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PROCESS AND COMPOSITION FOR THE HYDROCRACKING OF HYDROCARBON OILS

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This invention relates to catalytic hydrocracking. More particularly, this invention relates to a hydrocracking process and associated catalyst for petroleum distillates boiling in or above the furnace oil range to obtain petroleum-based fuels, including gasoline of enhanced aromatic content.

To satisfy the large and growing demand for hydrocarbon fuels, such as gasoline, diesel fuel, and furnace oil, it has recently been found desirable to supplement the older refinery procedures of distillation and catalytic cracking by hydrogenative cracking, known in the art as hydrocracking. In this process, a suitable feedstock, which may range from furnace oil to heavy gas oils and even to high boiling residues, is passed in admixture with hydrogen over a catalyst having both hydrogenative and cracking ability. There results a spectrum of products containing a substantial percentage of components in a boiling range lower than that of the charge. These products, moreover, have desirable properties, for example, low contents of sulfur and nitrogen compounds. These compounds, in unreduced quantities, can cause corrosion of metals and deterioration of the products during storage. In addition, the combustion products of these compounds can pollute the atmosphere.

In hydrocracking, the hydrogen mixed with the feed performs several functions. For one, it prevents heavy deposition of coke on the catalyst. Practitioners of the art believe this is accomplished by hydrogenation of aromatic coke precursors. Thus, the presence of hydrogen allows cracking of feedstocks which would not be susceptible to ordinary catalytic cracking because they would form excessive coke deposits on the catalyst. Another role of the hydrogen in hydrocracking is to upgrade the feed. Thus, as mentioned above, any corrosive and otherwise undesirable sulfur- and nitrogen-containing compounds remaining in the feedstock after hydrofining pretreatment, when such pretreatment is employed, tend to be destroyed during hydrocracking, the nitrogen and sulfur appearing in the gaseous portion of the reactor effluent as ammonia and hydrogen sulfide.

The outstanding advantages of hydrocracking are somewhat offset by the fact that in hydrocracking, as ordinarily now practiced, valuable aromatic hydrocarbons boiling in the gasoline range and produced by the cracking function of the hydrocracking catalyst may be hydrogenated by its hydrogenative function to form the corresponding naphthenic hydrocarbons, these products being of relatively less value as gasoline constituents. This lower value is due to the relatively lower octane numbers of the naphthenes as compared with the octane numbers of the aromatics to which they correspond. This synthesis of naphthenes is additionally disadvantageous because it increases the consumption of hydrogen per barrel of feed processed, and thus adds to the cost of the hydrocracked products.

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In accordance with the present invention, it has been discovered that the aromatic content of gasoline produced in hydrocracking can be increased and the consumption of hydrogen decreased, while at the same time retaining the advantageous results of hydrocracking, when the hydrocracking is carried out over a catalyst comprising metalliferous hydrogenating components composited with a silica-alumina cracking component prepared by a novel procedure. More particularly, in accordance with the process of this invention, a petroleum hydrocarbon distillate, at least 90 percent of which boils above 400° F., is contacted with hydrogen in the presence of a minor amount of a hydrogenating catalyst composited with a major amount of a silica-alumina refractory carrier composition prepared by a specified novel procedure.

When so prepared, this composition, when dried and calcined, is substantially free of alkali metal contaminants, that is, contains less than about 0.01 percent alkali metal, has a predominant proportion of its pore volume in pores of very small radius, that is, has more than 50 percent of its pore volume in pores of radius less than 50 Angstroms, and has a high cracking activity, indicated by a high surface acidity, that is, a surface acidity equivalent at 600° F. to more than 0.25 milliequivalents of ammonia per gram, as determined by ammonia adsorption and desorption as described by R. G. Barth and E. V. Ballou in Analytical Chemistry 33, pages 1080 to 1084 (1961). The specified novel procedure comprises mixing a dilute, cation-free silica sol, for example, a silica sol prepared by flowing sodium silicate through a preacidified ion-exchange resin, with an aqueous solution of an aluminum compound, for example, aluminum chloride hexahydrate, which yields aluminum cations in aqueous solution. Gelation of the resultant mixture is then brought about as by addition to the mixture of aqueous ammonia. Desirably the gel is washed to remove the anion whose source was the aluminum salt used as starting material. This gel can be composited with other catalytic components in a variety of ways. For example, the gel can be dried, calcined, and the preformed carrier can be impregnated with compounds which will produce, on further drying and calcining, the metalliferous hydrogenative components of the catalyst. Alternatively, the silica-alumina gel can be impregnated before drying and before calcination, or after drying and before calcination, with compounds which produce the hydrogenative, metalliferous components of the catalyst. It is also within the scope of this invention to incorporate in the ion-free silica starting material precursors of the metalliferous components of the catalysts associated with the process of this invention. These precursors may also be admixed with the aqueous solution of the aluminum compound. They may also be incorporated in both the cation-free silica sol and the aqueous solution of the aluminum compound.

A number of methods are available for preparing the cation-free, dilute silica sol used as starting material for the preparation of the catalysts associated with the process of the present invention. Preferably a dilute solution of sodium silicate is flowed as by percolation or pumping, through a bed of protonated cation-exchange material to recover an effluent dilute silica sol substantially free of cationic contaminants. Any soluble silicate may be used in this method. We prefer, however, sodium silicate solutions going commonly under the name of "water glass" because the solutions are cheap and easily available.

Because the silica sol starting material used in preparing

the catalyst associated with the process of this invention must be dilute, that is, should contain less than the equivalent of 5 percent sliica and preferably should contain the equivalent of between 1 and 3 percent silica, we prefer to employ for its preparation a dilute solution of soluble silicate—that is, one containing no more than the equivalent of about 5 percent by weight of silica, preferably the equivalent of between 1 and 3 percent by weight of silica. Solutions more dilute than one containing the equivalent of 1 percent silica are satisfactory but entail handling more liquid in making a given amount of the silica-alumina gel component of the catalyst associated with the process of the present invention.

Any solid cation-exchange material insoluble in water may be employed in the preparation of the dilute silica sol. Cation-exchanging resins of high cation-exchange capacity, such for example as sulfonated phenol formaldehyde resins or divinylbenzene cross-linked sulfonated polystyrene resins, like Amberlite IR–120 (Rohm & Haas), have given excellent results in the production of dilute silica sols. Other cation-exchange materials may be used, such as sulfuric acid-treated coal or wood. In every instance the ion-exchange material must be in acid form. It may be placed in this form by flushing with a suitable strong acid, such as sulfuric acid or hydrochloric acid. The residual acid adhering to the granules of the ion-exchange material or remaining within the interstices of the bed of ion-exchange material can be removed by washing with water.

In producing the cation-free silica sol, a single bed of cation-exchange material can be employed or a plurality of beds arranged in series, in parallel, or both. When beds are employed in series, it is advantageous to feed the fresh silicate solution to the most nearly spent bed of cation-exchange material with a substantially cation-free silica sol emanating from the most recently regenerated bed of ion-exchange material. Regeneration is accomplished by acid washing, as described above for the initial preparation of the ion-exchange material. To determine when a bed is spent, it is convenient to measure continuously or from time to time the pH or conductivity of the effluent silica sol. The pH of a satisfactory sol is in the neighborhood of 3 and its specific conductance is in the neighborhood of 10^{-5} ohm^{-1} $cm.^{-1}$. When the pH rises to about 5, the processing must be interrupted for regeneration, and advantageously permutation, of beds of ion-exchange material.

It is also within the purview of this invention to employ dilute silica sol made by other methods, which is substantially free of cationic contaminants. For example, satisfactory dilute cation-free silica sol can be made by hydrolysis of ethylorthosilicate or of silicon tetrachloride.

In preparing the silica-alumina component of the catalyst associated with the process of this invention, it is preferred that the dilute cation-free silica sol be mixed promptly with an aqueous solution of an aluminum compound which yields aluminum cations in aqueous solution. Aluminum salts of strong acids can be used, for example, aluminum chloride hexahydrate, aluminum nitrate, or aluminum sulfate. Aluminum chloride hexahydrate, which is plentiful and cheap, has been employed with excellent results.

Mixing of the cation-free silica sol with the aqueous solution of the aluminum compound should be thorough enough to produce a completely homogeneous liquid. Because cation-free dilute silica sols are unstable, having a tendency to gel, it is essential that the silica sol be used soon after its preparation, for example, within 12 hours after its preparation, preferably within one hour after its preparation. Indeed, when the silica sol is prepared by flowing a soluble silicate through an ion-exchange resin column, an excellent practice in accordance with the instant invention is to add the column effluent directly to the solution of the aluminum compound. Before gelation of silica sol, a subtle change takes place in the sol, akin perhaps to polymerization. In the preferred practice of the instant invention, the silica sol freshly prepared is mixed with the aqueous solution of the aluminum compound before such subtle change has advanced, that is, immediately or shortly after preparation of the ion-free silica sol.

Silica sols available on the market and characterized as "stabilized" are unsuitable for the preparation of the catalysts of the process of the instant invention. These silica sols are not substantially free of cationic contaminants.

In selecting the aluminum compound, it is important to distinguish those compounds which yield aluminum cations in aqueous solution from those compounds which do not. Examples of the latter are aluminum oxides and organo aluminum compounds, such as aluminum triethyl or aluminum isopropylate. Such aluminum compounds do not produce silica-alumina hydrocracking catalyst components which assure enhanced aromatic content of the gasoline produced in hydrocracking.

After thorough homogenization of the mixture of the aqueous solution of the aluminum compound and dilute, freshly prepared silica sol, gelation is brought about by increasing the pH of the mixture. This may be done conveniently by addition of aqueous ammonia with stirring or by addition of gaseous ammonia, as through a sparger. The alkaline agent chosen for raising the pH of the silica sol-aluminum compound mixture should be such as to leave no harmful residue in the resulting silica-alumina composition. For this reason alkali metal hydroxide solutions are unsatisfactory for they leave in the product a residue of alkali metal that is difficult, if not impossible, to remove by washing. Ammonia, on the other hand, is cheap and easily available, and leaves no residue upon calcination of the resulting gel or the ultimate catalyst. Other bases, such as trimethyl ammonium hydroxide, hydrazine, or quinolinium hydroxide, may be employed, but they are expensive and are considered to have no particular advantages.

The resulting gel is separated, as by filtration or centrifugation, and washed. The gel also can be dried and calcined at this point. If desired, however, it can be impregnated before drying or before calcining with compounds which yield the metalliferous hydrogenative components of the hydrocracking catalyst of the process of the instant invention. Accordingly, by the expression 'dried and calcined refractory carrier' we mean both carriers that have been dried and calcined before impregnation, as well as those that have been dried and calcined after impregnation.

It is emphasized that the refractory carrier compositions which form a component of the novel catalyst associated with the process of the instant invention possess high cracking activity, as measured, for example, in a modification of the Indiana Downflow Test, as described by A. C. Whitaker and A. D. Kinzer in Industrial & Engineering Chemistry 47, pages 2153 to 2157 (1955). High cracking activity is a necessary, but not in itself sufficient, property of the refractory carrier component of hydrocracking catalysts. More particularly, cracking activity of a hydrocracking catalyst's refractory carrier component does not, alone, correlate with the tendency of the catalyst to produce relatively less aromatic hydrocracked products.

To composit the silica-alumina component of the hydrocracking catalyst of the process of the instant invention with the metalliferous hydrogenating component, any conventional procedure for preparation of a multi-component catalyst may be used. Preferably, the silica-alumina gel prepared as specified above, is after washing, drying and calcining, impregnated with a salt of the metalliferous hydrogenating component. The impregnated silica-alumina composition is then dried and calcined to obtain the finished hydrocracking catalyst. If a plurality of metalliferous hydrogenating components are employed,

they may be composited with the silica-alumina composition in one impregnation or a plurality of impregnations.

Any hydrogenating component or components may be employed. For example, any Group VI and/or Group VIII metals, metal oxides, or metal sulfides may be composited with the silica-alumina compositions of the catalysts of the process of the instant invention. It is frequently desirable to employ mixtures of hydrogenative components—for example, mixtures of nickel and tungsten or nickel and tungsten and cobalt or their oxides and/or sulfides. Also, excellent hydrocracking is achieved when noble metals, for example, platinum or palladium, or their sulfides, are composited with the silica-alumina compositions of catalysts associated with the process of the instant invention. By the expression "sulfides" we do not mean to imply any particular chemical compounds, but merely a sulfided form of the corresponding metals. Thus, a sulfided nickel tungsten hydrogenating component can be present as nickel thiotungstate, or as other complex, sulfur-containing compounds or mixtures thereof.

The reaction conditions employed in the instant invention depend in part upon the nature of the feedstock. For relatively lower-boiling feedstocks, e.g., those boiling in the furnace oil range, milder conditions, that is, lower temperatures and higher space velocities, are employed, whereas for heavy distillates, such as heavy gas oils, more severe conditions are appropriate. For example, in hydrocracking a furnace oil 90 percent of which boils above 475° F., the hydrocracking temperature may vary between 550° and 700° F. and is preferably in the range 625° to 675° F. During hydrocracking, the catalyst undergoes a gradual loss in activity, and it is customary to increase the temperature of the catalyst bed so to compensate for this loss in activity that the conversion remains roughly constant during the onstream period of the use of the catalyst. Thus, initially the catalyst will be used near the lower part of the above-stated range in temperature and the temperature will be raised during the onstream period to maintain the conversion essentially constant. For hydrocracking heavier feedstocks, for example, for hydrocracking a heavy gas oil boiling between about 650° and about 1100° F. and containing more than 220 p.p.m. of nitrogen, higher hydrocracking temperatures, for example, from 700° to 950° F., are appropriate, preferably from 750° to 850° F.

The hydrogen partial pressure may vary over a wide range, for example, from 500 to 10,000 p.s.i. More often, hydrogen partial pressures between 750 and 2000 p.s.i. are employed, and excellent results are achieved with pressures of 1000 to 1500 p.s.i. Hydrogen recycle rates, that is, hydrogen:oil ratios, may vary from 2000 or less to 30,000 or more s.c.f/bbl. of liquid feed. Excellent results have been achieved with hydrogen rates between 4000 and 10,000 s.c.f./bbl.

Space velocities may range from 0.5 to 10.0 volumes of liquid feed per volume of catalyst bed per hour. Space velocities in the range of 0.5 to 3.0 are preferred.

The advantages of the process of the instant invention are most pronounced when the petroleum distillate feedstock contains at most a small proportion of nitrogen; preferably it will contain less than 100 parts per million of nitrogen. Not only is the relative enhancement in aromaticity of the product of hydrocracking over the novel catalysts associated with the instant invention greater, in comparison to that of products of hydrocracking over catalysts of the prior art, when low-nitrogen feeds are employed, but also the rate of aging of catalysts is lower when such feeds are processed. Therefore, when feeds of relatively higher nitrogen content are to be hydrocracked in accordance with the instant invention, it has been found advantageous to reduce their nitrogen content by pretreatment. Effective hydrogenative pretreatments for reduction of nitrogen content are well known in the art. For example, the nitrogen content of petroleum distillates can be reduced by contacting the distillates with hydrogen at a partial pressure between 500 and 2500 p.s.i. at a rate between 4000 and 20,000 s.c.f. of hydrogen per barrel of distillate over a hydrofining catalyst, such as nickel-tungsten on an alumina or silica-alumina carrier or cobalt-molybdenum on an alumina or silica-alumina carrier, at a liquid hourly space velocity between 0.2 and 10 volumes of liquid distillate per volume of catalyst per hour and at a temperature between 500° and 800° F. In this contacting, the liquid hourly space velocity is adjusted to provide a pretreated feed of the desired nitrogen content, advantageously less than 100 parts per million.

The practice of the instant invention is illustrated, but not limited, by the following examples.

EXAMPLE I

To make a dilute, substantially cation-free silica sol, 1220 grams of water glass (28.7 percent SiO_2) were mixed with 12 liters of water. The mixture was flowed through a bed of 3000 grams of protonated Amberlite IR–120 cation-exchange resin (a sulfonated styrene polymer cross-linked by a small proportion of divinylbenzene and manufactured by the Rohm & Haas Company). Dilute silica sol issued from the bed. The bed was rinsed with 3 liters of dilute hydrochloric acid, the liquid rinsed from the bed being added to the dilute silica sol.

In 5 liters of water were dissolved 710 grams of aluminum chloride hexahydrate. The resulting solution was added with mixing to the dilute silica sol prepared as described above. To the resulting mixture was added, with constant mixing, in a flow stream, dilute aqueous ammonia (9 percent NH_3) in an amount sufficient to raise the pH of the resultant mixture to 8. This resulted in formation of a gel, which was separated by filtration. The gel was washed with water containing 1 millilter of aqueous ammonia (28 percent NH_3) per liter until the conductivity of the washings had fallen to a constant level. The washed gel was dried at 250° F. and formed into pellets $\frac{3}{16}$-inch in diameter. These were calcined at 1000° F. for 16 hours. The pore size distribution of the calcined pellets was determined by nitrogen adsorption measurement; 77.4 percent of the pore volume was in pores of radius less than 50 Angstroms. The sodium content of the calcined pellets was determined to be less than 0.01 percent. The surface acidity of a sample of silica-alumina gel of the same chemical composition and prepared in the same way was determined to be equivalent to 0.40 milliequivalents of ammonia per gram at 600° F., as determined by ammonia adsorption and desorption, by the method previously referred to herein. The calcined pellets, containing the equivalent of 30 percent Al_2O_3 and 70 percent SiO_2, were broken up and classified by sieving. Those passing through the 10 mesh screen and being retained on the 20 mesh screen were impregnated with a solution containing ammonium fluoride, ammonium metatungstate, and nickel nitrate to produce a catalyst which, after drying at 250° F. for 16 hours and calcination at 1000° F. for 16 hours, contained 6 percent nickel, 19 percent tungsten, and 2 percent fluorine.

The catalyst whose preparation was described above was employed in hydrocracking of fluid catalytically cracked furnace oil which had been catalytically hydrofined to reduce its content of sulfur- and nitrogen-containing compounds. Before the catalyst was placed onstream, it was pretreated in the hydrocracking reactor for one hour at 600° F. and atmospheric pressure with a stream of gas containing 8 percent hydrogen sulfide and 92 percent hydrogen. After this the hydrocracking reactor was placed onstream, a mixture of the described FCC furnace oil and hydrogen being passed over the catalyst, the liquid hourly space velocity of the furnace oil being 1.5 volumes of oil per volume of catalyst per hour and the hydrogen rate being 10,000 s.c.f./Bbl. at a hydrogen partial pressure of 1200 p.s.i. The products

from this hydrocracking run were collected and distilled to recover light gasoline, naptha, and higher-boiling material. Yields of these products and their properties are listed in Table I.

Table I.—Hydrocracking FCC furnace oil

Catalyst of Example I:	
Conditions: 600° F., 1200 p.s.i.g. H_2, 1.5 LHSV, 10,000 s.c.f. H_2/bbl. oil.	
Yields (percent by volume of charge, except for C_1–C_2):	
C_1–C_2 (percent by weight)	0.14
C_3	3.7
C_4	6.0
C_5–180° F.	41.1
180°–400° F.	68.6
400° F. +	13.7
Hydrogen consumption: s.c.f./bbl.	1470
Inspections:	
Light Gasoline:	
Octane No. (Research, plus 3 cc. lead tetraethyl)	104.7
Naphtha:	
Aromatics: (percent by volume)	24.2
Octane Nos.:	
Research, plus 3 cc. lead tetraethyl	89.3
Motor, plus 3 cc. lead tetraethyl	83.9
400° F. +:	
Aromatics	23.1

It is evident from the data listed in Table I that the process and associated catalyst of the instant invention produce gasoline and naphtha of excellent quality in high yields. In addition, production of fixed gases, methane and ethane-ethylene, which have low value compared to liquid products, is desirably low. On the other hand, yields of C_3's and C_4's, of value in themselves as fuels and also of value as intermediates for making petrochemicals and fuels, for example, for production of alkylate gasoline, are comparatively high.

The light gasoline, produced in high yield, is of excellent quality. Leaded, its octane number more than meets the requirements of modern automotive engines. It can, therefore, be blended with gasolines of lower quality to bring their performance up to standards of acceptance.

The 180°–400° F. naphtha has high aromatic content and, when leaded, a relatively high octane number, as measured by both Research and Motor methods. The sensitivity, that is, the difference between research and motor octane ratings, is rather low for this naphtha, another desirable quality. This naphtha is produced in remarkably high yield by the process and associated catalyst of the instant invention.

The aromatic content of the fuel oil is also relatively high. This signifies an advantageously low hydrogen consumption—advantageous because, even when hydrogenated, the fuel oil fractions have a relatively lower value than that of gasolines and naphthas.

Finally, attention is called to the high volumetric yield (greater than 130 percent) of liquid products obtained with very moderate hydrogen consumption by the method and associated catalyst of the instant invention.

EXAMPLE II

To make ion-free silica sol, water glass (2152 grams, 28.7 percent SiO_2) was mixed with 20 liters of water and was passed through a column containing 1500 grams of the ion-exchange resin of Example I, which had been activated by treatment with dilute hydrochloric acid and washed to remove excess acid. Ion-free silica sol emerged from the column. The bed of resin was then rinsed with 1 liter of water, and the effluent rinse water was added to the silica sol.

Aluminum chloride hexahydrate (1182 grams) was dissolved in 10 liters of water. The resulting solution was mixed with the silica sol whose preparation is described above.

To this mixture was added aqueous ammonia (8 percent NH_3) until the pH of the mixture had risen to 8. This resulted in the formation of a silica-alumina gel, which was separated by filtering. The filter cake was washed with water containing 1 milliliter of concentrated (28 percent NH_3) ammonia per liter of wash water. Washing was continued until the conductivity of the wash water fell to a constant level.

The washed cogel was dried at 250° F., formed into 3/16-inch pellets, and calcined at 1000° F. for about 8 hours. The calcined pellets were determined to contain less than 0.01 percent sodium. The calcined pellets, having a chemical composition corresponding to 75 percent silica and 25 percent aluminum, were then broken and classified to obtain particles passing a 10 mesh screen and being retained on a 20 mesh screen. This class of particles was then impregnated to incipient wetness with a solution containing ammonium metatungstate, nickel nitrate, and ammonium fluoride. The impregnated material was then dried and calcined at 1000° F. to give a catalyst containing 6 percent nickel, 19 percent tungsten, and 2 percent fluorine.

The above-described catalyst was employed in the hydrocracking of fluid catalytically cracked furnace oil which had been treated to reduce its content of sulfur- and nitrogen-containing compounds. Before the catalyst was placed onstream, it was pretreated in the hydrocracking reactor for 1 hour at 600° F. and atmospheric pressure with a stream of gas containing 8 percent hydrogen sulfide and 92 percent hydrogen. After this pretreatment, the hydrocracking reactor was placed onstream, a mixture of the described furnace oil and hydrogen being passed over the catalyst, the liquid hourly space velocity of the furnace oil being 2 volumes of oil per volume of catalyst per hour, and the hydrogen rate being 10,000 s.c.f./bbl. at a hydrogen partial pressure of 1000 p.s.i.g. The temperature of the catalyst bed was about 600° F.

The effluent from the hydrocracking reactor was collected in a low-pressure separator. The liquid product was analyzed for its aromatics content by the FIA (fluorescent-indicator adsorption) method. Its aromatics content so determined was 28.5 percent.

The conversion was defined as the difference between 100 and the volume of product boiling above 400° F. per 100 volumes of furnace oil fed to the reactor. The conversion in the above-described hydrocracking run was 51 percent.

A commercial silica-alumina cracking catalyst containing 75 percent silica and 25 percent alumina, prepared by a method other than that disclosed herein, and having a typical sodium content of 0.01 percent, was impregnated with the solution containing ammonium metatungstate, nickel nitrate, and ammonium fluoride, just as described in the preparation of the catalyst of Example II. This catalyst was then employed for hydrocracking the furnace oil of Example I under the same conditions used in the hydrocracking of Example II. A conversion of 50.0 percent was achieved. The aromatics content of the liquid product corresponding to the liquid product of Example II was 26 percent.

It is immediately apparent from a comparison of results of Example II with those obtained in hydrocracking with a catalyst of essentially the same gross chemical composition but made with a commercial silica-alumina that by the process of the instant invention a product of significantly higher aromaticity is made, and at the same time this does not have to be paid for by a loss in conversion or by any adjustment in the operating variables—temperature, pressure, space velocity, and hydrogen rate—of the hydrocracking process. Indeed, the improvement in product quality, namely, a higher content of aromatics, is attributable to the use of the specified catalyst of the

process of the instant invention. The enhanced aromatic content of the product of hydrocracking in accordance with the specification of the instant invention has significance in that it furnishes a gasoline of higher octane number, useful in itself and as a blending agent. In the latter capacity, it may be mixed with fuels of lower octane number to produce a blend meeting the higher antiknock requirements of the modern gasoline engine. It also effects a saving in lead tetraethyl, which must be added to relatively poorer fuels to inhibit their tendency to knock. The aromatic portion of the hydrocracked product of the process of the instant invention can also serve as an intermediate for production of aromatic petrochemicals. It will be understood that in a hydrocracking unit processing 30,000 barrels of distillate fuel oil per day, even a 1 percent enhancement in aromatic content corresponds to 150 barrels per day of aromatic hydrocarbons, a large and valuable increment in terms of aromatic petrochemical specialties.

The process of this invention is not limited to use of catalysts containing silica and alumina in the proportion 75 to 25. The following examples illustrate the practice of this invention with catalysts containing silica-alumina components with other silica-to-alumina ratios. A catalyst whose silica-alumina component contains 70 percent silica and 30 precent alumina has been found to give particularly advantageous results in the hydrocracking of furnace oils. Indeed, for the hydrocracking of furnace oils and heavy gas oils to produce gasoline, catalysts whose silica-alumina component contains between 25 percent and 55 percent alumina and between 75 percent and 45 percent silica are preferred. For hydrocracking of heavy gas oil to produce furnace oil, on the other hand, catalysts whose silica-alumina component contains between 75 percent and 95 percent alumina and between 25 percent and 5 percent silica have been found to furnish high selectivity for furnace oil in the hydrocracked product.

EXAMPLE III

Water glass (1220 grams, 28.7 percent SiO_2) was mixed with 12 liters of water. The resulting solution was passed through a column of 1500 grams of Amberlite IR–120 (Rohm & Hass Company) ion-exchange resin which had been activated by treatment with dilute hydrochloric acid and washing to remove excess acid. A dilute silica sol issued from the column. The column was then rinsed with 1 liter of water and the rinse water issuing from the column was added to the silica sol.

Aluminum chloride hexahydrate (710 grams) was dissolved in 5 liters of water. This solution was mixed with the silica sol prepared as described above. To the mixture was added aqueous ammonia (8 percent NH_3) until the pH of the mixture had risen to 8. This resulted in formation of a gel, which was separated by filtration. The filter cake was washed with water containing 1 milliliter of concentrated ammonia (28 percent NH_3) per liter. Washing was continued until the conductivity of the wash water had fallen to a constant low.

The washed gel was dried at 250° F., formed into 3/16-inch pellets, and calcined at 1000° F. for about 8 hours. The sodium content of this calcined material was found to be less than 0.01 percent. Its pore volume distribution was determined as described under Example I; 83.3 percent of the pore volume was in pores of radius less than 50 Angstroms. The surface acidity of a sample typical of this material, determined as described under Example I, was equivalent to 0.40 milliequivalents per gram at 600° F. The calcined pellets, having a chemical composition corresponding to 70 percent SiO_2 and 30 percent Al_2O_3, were broken and classified by sieving to obtain a class passing through a 10 mesh sieve and being retained on a 20 mesh sieve. This class was then impregnated with a solution containing amonium metatungstate, nickel nitrate, and ammonium fluoride, just as in Example II, to give a catalyst containing 6 percent nickel, 19 percent tungsten, and 2 percent fluorine. The impregnated material was dried at 250° F. and calcined at 1000° F. This catalyst was employed, after pretreating as in Example II, to hydrocrack the same furnace oil feed and under the same conditions as in Example II. Collection and analysis of the products reveal that under these conditions a conversion of 80 percent was achieved and that the liquid product had an aromatic content of 18 percent.

EXAMPLE IV

To make ion-free silica sol, water glass (871 grams, 28.7 percent silica) was mixed with 9 liters of water and passed through a column of 1500 grams of ion-exchange resin, IR–120 (Rohm & Haas Company), which had been activated by treatment with dilute hydrochloric acid and washed to remove the excess acid. Ion-free silica sol issued from the column. The column of ion-exchange resin was rinsed with 1 liter of water and the rinse water issuing from the column was combined with the silica sol.

Aluminum chloride hexahydrate (1182 grams) was dissolved in 10 liters of water, and this solution was mixed with the silica sol prepared as described above. To the mixture was added dilute aqueous ammonia (8 percent NH_3) until the pH of the mixture rose to 8. This resulted in the formation of a cogel, which was separated by filtration. The filter cake was washed with water containing for each liter of water 1 milliliter of concentrated aqueous ammonia (28 percent NH_3). Washing was continued until the conductivity of the wash water had fallen to a constant value. The gel was then dried at 250° F., formed into 3/16-inch pellets, and calcined at 1000° F. The sodium content of this calcined material was found to be less than 0.01 percent. The pore volume distribution of a sample representative of this material was determined as described under Example I; 51.8 percent of the pore volume was in pores of radius less than 50 Angstroms. The surface acidity, determined as described under Example I, of a sample typical of the calcined material was equivalent to 0.42 milliequivalents of ammonia per gram at 600° F. The calcined pellets, having a chemical composition corresponding to 50 percent SiO_2 and 50 percent Al_2O_3, were broken and classified to obtain a class passing through a 10 mesh sieve and being detained on the 20 mesh sieve. This class was then impregnated by the incipient wetness technique with a solution containing ammonium metatungstate, nickel nitrate and ammonium fluoride to give a catalyst containing 6 percent nickel, 19 percent tungsten, and 2 percent fluorine. The impregnated material was dried at 250° F. and calcined at 1000° F.

The resulting catalyst was employed for hydrocracking the furnace oil of Example II under the hydrocracking conditions of Example II. A 50 percent conversion was achieved, and the liquid product was found to have an aromatic content of 28.5 percent.

EXAMPLE V

A catalyst containing nickel, tungsten, fluorine, silica and alumina, in which the ratio of silica to alumina was 60 to 40, was made exactly as in the procedure of Example IV except that 2090 grams of water glass in 20 liters of water were charged to a column of 1500 grams of ion-exchange resin and that a solution of 1892 grams of aluminum chloride hexahydrate in 10 liters of water was mixed with silica sol that had been produced. The silica-alumina component of this catalyst contained less than 0.01 percent sodium. A sample typical of this component was found to have a surface acidity at 600° F. corresponding to 0.44 milliequivalents of ammonia per gram and 79.5 percent of its pore volume in pores of radius less than 50 Angstroms. This catalyst, too, contained 6 percent nickel, 19 percent tungsten, and 2 percent fluorine. It was employed for the hydrocracking of the same FCC furnace oil of Example II under the

same conditions employed in Example II. A conversion of 57 percent was achieved. The aromatic content of the liquid product was determined to be 24 percent.

EXAMPLE VI

By procedures analogous to those recited in the preceding examples, catalysts were prepared containing 6 percent nickel, 19 percent tungsten, 2 percent fluorine, and silica-alumina with the silica and alumina in the ratio of 5 to 95, 10 to 90, 30 to 70, and 70 to 30. The sodium content of the silica-alumina components of these catalysts was less than 0.01 percent. Samples typical of these components had 88.2, 90.5, 93.2, and 82.3 percent, respectively, of their pore volumes in pores of radius less than 50 Angstroms. The samples had surface acidities at 600° F. corresponding to 0.31 milliequivalents of ammonia per gram for the sample with silica and alumina in the ratio 5 to 95, 0.38 milliequivalents per gram for that containing silica and alumina in the ratio 30 to 70, and 0.40 milliequivalents per gram for that containing silica and alumina in the ratio 70 to 30. These catalysts were employed in the hydrocracking of a Kuwait vacuum gas oil having a 20.7° API gravity and containing 3.2 percent sulfur and 970 p.p.m. nitrogen. The catalyst bed temperature was 800° F. and the hydrogen partial pressure 2000 p.s.i.g. The liquid hourly space velocity was 1.0 volume of charge per volume of catalyst per hour and the hydrogen rate was 10,000 s.c.f. of hydrogen per barrel of charge. For the runs for each catalyst the product was collected and fractionated to determine the activity of the catalyst and its selectivity for furnace oil production. The results of these hydrocracking runs are listed in Table II.

Table II.—Hydrocracking heavy gas oil

[Charge: Kuwait Vacuum Gas Oil (20.7° API, 3.2% S, 970 p.p.m. N). Conditions: 800° F., 2,000 p.s.i.g., 1.0 LHSV, and 10,000 s.c.f. H_2/bbl. Catalyst: 6% Ni, 19% W, 2% F.]

Percentage of Total (SiO_2+Al_2O_3):				
Percent SiO_2	5	10	30	70
Percent Al_2O_3	95	90	70	30
Activity, percent by Vol. off at ° F., ASTM:				
400	16	23	45	83
675	67	81	92	100(+)
Selectivity: $\frac{400°\text{-}675°\text{ F. Yield}}{C_5\text{-}400°\text{ F. Yield}}$	2.82	1.58	0.91	(1)

[1] Unavailable. Estimated to be approximately 0.20.

From the results shown in Table II, it can be seen that the proportion of furnace oil to gasoline produced in hydrocracking heavy petroleum fractions can be controlled by selecting the proportion of silica to alumina in the catalysts employed in the process of the instant invention. Thus, high alumina contents, as shown in the selectivity values listed in Table II, correspond to higher proportions of furnace oil in the hydrocracked product, whereas low proportions of alumina correspond to high proportions of gasoline in the hydrocracked product. Being able to control this ratio is important, for in some areas, such as Europe, consumption of furnace oil is high and gasoline low, whereas in other areas, as in the United States, consumption of gasoline is high and consumption of furnace oil is low. It is, of course, desirable to match the production of gasoline and furnace oil to the gasoline-furnace oil demand in the area a refinery serves.

EXAMPLE VII

To make ion-free silica sol, 1220 grams of water glass (28.7 percent SiO_2) is dissolved in 12 liters of water and the solution passed through a column of 1500 grams of ion-exchange resin, IR–120 (Rohm & Haas Company), which has been activated by treatment with dilute hydrochloric acid and then washed to remove excess acid. The column is rinsed with 1 liter of water and the rinse water is added to the silica sol.

Aluminum chloride hexahydrate (710 grams) is dissolved in 5 liters of water, and the resulting solution is mixed with the silica sol prepared as described above. Aqueous ammonia (8 percent NH_3) is added to the silica sol-aluminum chloride mixture until the pH reaches 8. This results in the formation of a silica-alumina gel which is separated by filtration and washed with water containing 1 milliliter of concentrated aqueous ammonia (28 percent NH_3) per liter of wash water. Washing is continued until the conductivity falls to a constant level.

The washed gel is dried at 250° F., formed into 3/16-inch pellets, and calcined at 1000° F. The calcined material contains less than 0.01 percent sodium. It has a preponderance of its pore volume in pores of radius less than 50 Angstroms and has a surface acidity greater than 0.25 milliequivalents of ammonia per gram at 600° F. The calcined material is broken and sieved to obtain a class passing through the 10 mesh sieve and being retained on the 20 mesh sieve. This class is impregnated with a dilute chloroplatinic acid solution by the incipient wetness technique to obtain a catalyst containing 0.5 percent platinum. The impregnated material is dried at 250° F. and calcined at 1000° F. It is employed in hydrocracking furnace oil to obtain gasoline.

EXAMPLE VIII

To make ion-free silica sol, 1220 grams of water glass (28.7 percent SiO_2) is dissolved in 12 liters of water and the solution passed through a column of 1500 grams of ion-exchange resin, IR–120 (Rohm & Haas Company), which has been activated by treatment with dilute hydrochloric acid and then washed to remove excess acid. The column is rinsed with 1 liter of water and the rinse water is added to the silica sol.

Aluminum chloride hexahydrate (710 grams) is dissolved in 5 liters of water, and the resulting solution is mixed with the silica sol prepared as described above. Aqueous ammonia (8 percent NH_3) is added to the silica sol-aluminum chloride mixture until the pH reaches 8. This results in the formation of a silica-alumina gel which is separated by filtration and washed with water containing 1 milliliter of concentrated aqueous ammonia (28 percent NH_3) per liter of wash water. Washing is continued until the conductivity falls to a constant level.

The washed gel is dried at 250° F., formed into 3/16-inch pellets, and calcined at 1000° F. The calcined material contains less than 0.01 percent sodium. It has a preponderance of its pore volume in pores of radius less than 50 Angstroms and has a surface acidity greater than 0.25 milliequivalents of ammonia per gram at 600° F. The calcined material is broken and sieved to obtain a class passing through the 10 mesh sieve and being retained on the 20 mesh sieve. One-hundred sixty grams of the calcined material is, after evacuation, contacted with 85 milliliters of an oxalic acid solution containing 17.8 grams of molybdenum oxide and 16.5 grams of oxalic acid dihydrate. The resultant product is dried at 250° F. for 16 hours and calcined at 1000° F. The resultant catalyst is used to hydrocrack furnace oil to produce gasoline.

We claim:

1. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F., said

process comprising contacting the said distillate with hydrogen at a partial pressure between 750 and 2000 p.s.i. at a temperature between 625° and 850° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said distillate in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said refractory carrier containing the equivalent of between 25 and 55 percent Al_2O_3 and between 75 and 45 percent SiO_2, at a liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said petroleum distillate per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the gasoline range.

2. A process for hydrocracking a furnace oil, said process comprising contacting the said furnace oil with hydrogen at a hydrogen partial pressure between 500 and 10,000 p.s.i. at a temperature between 550° and 700° F., the hydrogen being fed at a rate between 2000 and 30,000 s.c.f./bbl. of said furnace oil in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, at a liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said furnace oil per volume of said catalytic composition per hour.

3. A process for hydrocracking a furnace oil containing less than 100 parts per million of nitrogen, said process comprising contacting the said furnace oil with hydrogen at a hydrogen partial pressure between 750 and 2000 p.s.i. at a temperature between 625° and 675° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said furnace oil in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said calcined refractory carrier having a composition corresponding to between 25 and 55 percent Al_2O_3 and between 75 and 45 percent SiO_2, at a liquid hourly space velocity lying between 0.5 and 3.0 volumes, as liquid, of said furnace oil per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the gasoline range.

4. A process for hydrocracking a gas oil, said process comprising contacting the said gas oil with hydrogen at a hydrogen partial pressure between 500 and 10,000 p.s.i. at a temperature between 700° and 950° F., the hydrogen being fed at a rate between 2000 and 30,000 s.c.f./bbl. of said gas oil in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silical sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, at a liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said gas oil per volume of said catalytic composition per hour.

5. A process for hydrocracking a petroleum gas oil boiling between 650° and 1100° F. and containing less than 100 parts per million of nitrogen, said process comprising contacting the said gas oil with hydrogen at a hydrogen partial pressure between 750 and 2000 p.s.i. at a temperature between 750° and 850° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said gas oil in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said calcined refractory carrier having a composition corresponding to between 75 and 95 percent Al_2O_3 and between 25 and 5 percent SiO_2, at a liquid hourly space velocity lying between 0.5 and 3.0 volumes, as liquid, of said gas oil per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the furnace oil range.

6. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F., said process comprising contacting under hydrocracking conditions the said distillate with hydrogen in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution.

7. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F., said process comprising contacting the said distillate with hydrogen at a partial pressure between 500 and 10,000 p.s.i. at a temperature between 550° and 950° F., the hydrogen being fed at a rate between 2000 and 30,000 s.c.f./bbl. of said distillate in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, at a liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said petroleum distillate per volume of said catalytic composition per hour.

8. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F., said process comprising contacting the said distillate with hydrogen at a partial pressure between 750 and 2000 p.s.i. at a temperature between 625° and 850° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said distillate in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier hav-

ing been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, at a liquid hourly space velocity lying between 0.5 and 3.0 volumes, as liquid, of said petroleum distillate per volume of said catalytic composition per hour.

9. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F. and which contains less than 100 parts per million of nitrogen, said process comprising contacting the said distillate with hydrogen at a partial pressure between 750 and 2000 p.s.i. at a temperature between 625° and 850° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said distillate in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said refractory carrier containing the equivalent of between 25 and 55 percent Al_2O_3 and between 75 and 45 percent SiO_2, at a liquid hourly space velocity between 0.5 and 3.0 volumes, as liquid, of said petroleum distillate per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the gasoline range.

10. A process for hydrocracking a furnace oil, said process comprising contacting the said furnace oil with hydrogen at a hydrogen partial pressure between 500 and 10,000 p.s.i. at a temperature between 550° and 700° F., the hydrogen being fed at a rate between 2000 and 30,000 s.c.f./bbl. of said furnace oil in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, the liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said furnace oil per volume of said catalytic composition per hour.

11. A process for hydrocracking a furnace oil, said process comprising contacting the said furnace oil with hydrogen at a hydrogen partial pressure between 750 and 2000 p.s.i. at a temperature between 625° and 675° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said furnace oil in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said calcined refractory carrier having a composition corresponding to between 25 and 55 percent Al_2O_3 and between 75 and 45 percent SiO_2, the liquid hourly space velocity lying between 0.5 and 3.0 volumes, as liquid, of said furnace oil per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the gasoline range.

12. A process for hydrocracking a gas oil, said process comprising contacting the said gas oil with hydrogen at a hydrogen partial pressure between 500 and 10,000 p.s.i. at a temperature between 700° and 950° F., the hydrogen being fed at a rate between 2000 and 30,000 s.c.f./bbl. of said gas oil in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, the liquid hourly space velocity lying between 0.5 and 10.0 volumes, as liquid, of said gas oil per volume of said catalytic composition per hour.

13. A process for hydrocracking a petroleum gas oil boiling between 650° and 1100° F., said process comprising contacting the said gas oil with hydrogen at a hydrogen partial pressure between 750 and 2000 p.s.i. at a temperature between 750° and 850° F., the hydrogen being fed at a rate between 4000 and 10,000 s.c.f./bbl. of said gas oil in the presence of a catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said calcined refractory carrier having a composition corresponding to between 75 and 95 percent Al_2O_3 and between 25 and 5 percent SiO_2, the liquid hourly space velocity lying between 0.5 and 3.0 volumes, as liquid, of said gas oil per volume of said catalytic composition per hour, to form a liquid product composed chiefly of hydrocarbons boiling in the furnace oil range.

14. A catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations, in aqueous solution, said calcined refractory carrier having a composition corresponding to between 25 and 55 percent Al_2O_3 and between 75 and 45 percent SiO_2.

15. A catalytic composition comprising a hydrogenating component composited with a preformed, dried, and calcined refractory carrier having cracking activity and having a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali metal content less than 0.01 percent, and a surface acidity at 600° F.

greater than 0.25 milliequivalents of ammonia per gram, said carrier having been prepared by gelling a mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution, said calcined refractory carrier having a composition corresponding to between 75 and 95 percent Al_2O_3 and between 25 and 5 percent SiO_2.

16. A process for hydrocracking a petroleum distillate at least 90 percent of which boils above 400° F., said process comprising contacting under hydrocracking conditions said distillate with hydrogen in the presence of a catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution.

17. The process of claim **16** wherein said contacting with hydrogen is carried out at a hydrogen partial pressure in the range of about 500 to 10,000 p.s.i. at a temperature in the range of about 550° to 950° F., at a liquid hourly space velocity in the range of about 0.5 to 10.0 volumes of liquid per volume of catalyst per hour and at a hydrogen:oil ratio in the range of about 2000 to 30,000 s.c.f./bbl. of said distillate.

18. The process of claim **16** wherein said contacting with hydrogen is carried out at a hydrogen partial pressure in the range of about 750 to 2000 p.s.i. at a temperature in the range of about 625° to 850° F., at a liquid hourly space velocity in the range of about 0.5 to 3.0 volumes of liquid per volume of catalyst per hour and at a hydrogen:oil ratio in the range of about 4000 to 10,000 s.c.f./bbl. of said distillate.

19. A catalytic composition comprising a hydrogenating component composited with a dried and calcined refractory carrier having cracking activity and having been prepared from a gelled mixture of a freshly prepared, cation-free silica sol obtained by ion exchange of a water glass solution with a solid, water insoluble, cation exchange material in acid form, and an aqueous solution of a compound yielding aluminum cations in aqueous solution.

20. The composition of claim **19** wherein said calcined refractory carrier has a preponderance of pore volume in pores of radius less than 50 Angstroms, an alkali-metal content less than 0.01 percent, and a surface acidity at 600° F. greater than 0.25 milliequivalents of ammonia per gram.

References Cited by the Examiner

UNITED STATES PATENTS

3,041,140	6/1962	Alexander	23—182
3,078,221	2/1963	Beuther et al.	208—111
3,169,106	2/1965	Lefrancois	208—111
3,182,012	5/1965	Browning et al.	208—111

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