to be employed at the start of such period. The exact proportions of hydrogen and hydrogen sulfide are not critical, and mixtures containing low or high proportions of hydrogen sulfide can be used. Relatively low proportions are preferred for economic reasons. When the unused hydrogen and hydrogen sulfide utilized in the presulfiding operation is recycled through the catalyst bed, any water formed during presulfiding is preferably removed prior to recycling through the catalyst bed. It will be understood that elemental sulfur or sulfur compounds, e.g., mercaptans, that are capable of yielding hydrogen sulfide at the sulfiding conditions, can be used in lieu of hydrogen sulfide.

Although presulfiding of the catalyst is preferred, it is emphasized that this is not essential as the catalyst will normally become sulfided in a very short time by contact, at the process conditions disclosed herein, with the high sulfur content feed stocks to be used.

## EXAMPLE 1

In a specific embodiment, a catalyst representative of the class disclosed herein was prepared by deposition of the desired hydrogenating components on a commercial, calcined alumina base having a density of 39.0 pounds per cubic foot, a surface area of 299.6 square meters per gram, a pore volume of 0.79 milliliter per gram and an average pore radius of 79.1 Angstrom units. A typical sample of the calcined base had a pore volume distribution over the range of pores having a radius from 0 to 300 Angstrom units as follows:

| Pore radius, A.: | Pore volume, percent |
|---|---|
| 300–250 | 1.3 |
| 250–200 | 2.9 |
| 200–150 | 5.0 |
| 150–120 | 15.2 |
| 120–110 | 7.6 |
| 110–100 | 7.6 |
| 100–90 | 6.6 |
| 90–80 | 8.2 |
| 80–70 | 8.2 |
| 70–60 | 8.1 |
| 60–50 | 6.8 |
| 50–40 | 7.4 |
| 40–30 | 7.7 |
| 30–20 | 9.6 |
| 20–10 | 2.9 |
| 10–7 | 0.0 |

The hydrogenating components comprised a combination of 8 percent molybdenum, 1 percent cobalt and 0.5 percent nickel. The atomic ratios of these metals were as follows: 0.2 Co and 0.1 Ni:Mo. A catalyst of equivalent makeup and properties is suitably prepared by impregnating an alumina base having the pore volume distribution indicated with a solution of ammonium paramolybdate in an aqueous ammoniacal solution. The amount of ammonia used in the solution was sufficient to yield ammonium monomolybdate. The catalyst base is impregnated with the ammonium molybdate solution using the incipient wetness technique. Following the initial impregnation, the material is dried for 24 hours at a temperature above that required to evaporate water of impregnation.

After drying, the nickel and cobalt metals are deposited on the molybdenum-alumina from a water solution of the metal nitrates. The thus-impregnated base is then dried as described and calcined at 900° to 1000° F. in an oxygen-containing gas, whereby the hydrogenating metal components are converted to the oxide form.

The finished catalyst employed in the runs described below had a total pore volume of 0.46 ml./g., a surface area of 165.8 m.$^2$/g., and an average pore radius of 74.5 Angstrom units and a pore volume distribution, over the range of pores having a radius from 0 to 300 Angstrom units, as follows:

| Pore radius, A.: | Pore volume, percent |
|---|---|
| 300–250 | 0.8 |
| 250–200 | 1.5 |
| 200–150 | 2.5 |
| 150–120 | 5.7 |
| 120–110 | 4.6 |
| 110–100 | 7.1 |
| 100–90 | 9.5 |
| 90–80 | 11.7 |
| 80–70 | 11.6 |
| 70–60 | 10.2 |
| 60–50 | 8.6 |
| 50–40 | 8.7 |
| 40–30 | 7.9 |
| 30–20 | 8.8 |
| 20–10 | 1.1 |
| 10–7 | 0.0 |

The above-described catalyst was used in the catalytic hydrodesulfurization of a Kuwait crude oil containing approximately 2.5 percent sulfur and approximately 30 p.p.m. vanadium. The sulfur content of the residual fuel oil component of the crude (650° F. plus residue) was 4.0 percent. The conditions employed in the reaction were 2400 p.s.i.g. total reaction pressure (2000 p.s.i.g. hydrogen partial pressure) and a space velocity of 3.28 liquid volumes of oil per volume of catalyst, while maintaining a hydrogen to oil ratio of 5000 s.c.f./bbl. In this operation, the initial stabilized reaction temperature, following initial rapid temperature increase during startup, was 726° F. after four days of operation. At that time the sulfur content of the residual fuel oil component of the product (650° F. plus residue) was approximately 1.16 percent. The reaction was allowed to continue with temperature elevation as required to maintain the sulfur content of the residual fuel oil component of the crude oil feed stock below 1.3 percent sulfur. After 56½ days of continuous operation, the sulfur content of the residual fuel oil component of the product had not exceeded 1.3 percent and the temperature of the reaction had not exceeded 760° F.

By way of contrast, in a similar aging run carried out at 2400 p.s.i.g. total reactor pressure (2000 p.s.i.g. hydrogen partial pressure), a space velocity of 3.0 liquid volumes of oil per volume of catalyst per hour, while maintaining a hydrogen to oil ratio of 5000 s.c.f./bbl. oil, using a catalyst containing the same quantities of nickel, cobalt and molybdenum deposited on a commercial alumina carrier, where the finished catalyst had 28.4 percent of the pore volume of pores having a radius of 0 to 300 Angstrom units in pores having a radius of 30–40 Angstrom units and 28.8 percent of such pore volume in pores having a radius of 20–30 Angstrom units, but only 7.1 percent of such pore volume in pores having a radius of 50 to 60 Angstrom units, 2.4 percent in the 60 to 70 Angstrom unit range, 0.5 percent in the range of 70 to 80 Angstrom units, 0.4 percent in the range of 80 to 90 Angstrom units, 0.2 percent in the range of 90 to 100 Angstrom units, and which was known to be very effective for desulfurization of petroleum distillate fractions, the percent sulfur in the residual fuel oil component of the product was 1.1 percent at 704° F. after two days. After 20 days the temperature had been raised to 769° F., and the percent sulfur in the residual fuel oil component of the product was 1.52 percent.

Similarly, still another aging run was carried out with the same Kuwait crude oil charge stock at a total reaction pressure of 2300 p.s.i.g. (2000 p.s.i.g. hydrogen partial pressure), a 3.1 liquid hourly space velocity, using a hydrogen to oil ratio of 9000 s.c.f./bbl. wherein there was employed a catalyst containing the same portions of nickel, cobalt and molybdenum as in the above-indicated catalyst, deposited on a commercial alumina having 20.2 percent of the pore volume of the pores having a radius of 0 to 300 Angstrom units in pores having a radius of 10–20 Angstrom units and 25.2 percent of such pore volume in pores having a radius of 20–30 units, but only 6.9 percent in the range of 50 to 60 Angstrom units, 3.2 percent in the range of 60 to 70 Angstrom units, 1.9 percent in the range of 70 to 80 Angstrom units, 1.5 percent in the range of 80 to 90 Angstrom units, and 1.0 percent in the range of 90 to 100 Angstrom units. Although this catalyst had been found highly effective for desulfurization of petroleum distillates, the sulfur content of the residual fuel oil component of the product increased from about 1.16 percent at two days and a temperature of 735° F. to 1.64 percent after 20 days, in spite of an increase in temperature to 765° F. during that time.

## EXAMPLE 2

In another specific embodiment, the charge stock of Example 1 is hydrodesulfurized at the conditions of Example 1 with a catalyst of 6 percent nickel and 19 percent tungsten, in sulfided form, deposited on the alumina of Example 1.

The unusual coaction during hydrodesulfurization, between catalysts of the class disclosed herein and high-sulfur petroleum oils containing residual components, has been demonstrated by comparative experiments in which separate samples of a Kuwait crude oil containing 2.50 percent sulfur and approximately 30 p.p.m. vanadium were hydrodesulfurized at the same process conditions, over an alumina-supported catalyst representative of the class disclosed herein and another catalyst containing the same hydrogenating components in the same proportions. In both runs the hydrodesulfurization was effected at a hydrogen partial pressure of 1000 p.s.i.g. at a temperature of 790° F. and at a space velocity of 2.0 liquid volumes of oil per volume of catalyst per hour, while maintaining a hydrogen to oil ratio of 10,000 s.c.f./bbl. In each instance the catalyst was an alumina having deposited thereon 0.5 percent nickel, 1 percent cobalt and 8 percent molybdenum. In each case the catalyst was obtained by impregnation of the calcined alumina base with aqueous solutions containing the metallic impregnants in soluble form, followed by drying and calcining to the oxide form. The physical properties of the respective catalysts, including the pore volume distribution, is indicated in the following table in which Catalyst A is a catalyst representative of the class disclosed herein and in which Catalyst B is a catalyst obtained from another commercial alumina base.

| Pore Radius, Angstrom Units | Catalyst A, Volume, percent | Catalyst B, Volume, percent |
|---|---|---|
| 300-250 | 1.3 | 0.1 |
| 250-200 | 3.1 | 0.2 |
| 200–150 | 9.8 | 0.4 |
| 150–120 | 14.5 | 0.3 |
| 120–110 | 8.7 | 0.2 |
| 110–100 | 6.8 | 0.2 |
| 100–90 | 6.7 | 0.2 |
| 90-80 | 6.4 | 0.4 |
| 80-70 | 6.5 | 0.5 |
| 70-60 | 5.2 | 2.4 |
| 60–50 | 5.5 | 7.1 |
| 50–40 | 5.0 | 19.3 |
| 40-30 | 3.8 | 28.4 |
| 30-20 | 4.9 | 28.8 |
| 20–10 | 11.9 | 11.5 |
| 10–7 | 0.0 | 0.0 |
| Total Pore Vol., ml./g. | 0.47 | 0.27 |
| Surface Area, m.$^2$/g. | 221.2 | 175.5 |
| Average Pore Radius, A. | 91.7 | 33.2 |

In carrying out the above experiments the initial activity in terms of percent sulfur removed from charge stock was determined after stabilization of the temperature at the level indicated, following the initial rapid increase of temperature during startup. Thereafter, in order to induce accelerated aging of the catalysts, the same samples on which initial activity with the Kuwait crude charge stock referred to above had been determined were then contacted with a Ceuta crude oil feed stock at 2,000 p.s.i.g. hydrogen partial pressure, 790° F., and a space velocity of 2 liquid volumes of oil per volume of catalyst per hour, while maintaining a hydrogen to oil ratio of 10,000 s.c.f./bbl. of oil. The Ceuta crude charge stock used for aging the catalysts had a gravity of 33.5° API, a sulfur content of 1.10 percent, a nitrogen content of 0.15 percent by weight, a carbon residue of 3.39, a vanadium content of 104 p.p.m., and a nickel content of 13 p.p.m. Contact of the catalysts with the Ceuta crude was continued at the conditions indicated for 17½ days. Owing to the high metals content and high coke-forming tendencies of the Ceuta crude, this period of time was equivalent to about 70 days of contact with the Kuwait crude. After this accelerated aging period with the Ceuta crude feed stock, the catalysts were again contacted with the Kuwait crude charge stock described above, without intermediate regeneration of the catalyst, to determine what activity remained in the respective catalysts for desulfurization of the Kuwait crude. Analyses of the aged catalysts were also obtained to determine the amount of coke and vanadium deposited thereon. The results of these experiments are set forth in the following table:

| Catalyst | Desulfurization, percent by wt. | | Deposits on Aged Catalyst, percent by wt. | |
|---|---|---|---|---|
| | Fresh | Aged | Coke | Vanadium |
| Catalyst A | 79.2 | 47.0 | 18.8 | 6.4 |
| Catalyst B | 88.0 | 24.0 | 14.0 | 2.2 |

Comparison of the desulfurization activity of fresh Catalyst A with that of fresh Catalyst B indicates that catalysts having a relatively uniform pore volume distribution in the range of pores having a radius of 0 to 120 Angstrom units, i.e., catalysts of the class disclosed herein, have poorer initial desulfurization activity for residual fuel oils than conventional alumina-supported desulfurization catalysts having a high concentration of pores of about the same particular size, i.e., catalysts representative of the type found useful for desulfurizing distillates. Surprisingly, however, it will be noted that after severe aging, Catalyst A retained sufficient activity still to remove 47 percent of the sulfur from the charge stock, whereas Catalyst B had lost so much activity through aging that it was capable of removing only 24 percent of the sulfur from the charge stock, at the same conditions. Not only is this surprising, taking into consideration the fresh activities of the respective catalysts, but also these results are further unexpected in view of the fact that Catalyst A had accumulated markedly greater amounts of coke and vanadium during the accelerated aging cycle than had Catalyst B.

As indicated previously, the catalysts of the class disclosed herein are also advantageous as compared with catalysts normally considered superior for hydrodesulfurization of distillates in that they produce a total liquid product of higher API gravity and which is lower in sulfur, nitrogen, carbon residue and metals. In addition, catalysts of the class disclosed herein produce substantially larger quantities of gasoline and furnace oil distillate, and the desulfurized residue yields are relatively smaller, of higher quality and of markedly lower viscosity. The latter feature is important since lower viscosity residual oils require smaller proportions of cutter oil to render them useful as residual fuels.

The advantages indicated above have been demonstrated by comparative experiments in which a residual oil obtained as bottoms from the vacuum distillation of the atmospheric residue of a Kuwait crude oil was hydrodesulfurized at equivalent conditions over a catalyst of the class disclosed herein and a similarly prepared catalyst having identical hydrogenating components deposited thereon but which did not have the pore volume distribution of the herein disclosed catalysts. In each instance the catalyst was an alumina having deposited thereon 0.5% nickel, 1% cobalt and 8% molybdenum. In each case the catalyst was obtained by impregnation of the calcined alumina base with aqueous solutions containing the metallic impregnants in soluble form, followed by drying and calcining to the oxide form. In these runs the catalysts were presulfided by contact with a hydrogen-hydrogen sulfide mixture at the reaction conditions. The physical properties of typical samples of the respective catalysts, including the pore volume distribution, are indicated in the following table, wherein Catalyst C is a catalyst representative of the class disclosed herein and in which Catalyst D is a catalyst prepared in equivalent fashion from another commercial alumina base.

| Pore Radius, Angstrom Units | Catalyst C, Pore Vol., percent | Catalyst D, Pore Vol., percent |
|---|---|---|
| 300-250 | 1.2 | 0.2 |
| 250-200 | 1.7 | 0.2 |
| 200-150 | 2.9 | 0.7 |
| 150-120 | 2.8 | 0.4 |
| 120-110 | 5.9 | 0.2 |
| 110-100 | 6.1 | 0.2 |
| 100-90 | 8.3 | 0.3 |
| 90-80 | 11.2 | 0.3 |
| 80-70 | 11.5 | 1.6 |
| 70-60 | 11.4 | 7.4 |
| 60-50 | 9.5 | 32.9 |
| 50-40 | 9.5 | 27.1 |
| 40-30 | 8.0 | 15.5 |
| 30-20 | 9.1 | 12.9 |
| 20-10 | 0.7 | 0 |
| 10-7 | 0.0 | 0 |
| Total Pore Vol., ml./g | 0.45 | .5128 |
| Surface Area, m.$^2$/g | 165.0 | 190.9 |
| Average Pore Radius, A | 71.6 | 53.2 |

The hydrodesulfurization conditions employed in the comparative runs and the significant product inspections, along with the corresponding charge stock inspections, are set forth in the following table:

| | Charge Stock | Catalyst C | Catalyst D |
|---|---|---|---|
| Operating Conditions: | | | |
| Pressure, p.s.i.g | | 1,000 | 1,000 |
| Average Temperature, ° F | | 792 | 791 |
| Hydrogen Rate, s.c.f./bbl | | 9,284 | 9,750 |
| Run Length, hours | | 80 | 80 |
| Liquid Hourly Space Velocity, vol./hr./vol | | 0.50 | 0.53 |
| Catalyst Inspection: Carbon, percent by wt | | 28.39 | 15.88 |
| Total Liquid Product Inspections: | | | |
| Gravity, ° API | 5.5 | 19.5 | 17.2 |
| Sulfur, percent by wt | 5.45 | 0.88 | 1.24 |
| Nitrogen, percent by wt | 0.43 | 0.32 | 0.36 |
| Carbon Residue, Conradson, percent by wt | 23.11 | 10.19 | 11.61 |
| Vanadium, p.p.m | 102 | 5.1 | 7.3 |
| Nickel, p.p.m | 32 | 8.4 | 13.6 |
| Liquid Product Fractions: Gasoline (IBP-400° F.) Yield, percent by vol. of charge | | 9.3 | 6.1 |
| Furnace Oil (400°-670°) Yield, percent by vol. of charge | | 17.9 | 15.3 |
| Residue (670° F.): | | | |
| Yield, percent by vol. of charge | | 71.1 | 77.9 |
| Inspections: | | | |
| Gravity, °API | | 13.5 | 12.3 |
| Viscosity, SUV, sec.: | | | |
| 100° F | | 13,227 | 24,235 |
| 200° F | | 235 | 384 |
| Vanadium, p.p.m | | 5.8 | 9.6 |
| Nickel, p.p.m | | 10.1 | 16.5 |

From a comparison of the inspections of the products obtained over Catalyst C with the corresponding product inspections obtained from Catalyst D, it will be seen that in the case of the run carried out with Catalyst C, a catalyst representative of the class disclosed herein, the total liquid product had a higher API gravity and was lower in sulfur, nitrogen, carbon residue and metals than the product obtained in the run in which Catalyst D, a catalyst representative of the class of catalysts known to be useful for hydrosulfurization of distillates is utilized. In addition, it will be seen that the total liquid product obtained with Catalyst C contained relatively larger proportions of gasoline and furnace oil, and correspondingly lower yields of residue. Finally, the residue produced with Catalyst C is of higher quality than that produced with Catalyst D. All of these results are the more surprising in view of the fact that Catalyst C at the end of the run had accumulated a markedly greater carbon content than had Catalyst D.

We claim:

1. A process for catalytically hydrodesulfurizing a sulfur-containing petroleum oil that contains residual components and metallic contaminants normally capable of acting as catalyst poisons, comprising contacting said oil with hydrogen at hydrodesulfurization conditions in the presence of a catalyst comprising a hydrogenating component composited with an alumina base, said composite catalyst having not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment, starting at 0 Angstrom units, of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units.

2. A process for catalytically hydrodesulfurizing a sulfur-containing petroleum oil that contains residual components and metallic contaminants that are normally capable of acting as catalyst poisons, comprising contacting said oil with hydrogen at a partial pressure in the range of about 500 to 4000 p.s.i.g., at a temperature, after startup, in the range of about 600° to 850° F., at a space velocity in the range of about 0.1 to 10 volumes of liquid per volume of catalyst per hour, while maintaining a hydrogen:oil ratio in the range of about 1000 to 15,000 s.c.f./bbl. oil, in the presence of a catalyst comprising a hydrogenating component composited with an alumina base, said composite catalyst having not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment, starting at 0 Angstrom units, of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units.

3. The process of claim 2 wherein the hydrogen partial pressure is in the range of about 1000 to 2000 p.s.i.g., the temperature, after startup, is in the range of about 650° to 800° F., the space velocity is in the range of about 0.5 to 5 volumes of liquid per volume of catalyst per hour, and the hydrogen:oil ratio is in the range of about 4000 to 10,000 s.c.f./bbl. oil.

4. The process of claim 2 wherein the catalyst also has a surface area of at least 100 square meters per gram.

5. The process of claim 2 wherein the hydrogenating component of the catalyst is at least one member of the group consisting of metals of Group VI–B and Group VIII in a form capable of promoting hydrogenation reactions.

6. The process of claim 5 wherein the hydrogenating component is selected from the group consisting of sulfides and oxides of (a) a combination of about 2 to 25 percent by weight molybdenum and at least two iron group metals where the iron group metals are present in such proportions that the atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4, and (b) a combination of about 5 to 40 percent by weight of nickel and tungsten where the atomic ratio of tungsten:nickel is about 1:0.1 to 5.

7. The process of claim 6 wherein the hydrogenating component is selected from the group consisting of sulfides and oxides of (a) a combination of about 4 to 16 percent by weight molybdenum and at least two iron group metals, where the iron group metals are present in such proportions that the atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4, and (b) a combination of about 10 to 25 percent by weight of nickel and tungsten where the atomic ratio of tungsten:nickel is about 1:0.3 to 4.

8. A process for catalytically hydrodesulfurizing a sulfur-containing petroleum oil that contains residual components and metallic contaminants that are normally capable of acting as catalyst poisons, comprising contacting said oil with hydrogen at a hydrogen partial pressure in the range of about 1000 to 2000 p.s.i.g. at a temperature, after startup, in the range of about 650° to 800° F., at a space velocity in the range of about 0.5 to 5 volumes of liquid per volume of catalyst per hour, while maintaining a hydrogen:oil ratio in the range of about 1000 to 15,000 s.c.f./bbl. oil, in the presence of a catalyst comprising a hydrogenating component composited with an alumina base, said composite catalyst having not more than 15 percent of the volume of the pores having a radius in the range of 0 to 300 Angstrom units in any 10 Angstrom unit increment, starting at 0 Angstrom units, of pore radius in the range of pores having a 0 to 120 Angstrom unit radius, and also having at least about 10 percent of such pore volume in pores having a radius of less than 30 Angstrom units, at least 15 percent of such pore volume in pores having a radius greater than 30 Angstrom units and less than 70 Angstrom units, and at least 30 percent of such pore volume in pores having a radius of greater than 70 Angstrom units and less than 120 Angstrom units, and where the hydrogenating component is selected from the group consisting of sulfides and oxides of (a) a combination of about 4 to 16 percent by weight molybdenum and at least two iron group metals, where the iron group metals are present in such proportions that the atomic ratio of each iron group metal with respect to molybdenum is less than about 0.4, and (b) a combination of about 10 to 25 percent by weight of nickel and tungsten where the atomic ratio of tungsten to nickel is about 1:0.3 to 4, the reaction temperature and the space velocity being so controlled as to effect hydrogen consumption in the range of about 1 to 5 gram mols of hydrogen per gram atomic weight of sulfur removed from said oil.

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