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HYDROFINING CATALYST AND PROCESS USING SAME

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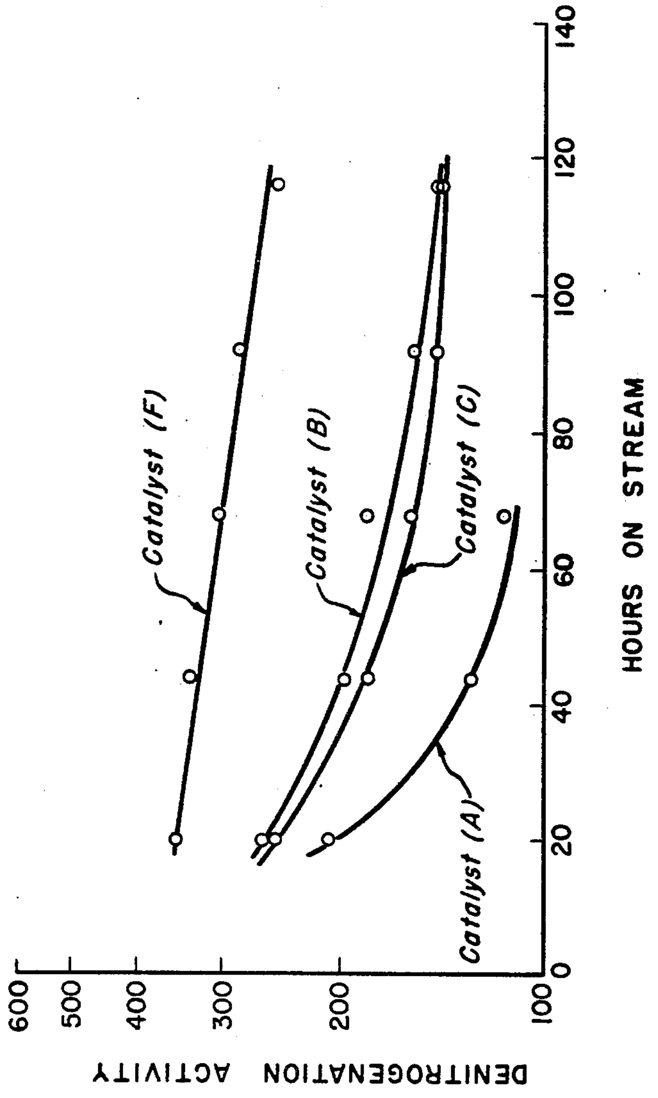

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HYDROFINING CATALYST AND PROCESS USING SAME

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This invention relates to the hydroprocessing of heavy gas oils and hydrocarbon residua. More particularly, it relates to a novel catalyst for the hydroprocessing of heavy gas oils and hydrocarbon residua and a process employing same.

Petroleum crudes are composed of a large variety of hydrocarbons, which include heavy distillates and hydrocarbon residua. Heavy distillates boil at temperatures above about 570° F. and include the heavy gas oils and light lubricating oils. The hydrocarbon residua, which are made up of saturates, monoaromatics, polyaromatics, resins and asphalt, are found to have molecular weights ranging from about 600 to about 1200 or above. At this time, the complete composition of petroleum is not known. There are many areas in the makeup of the crude where the molecular compositions of the compounds remain unknown. This is particularly true in the case of the heavy and residual fractions.

Today there are various processes employing numerous refining techniques which are used by petroleum refiners to upgrade the petroleum fractions obtained from the crudes. These processes, such as isomerization, reforming, hydrocracking, and alkylation are well-known in the art and may be used successfully to convert various hydrocarbon fractions into useful products. However, such processes do not convert effectively the higher-boiling feed stocks and fractions into sufficient quantities of useable products, such as motor fuels and heating fuels. Among these higher-boiling hydrocarbons are the heavy gas oils and the hydrocarbon residua. Such fractions have not been exploited fully by the refiner. Attempts to refine these heavy materials have shown, for the most part, that the processing must be done at such high severities that such processing is unattractive. These refractory materials give relatively low yields of usable products. The normal refining processes will not convert them into economical quantities of products. In general, the typical hydrocracking process will not convert efficiently such refractory heavy hydrocarbons to useable products. Accordingly, a primary object of the present invention is to provide a catalyst that can be used effectively to convert the refractory, higher-boiling gas oils and residual hydrocarbons to more useable products and a process using such a catalyst.

Hydrocarbon residua are, for the most part, byproducts of processes which are primarily used to obtain other petroleum products. The residual fuel oils are examples of such hydrocarbon residua. Commercial residual fuel oils have gravities which may vary between 8.9 and 23.5° API, flash points within the range of about 150° to about 450° F., and pour points within a range of about −55° to about 50° F. Their Conradson carbon residues may fall within a range of about 0.1 to about 11.5% and their boiling points may fall within a range of about 300° to about 1100° F. Such residual fuel oils have been used generally to supply heat.

The heavier fractions of the various petroleum crudes will contain appreciable amounts of sulfur and nitrogen, as well as certain so-called heavy metals. For example, a vacuum reduced crude may be found to contain as much as 100 parts per million nickel. Metals such as these deleteriously affect the life of any catalyst over which the hydrocarbons containing such metals are being processed.

In upgrading the heavier fractions of a petroleum crude, it is ultimately required that a portion of the nitrogen be removed from the heavy-gas-oil fraction and that a substantial amount of the heavy metals be removed from the fraction boiling above 650° F., this latter material being sent usually to a catalytic cracker for an additional treatment.

Hydroprocessing may be used in the upgrading of heavier petroleum fractions to usable petroleum products. It comprises the contacing of the hydrocarbon material that is being processed with a suitable catalyst under suitable conditions in the presence of hydrogen. The outstanding growth of catalytic reforming and the large amounts of hydrogen resulting therefrom have advanced the economic attractivenes of hydroprocessing. In such a process, not only are a great deal of the sulfur and a large percentage of the nitrogen removed from the hydrocarbon material being processed, but also the hydrocarbon material is hydrocracked to yield some usable hydrocarbon products.

Hydrocracking is a general term which is applied to petroleum refining process employing destructive hydrogenation wherein hydrocarbon feed stocks which have relatively high molecular weights are converted to lower-molecular-weight hydrocarbons at elevated temperature and pressure in the presence of a suitable catalyst and a hydrogen-containing gas. Hydrogen is consumed in the conversion of organic nitrogen to ammonia and sulfur to hydrogen sulfide, in the splitting of high-molecular-weight compounds into lower-molecular-weight compounds, and in the saturation of olefins and other unsaturated compounds.

Suitable catalysts have been developed for the hydroprocessing of hydrocarbon fractions boiling at temperature within the light-gas-oil boiling range. In this hydroprocessing treatment, the feed stock is destructively hydrogenated to lower-molecular-weight material. Typically, such catalysts comprise cobalt, molybdenum, and their oxides and sulfides on a solid inorganic-oxide support such as alumina. However, these catalysts will not convert in an efficient manner such refractory hydrocarbon materials as the heavy gas oils and hydrocarbon residua. We have found a catalyst which will convert the heavy gas oils and hydrocarbon residua into more usable materials and a hydroprocessing process that uses such a catalyst.

Briefly, we have prepared a catalyst which is surprisingly useful for hydroprocessing heavy gas oils and hydrocarbon residua. This catalyst is a solid catalytic composition which comprises at least one hydrogenation component on a solid inorganic-oxide support comprising a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms. Suitably, this catalyst comprises a hydrogenation metal of Group VI–A of the Periodic Table and a hydrogenation metal of Group VIII of the Periodic Table on a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms. The Periodic Table to which we have referred is published on page 2 of Modern Aspects of Inorganic Chemistry, H. J. Emeleus and J. S. Anderson, D. Van Nostrand Company, Inc., New York, N.Y., 1949.

We have also prepared a solid catalytic composition wherein the support is further characterized in that a zeolitic molecular sieve is suspended in the matrix of the alumina and have found that this is an effective catalyst for the hydroprocessing of heavy gas oils and hydrocarbon residua.

Our catalyst and a process employing such a catalyst can be understood more easily through the studying of the following discussion and figure. The figure presents a comparison of the denitrogenation activities of four catalysts, three of which art typical of our invention, obtained under hydroprocessing conditions.

We have prepared a catalyst that can be used for the hydroprocessing of heavy gas oils and hydrocarbon residua. This catalyst typically comprises a hydrogenation metal of Group VI–A of the Periodic Table and a hydrogenation metal of Group VIII of the Periodic Table on a solid inorganic-oxide support comprising a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms. It is desirable that such an alumina be in one of the well-known catalytically active forms, such as gamma-alumina. Although such alumina may be pure, it may contain also minor amounts of other oxides that are inert under the conditions at which it will be used. Such an alumina can contain a small amount of silica for stability without creating undesirable effects in our process. Desirably, the amount of silica is within the range of about 1 to about 10 weight percent. It is essential that the alumina in our catalyst have large pore diameters. The average pore diameter of the alumina should be within the range of about 100 to about 200 angstroms, suitably within the range of about 125 to about 180 angstroms, and preferably within the range of about 135 to about 160 angstroms; the surface area should be within the range of about 150 to about 500 square meters per gram, suitably within the range of about 300 to about 350 square meters per gram, and preferably within the range of about 320 to 340 square meters per gram. Suitable aluminas can be purchased from manufacturers of reforming catalysts. For example, Nalco HF-type aluminas having surface areas within the range of about 300 to about 350 square meters per gram are available from the Nalco Chemical Company. These HF-type aluminas can be obtained with pore volumes varying from as low as 0.54 cubic centimeters per gram to as high as 2.36 cubic centimeters per gram and corresponding average pore diameters within the range of about 72 to about 305 angstroms. Therefore, those Nalco HF-type aluminas which have the desired physical properties are suitable as the inorganic-oxide support of our catalyst.

The alumina desired as a support in our catalyst has a much higher average pore diameter than the aluminas used in conventional catalyst. The use of the alumina having a large average pore diameter as a support in a catalyst for hydroprocessing heavy gas oils and hydrocarbon residua results in a catalyst having improved denitrogenation activity, improved desulfurization activity, and improved hydrocarbon-conversion activity.

We have found that a suitable embodiment of our solid catalytic composition comprises a hydrogenation metal of Group VI–A of the Periodic Table and a hydrogenation metal of Group VIII of the Periodic Table on an inorganic-oxide support of a large-pore-diameter alumina having an average pore diameter within the range of about 100 to about 200 angstroms and a surface area within the range of about 150 to about 500 square meters per gram. The combined amounts of the hydrogenation metals are within the range of about 3 to about 35 weight percent based upon said composition. Typically, the hydrogenation metal of Group VI–A is molybdenum and the hydrogenation metal of Group VIII is cobalt. When these two metals are the hydrogenation components, the molybdenum should be present in an amount within the range of about 4.5 to about 26 weight percent, calculated as molybdenum trioxide and based upon said composition, and the cobalt should be present in an amount within the range of about 1.3 to about 5.2 weight percent, calculated as cobalt oxide and based upon said composition. A typical embodiment of our catalyst comprises 3 weight percent cobalt and 14 weight percent molybdenum, both metals being calculated as the oxides, on a large-pore-diameter alumina having an average pore diameter within the range of about 100 to about 200 angstroms and a surface area within the range of about 150 to about 500 square meters per gram. A preferred embodiment of our catalyst comprises 3 weight percent cobalt and 14 weight percent molybdenum, both metals being calculated as the oxides, on a large-pore-diameter alumina having an average pore diameter within the range of about 125 to about 180 angstroms, and a surface area within the range of about 300 to about 350 square meters per gram.

We have found further that our catalytic composition is improved if a zeolitic molecular sieve is suspended in the matrix of the alumina. The molecular sieve may be present in an amount within the range of about 1 to about 50 weight percent based upon the combined weight of sieve and alumina. Preferably, the molecular sieve is present in an amount within the range of about 5 to about 30 weight percent based upon the combined weight of sieve and alumina.

Zeolitic molecular sieves are composed of porous crystalline metal alumino-silicates. The zeolitic structure excavities, which are interconnected by numerous smaller pores. These pores have essentially a uniform diameter at their narrowest cross section. Generally, this uniform diameter falls within the range of 4 to 15 angstroms. Basically, the network of cavities is a rigid 3-dimensional and ionic network of silica and alumina tetrahedra. These tetrahedra are cross-linked by the sharing of oxygen atoms. Cations are included in the crystal structure to balance the electrovalence of the tetrahedra. Examples of such cations are a metal ion, an ammonium ion and a hydrogen ion. One cation may be exchanged either entirely or partially by another cation. This cation exchange is conveniently accomplished through the use of ion-exchange techniques.

Both crystalline alumino-silicate clays and amorphous alumino-silicates may be readily distinguished from the zeolites. Crystalline alumino-silicate clays, e.g., bentonite, have 2-dimensional structures. Amorphous alumino-silicates, e.g., a synthetic silica-alumina cracking catalyst, have random structures.

In the case of a particular zeolitic molecular sieve, the intracrystalline pores can be varied in size by replacing at least a part of exchangeable cations with other suitable ions. Such zeolities may be used for drying purposes, for catalytic purposes, and for hydrocarbon-type-separation purposes.

Either natural or synthetic molecular sieves may be used in our proposed catalyst. Examples of natural molecular sieves are erionite, mordenite, chabazite, faujasite, gmelinite, and the calcium form of analcite. Examples of synthetic zeolitic molecular sieves are Type X, Type Y, Type A, Type D, Type L, Type R, Type S and Type T molecular sieves. Zeolitic molecular sieves can be activated by driving out of the sieves a major portion of the water of hydration. The characteristics of both natural and synthetic molecular sieves and the methods for preparing them have been presented in the chemical art.

The catalyst for hydroprocessing heavy gas oils and hydrocarbon residua, as proposed herein, can be prepared by incorporating the cobalt and molybdenum metals into the alumina support through the use of an aqueous solution of a heat-decomposable compound of the particular metal. In the case of cobalt, a solution of cobalt nitrate, cobalt acetate, cobalt formate, or a solution of such metal compound and a soluble complexing agent, can be used to impregnate the cobalt on the alumina support. In the case of molybdenum, an aqueous solution of ammonium-hepta-molybdate or a solution of molybdenum trioxide in ethanolamine may be used to impregnate the molybdenum on the support. Following these impregnations the resulting material is dried and calcined. In the case where a molecular sieve is suspended in the alumina, the catalyst support is prepared by reducing the zeolite to a small particle size, blending the zeolite particles with the alumina hydrogel, and drying the resultng blend. The cobalt and molybdenum may be impregnated then on the support comprising the molecular sieve suspended in the alumina by techniques discussed above. The resultant catalyst can be used under suitable hydroprocessing conditions to convert the refractory high-boiling hydrocarbons into lower-molecular-weight compounds, some of which may be used in motor fuels and heating fuels.

Although our catalyst is particularly suitable for the hydroprocessing of heavy gas oils and hydrocarbon residua, it may be used also to hydroprocess light gas oil, light catalytic cycle oils, and the like.

Such a ctalyst as discussed above may be used in a process for hydroprocessing heavy gas oils and hydrocarbon residua. In this process, heavy metals, such as vanadium and nickel need not be removed from the feed stock. For example, as much as 300 parts per milion vanadium and as much as 100 parts per milion nickel can be tolerated. In addition, the nitrogen does not have to be removed from the feed stock prior to our process. The total nitrogen content of more than 6,000 parts per million can be tolerated. Our process is carried out at a temperature within the range of about 750° to about 850° F., preferably, within a range of about 770° to about 825° F., and at an operating pressure within the range of about 1,000 to about 3,000 p.s.i.g., preferably, within the range of about 1,200 to about 2,200 p.s.i.g. The hydrocarbon feed is added at a liquid hourly space velocity within the range of about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, preferably, within the range of about 0.5 to about 1.5 volumes of hydrocarbon per hour per volume of catalyst. Hydrogen is added to our process at a rate within the range of about 3,000 to about 50,000 standard cubic feet of hydrogen per barrel of hydrocarbon, preferably within the range of 6,000 to 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon. The hydrogen partial pressure is at least 80% of the operating pressure.

Our process can be carried out in conventional equipment which has been designed to withstand the operating conditions. No novel pieces of separation and recovery equipment are necessary.

Our process can be used to upgrade high-boiling-hydrocarbon fractions. It is particularly useful in converting those hydrocarbon feeds which are composed mainly of hydrocarbons which boil above 650° F. An example of such a hydrocarbon feed stock is a Cyrus Crude which contains 69.8 volume percent material boiling at a temperature of at least 650° F. and which has a gravity of 8.9° API, a sulfur content of 4.5 weight percent and which contains 230 parts per million vanadium and 70 parts per milion nickel. A similar feed stock was used in the example set forth hereinafter.

The heavy metals in these various higher-boiling hydrocarbon feed stocks exist in compounds. During the hydroprocessing reactions, these compounds which contain metals are decomposed and the metals are subsequently deposited on the catalyst and in the coke. The coke and metals may be removed by suitable regeneration techniques; or, if the appropriate conditions exist, the spent catalyst advantageously may be discarded.

Example

Six different catalysts were prepared. These catalysts will be hereinafter referred to as Catalysts A through F, and each will be defined and its preparation discussed herein.

Catalyst A contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on an alumina support of the type prepared in the United States Patent Reissue 22,196. Catalyst A was prepared by blending 29.5 grams of cobalt nitrate with 2,770 grams of the required alumina sol in 300 milliliters of water. To this blend were added 51 grams of ammonium hepta-molybdate in 300 milliliters of hot water. The addition of this molybdenum-containing solution gelled the alumina sol. The gel was dried in air at a temperature of about 250° F. for 16 hours. The resulting powder was pelletted into ⅛" x ⅛" pellets. These pellets were subsequently calcined in air at a temperature of about 1000° F. for about 6 hours.

Catalyst B contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on a support of alumina which has suspended therein 25 weight percent of an ammonium-exchanged Type-Y molecular sieve based upon said support. Catalyst B was prepared by blending 41.5 grams of ammonium-exchanged type-Y molecular sieve with 2,080 grams of alumina sol of the type prepared in United States Patent Reissue 22,196. A cobalt solution containing 29.5 grams of cobalt nitrate was then added to the resulting blend. This was followed by the addition of a molybdate solution having been previously prepared by adding 49 grams of ammonium hepta-molybdate to 500 milliliters of water. The molybdate solution gelled the sol. The resulting gel was dried in air at a temperature of about 250° F. for 16 hours. The resulting powder was pelletted with Sterotex and subsequently calcined in air at a temperature of about 1000° F. for 6 hours.

Catalyst C contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on a support of Nalco HF-type alumina. Catalyst C was prepared by increasing the cobalt content and the molybdenum content of a catalyst containing 3 weight percent cobalt-oxide and 14 weight percent molybdenum trioxide which had been obtained from the Nalco Chemical Company. A solution was prepared by adding 18.2 grams of ammonium hepta-molybdate and 6.8 grams of cobalt nitrate to about 170 milliliters of water; then 189 grams of the Nalco catalyst were impregnated with this solution. The impregnated catalyst was then dried in air at a temperature of about 250° F. for about 16 hours and subsequently calcined in air at a temperature of 1000° F. for 6 hours.

Catalyst D contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on a support of alumina into the matrix of which ammonium-exchanged type-Y molecular sieves have been suspended. The molecular-sieve content of the support was 5 weight percent. This catalyst was prepared by blending 114 grams of ammonium-exchanged type-Y molecular sieves with 1770 grams of Nalco HF-type alumina hydrogel (weight is on a dry basis). After sufficient blending, the resulting blend was spray dried at 250° F. Cobalt and molybdenum were impregnated into the preparation by conventional commercial techniques.

Catalyst E contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on a support of alumina into which ammonium-exchanged type-Y molecular sieves have been suspended. The molecular-sieve content of the support was 10 weight percent. The catalyst was prepared by blending 340 grams of ammonium-exchanged type-Y molecular sieve with 1544 grams of Nalco HF-type alumina hydrogel (weight is on a dry basis). After sufficient blending, the resulting blend was spray dried at 250° F. Cobalt and molybdenum were impregnated into the preparation by conventional commercial techniques.

Catalyst F contains 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the metals, on a support of alumina into which ammonium-exchanged type-Y molecular sieves have been suspended. The support contained 25 weight percent molecular sieves. Catalyst F was prepared by blending 568 grams of ammonium-exchanged type-Y molecular sieves with 1316 grams of Nalco HF-type alumina hydrogel (weight is on a dry basis). The resulting blend was then spray dried at a temperature of about 250° F. Cobalt and molybdenum were impregnated into the preparation by conventional commercial techniques.

The above catalysts were tested individually in a micro unit to determine whether they would satisfactorily reduce the nitrogen and sulfur contents of a vacuum residuum. This vacuum residuum was in essence a vacuum reduced crude.. Its physical properties are summarized in the following table.

Gravity, ° API	10.9
ASTM IBP, ° F.	1000+
Ramsbottom carbon, weight percent	17
Sulfur, wt. percent	1.3
Pour point, ° F.	115
Viscosity:	
SSF @ 275° F.	125
SSF @ 325° F.	43
Total nitrogen, p.p.m.	6,300
Metals, p.p.m.:	
Alumina	5.4
Calcium	20
Iron	18
Magnesium	6.2
Sodium	75
Nickel	41
Vanadium	66

The reactor of the micro unit was 5/8" in diameter; and when it was filled with 40 cc.'s of catalyst, the catalyst-bed depth was 8.4 inches. A particular catalyst was charged to this reactor. It is presumed that the cobalt and molybdenum in each of these catalyst was present in the oxide form, since the catalyst had been calcined in air at 1000° F. prior to the charging. When a particular catalyst had been put in the reactor, the catalyst was heated to a temperature of about 700° F. in nitrogen at near-atmospheric pressure. Then a hydrogen stream containing 8 volume percent hydrogen sulfide was passed over the catalyst at a pressure of 100 p.s.i.g.. at a uniform rate so that 4 standard cubic feet of the gas mixture would pass over the catalyst in one hour. The system having the catalyst in an atmosphere of the gas mixture was then heated from 700° to 750° F. and subsequently pressured with hydrogen to 1400 p.s.i.g. At the hydrogen pressure of 1400 p.s.i.g., once-through hydrogen and hydrocarbon streams were introduced into the reactor. The hydrocarbon was charged to the reactor at a liquid hourly space velocity of about 0.6 volume of hydrocarbon per hour per volume of catalyst and the hydrogen was added at the rate of approximately 4 standard cubic feet of hydrogen per hour (about 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon). After the catalyst had been on stream for 20 hours, the temperature was raised from 750° to 810° F. and then maintained at this latter temperature for the remainder of the test. Each test was continued for a period of time of 2 to 4 days. Catalysts were evaluated for the maintenance of the activity of that catalyst over the time of the test. Denitrogenation activity, desulfurization activity, or both, were considered for each of these tests. Since previous data have indicated that denitrogenation for this particular feed stock followers a zero-order-reaction mechanism and that desulfurization follows a first-order-reaction mechanism, rate constants could be calculated for denitrogenation and desulfurization occurring in a particular test. Either the denitrogenation activity or the desulfurization activity was calculated as 100 times the ratio of the observed rate constant for the particular reaction from a particular test divided by a standard rate constant.

The results of tests made with Catalyst A, Catalyst B, Catalyst C, and Catalyst F are presented in the figure, which shows the denitrogenation activity of each of these catalysts over the length of the particular test run. The denitrogenation activity of Catalyst A, the catalyst having a support of the prior-art alumina, is inferior to those of the other three catalysts, which include Catalyst C. Catalyst C has a Nalco HF-type alumina support. Catalyst C and Catalyst B, containing the prior-art alumina and 25 weight percent molecular sieves based upon the support, have almost similar denitrogenation activities; however, Catalyst F, which contains Nalco HF-type alumina and 25 weight percent molecular sieves based upon the support, has a denitrogenation activity which is far superior to those of the other three catalysts.

In addition to the results shown in the figure, these tests furnished data which indicate that the desulfurization activities of these four catalysts are essentially equivalent.

The results of tests using Catalysts D, E, and F indicate that changing the molecular sieve content of the catalyst from the 5 weight percent in Catalyst D to the 25 weight percent in Catalyst F does not appreciably affect the denitrogenation activity of the catalyst. These amounts of molecular sieves are based upon the support. In each of the Catalysts D, E, and F, Nalco HF-type alumina was used.

The results of the above tests indicate that our catalytic composition has advantages over those presented in the prior art for hydroprocessing heavy gas oils and petroleum residua.

In a specific embodiment of our process for hydroprocessing hydrocarbon residua, approximately 71,000 barrels per stream day (BSD) of an atmospheric reduced crude fraction of a Cyrus Crude are introduced into the reaction zone. The raw crude has a sulfur content of 3.6 weight percent sulfur and a gravity of 17.7° API; the atmospheric reduced crude fraction, a sulfur content of 4.5 weight percent sulfur and a gravity of 9.3° API. Also introduced into the reaction zone are 125 million standard cubic feet of hydrogen per day and 6,000 standard cubic feet of recycle gas per barrel of hydrocarbon processed. Operating conditions in the reaction zone include a temperature of about 800° F., a pressure of 1500 p.s.i.g., and a liquid hourly space velocity of 0.7–.4 volumes of hydrocarbon per hour per volume of catalyst. The catalyst employed is a catalyst comprising 3 weight percent cobalt and 14 weight percent molybdenum, calculated as the oxides, on a support of Nalco HF-type alumina. Approximately 104,250 BSD of reconstituted Cyrus Crude are obtained. This reconstituted Cyrus Crude has a sulfur level of 1.5 weight percent sulfur and a gravity of 28.9° API. While the atmospheric reduced crude charged to the reaction zone is about 95% material boiling at a temperature of at least 650° F., the product is only about 67% material boiling at a temperature of at least 650° F.

It is to be understood that the examples and specific embodiment presented herein are for illustrative purposes only and are not intended to limit the scope of our invention.

What is claimed is:

1. A solid catalytic composition for the hydroprocessing of heavy gas oils and hydrocarbon residue, which composition comprises a hydrogenation metal of Group VI–A of the Periodic Table and a hydrogenation metal of Group VIII of the Period Table on a solid inorganic-oxide support comprising a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms.

2. The composition of claim **1** further characterized in that said metal of Group VI–A and said metal of Group VIII are present in a total amount within the range of about 3 to about 35 weight percent based upon said composition.

3. The composition of claim **1** wherein said metal of Group VI–A is molybdenum.

4. The composition of claim **1** wherein said metal of Group VIII is cobalt.

5. The composition of claim **1** wherein said metal of Group VI–A is molybdenum and is present in an amount

within the range of about 4.5 to about 26 weight percent, calculated as molybdenum trioxide and based upon said composition.

6. The composition of claim **1** wherein said metal of Group VIII is cobalt and is present in an amount within the range of about 1.3 to about 5.2 weight percent, calculated as cobalt oxide and based upon said composition.

7. The composition of claim **1** wherein said metal of Group VI–A is molybdenum and is present in an amount within the range of about 4.5 to about 26 weight percent, calculated as molybdenum trioxide and based upon said composition, and wherein said metal of Group VIII is cobalt and is present in an amount within the range of about 1.3 to about 5.2 weight percent, calculated as cobalt oxide and based upon said composition.

8. The composition of claim **1** wherein said support is further characterized in that a zeolitic molecular sieve is admixed with said alumina.

9. The composition of claim **8** wherein said molecular sieve is present in an amount within the range of about 1 to about 50 weight percent based upon said support.

10. The composition of claim **8** wherein said molecular sieve has been ion-exchanged with a salt selected from the group consisting of alkali-metal salts and alkaline-earth-metal salts.

11. The composition of claim **8** wherein said molecular sieve is present in the hydrogen form.

12. The composition of claim 8 further characterized in that said metal of Group VI–A is molybdenum and is present in an amount within the range of about 4.5 to about 26 weight percent, calculated as molybdenum trioxide and based upon said composition, said metal of Group VIII is cobalt and is present in an amount within the range of about 1.3 to about 5.2 weight percent, calculated as cobalt oxide and based upon said composition, and said molecular sieve is the hydrogen form of a Type-Y molecular sieve and is present in an amount within the range of about 1 to about 30 weight percent based upon said support.

13. The composition of claim **8** further characterized in that said metal of Group VI–A is molybdenum and is present in an amount of 21 weight percent, calculated as molydenum trioxide and based upon said composition, said metal of Group VIII is cobalt present in an amount of 3.8 weight percent, calculated as cobalt oxide and based upon said composition, and said molecular sieve is the hydrogen form of a Type-Y molecular sieve and is present in an amount within the range of about 5 to about 25 weight percent based upon said support.

14. A process for the hydroprocessing of a feed stock selected from the group consisting of heavy gas oils, hydrocarbon residue, and mixtures thereof, which process comprises contacting said feed stock under suitable hydroprocessing conditions with a catalyst comprising a metallic hydrogenation component on a solid inorganic-oxide support comprising a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms.

15. The process of claim **14** wherein said support is further characterized in that a zeolitic molecular sieve is admixed with said alumina.

16. The process of claim **14** wherein said catalyst comprises a hydrogenation metal of Group VI–A of the Periodic Table and a hydrogenation metal of Group VIII of the Periodic Table on a solid inorganic-oxide support comprising a large-pore-diameter alumina having a surface area within the range of about 150 to about 500 square meters per gram and an average pore diameter within the range of about 100 to about 200 angstroms.

17. The process of claim **14** wherein said contacting is carried out at a temperature within the range of about 750° to about 850° F., an operating pressure within the range of about 1000 to about 3000 p.s.i.g., a hydrogen partial pressure of at least 80% of said operating pressure, a liquid hourly space velocity within the range of about 0.25 to about 5.0 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen addition rate within the range of about 3,000 to about 50,000 standard cubic feet of hydrogen per barrel of hydrocarbon.

18. The process of claim **14** wherein said contacting is carried out at a temperature within the range of about 770° to about 825° F., an operating pressure within the range of about 1200 to about 2200 p.s.i.g., a hydrogen partial pressure of at least 80% of said operating pressure, a liquid hourly space velocity within the range of about 0.5 to about 1.5 volumes of hydrocarbon per hour per volume of catalyst, and a hydrogen addition rate within the range of about 6,000 to about 20,000 standard cubic feet of hydrogen per barrel to hydrocarbon.

19. The process of claim **17** wherein said catalyst has been subjected previously to a treatment comprising heating said catalyst to a temperature of about 700° F. in nitrogen, passing over said catalyst a gas containing hydrogen and hydrogen sulfide at a pressure of 100 p.s.i.g. for 1 hour, heating said catalyst in said gas to the desired operating pressure, and placing said catalyst under conditions that will be used in said process.

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DELBERT E. GANTZ, *Primary Examiner.*

SAMUEL P. JONES, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,393,148 July 16, 1968

Ralph J. Bertolacini et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 69 and 70, "as much as 100 parts per million nickel" should read -- as much as 500 parts per million vanadium and as much as 100 parts per million nickel --. Column 2, line 22, "process" should read -- processes --. Column 3, line 5, "art" should read -- are --. Column 4, lines 23 and 24, "The zeolitic structure ex-cavities" should read -- The zeolitic structure exists as a network of relatively small alumino-silicate cavities --. Column 5, line 54, "milion" should read -- million --. Column 6, line 15, "type-Y" should read -- Type-Y --. Column 7, line 61, "followers should read -- follows --. Column 10, line 36, "to" should read -- of --.

Signed and sealed this 20th day of January 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents