HYDROCRACKING OF HYDROCARBONS WITH THE USE OF A CATALYST COMPRISING NICKEL METAL AND A HETEROPOLY ACID ON ALUMINA

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This invention relates to the catalytic conversion of hydrocarbons, and more particularly concerns the catalytic hydrocracking of hydrocarbons to obtain predominantly gasoline boiling range products.

Most of the modern day petroleum refineries are geared to the production of maximum amounts of gasoline. To achieve this involves the utilization of a variety of processes to convert lower-than-gasoline and higher-than-gasoline boiling range hydrocarbons into fractions suitable for inclusion into high octane gasoline products. While many successful processes are available for accomplishing these conversions, nonetheless a number of high boiling feed stocks have effectively resisted commercial exploitation as sources of gasoline. For example, cycle oils from catalytic or thermal cracking processes, while often recycled for further cracking, are, in general, unattractive by reason of the high severities which they require for conversion. Moreover, these refractory cycle oils usually give relatively low yields of usable gasoline. Accordingly, a major object of the present invention is to provide a process for converting hydrocarbons, especially the higher boiling and refractory cycle oils, to products which predominantly boil in the gasoline boiling range—roughly butanes through about 400° F.

Briefly, in accordance with the invention, it has now been discovered that high boiling hydrocarbons may be catalytically cracked and hydrogenated, or "hydrocracked," to obtain predominantly gasoline boiling range products of high octane number, by contacting the hydrocarbons with hydrogen gas in the presence of a catalyst essentially comprising nickel metal and heteropoly acid on alumina. When such contact is effected at moderately low temperatures and high pressures, partial saturation of polynuclear aromatics occurs, with subsequent cracking of the saturated portion into alkylbenzenes and isoparaffins. An unusual feature of the invention is that only a very small portion of the hydrocarbon feed stocks are converted into usable dry gas.

Heteropoly acids refer to normally solid "complex inorganic substances of high molecular weight in which two or more different acid cations or oxides of metals or metalloids are associated with varying frequency indeterminate amounts of combined water as water of hydration," according to the definition given in Flick U.S. Patent 2,547,380. Illustrative of the heteropoly acids are phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, phosphovanadic acid, phosphomolybdate, silicic acid, sulfuric acid, peroxysulfuric acid, and chromic oxide. The catalytic composition used in the invention is a mixture of at least two of these heteropoly acids. The mixture is most preferably prepared in the manner described in U.S. Patent 2,547,380.

The alumina base or support advantageously comprises either gamma alumina or eta alumina, or mixtures of these allotropic forms. These definitions of alumina are the definitions adopted as standard nomenclature by Russell in his brochure entitled "Alumina Properties," Technical Paper No. 10, 1953, Aluminum Company of America, and by Stumpf et al., Ind. Eng. Chem., 42, 1950, pages 1398-1403.

The invention in its various aspects will be more fully described in the ensuing subsections.

Feed Stocks

A major advantage of the hydrocracking process is that it permits a wide variety of hydrocarbon feed stocks to be converted to predominantly gasoline boiling range products of high octane number. The feed stocks which may be satisfactorily hydrocracked may have compositions ranging from essentially all saturates to essentially all aromatics. Saturates, as noted earlier, are hydrocracked to gasoline-boiling-range paraffins which containing a higher-than-equilibrium concentration of isoparaffins in the product. In the case of polynuclear aromatics compounds these are partially hydrogenated to a tetrahydroanmaphtalene-type structure, and the hydrogenated ring portion is hydrocracked to afford an alkyl substituted benzene and an isoparaffin.

High boiling fractions of crude oil constitute exceedingly advantageous feed stocks for the hydrocracking process. These fractions may range from naphtha and kerosene through light and heavy virgin gas oils, to the light and heavy vacuum gas oils and even to paraffin wax. The individual compositions of each fraction will vary considerably in accordance with crude oil source, and similarly the boiling ranges of the respective fractions will depend on fractionation conditions. Speaking very roughly, naphtha boils at about 200-400° F., kerosene has a boiling range of about 325-500° F., and the virgin gas oils may have an initial boiling point of around 400° and a final boiling point of 700° F. and possibly higher. Vacuum gas oils are exceedingly high boiling. These virgin stocks may be hydrocracked to high octane gasoline. Yields will be significantly higher than can be obtained by conventional fluid bed catalytic cracking.

Cycle oils and cycle oil extracts from catalytic cracking constitute most valuable feed stocks. These cycle oils are the distillates boiling higher than gasoline and are obtained as a product or byproduct of catalytic cracking. Cycle oils normally are enriched in polynuclear aromatics and the hydrocracked product will have outstandingly high octane numbers. A typical light catalytic cycle oil may have a boiling range of about 400-600° F. (ASTM method) while a heavy catalytic cycle oil may have a boiling range of roughly 600-800° F.

Analogous to the light and heavy catalytic cycle oils are the light and heavy cycle oils derived from thermal cracking, delayed coking, and the like. These gas oils are also typically aromatic and olefinic in nature. In the light fraction, the heavy fraction, or both in admixture, may be hydrocracked successfully. In each case, the products have somewhat lower octane number than those obtained by hydrocracking catalytic cycle oils of corresponding boiling ranges, but the yield and octane curves are significantly higher than from fluid bed catalytic cracking of the same materials.

In the hydroforming of petroleum naphthas, say virgin naphthas chiefly boiling in the 200-400° F. range, with a platinum type catalyst (e.g., platinum on eta or gamma alumina) a small amount of polymer or higher boiling product is obtained. This polymer boils above about 425° F. and consists almost entirely of alkylated naphthenes with small amounts of still higher boiling poly-nuclear aromatics. This bottom fraction has heretofore had only limited utility as a high boiling solvent, but by means of the present invention it may be converted in
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In the production of lubricant oils, a virgin distillate of suitable boiling range may be subjected to extraction by selective solvents such as sulfur dioxide, Chlorox, phenol, or the like to remove an aromatic material. This aromatic extract, either alone or in admixture with other feeds, is an ideal feed stock.

The inventive process is also valuable for the mild hydrogenation of feed stocks boiling in the gasoline boiling range to obtain products of similar or only slightly lower boiling range of high octane number. Thus, light and heavy virgin gasoline, the raffinate remaining after solvent extraction of aromatics from a petroleum hydroformate, and other chiefly saturated feed stocks may be processed according to the invention.

Product yields are dependent upon many factors both with respect to feed stocks and hydrocracking conditions. Consequently, although generalizations may be developed, no detailed prediction or correlation of yields or octane numbers are possible without involving awkward inclusion of a multitude of variables. In general, however, the higher the aromatic content of the feed stock the higher will be product yield (gasoline boiling range materials) at any given product octane number. Other factors being equal, the higher the boiling range of the feed stock the greater is the gasoline boiling range product yield.

With any given feed stock, the amount of gasoline produced increases as the severity of operation goes up. It is convenient to express severity in terms of percentage of feed converted to gasoline and other products, that is, dry gas and coke. Conversion is then defined as 100 minus the percentage of unconverted feed remaining in the product. Thus, 40% conversion on a once-through basis would mean that 60% of original feed stock remained, while 40% of the original feed stock (on a weight basis) was converted to gasoline and lower boiling products. In tests at severities ranging from about 70% to over 95% conversion, the dry gas yield never exceeded about 5 weight percent on feed, and with heavy gas oil feeds substantially all of the product boiling below 400° F. comprised high octane number gasoline.

Although the inventive catalyst composition is especially rugged and stable, it nonetheless is subject to poisoning by relatively minor amounts of non-hydrocarbon material that may be in the feed stock. For this reason, it is usually necessary to pretreat all feeds and remove non-hydrocarbon materials, unless by the nature of the previous history of such feeds they have been freed of contaminants.

Sulfur apparently represents the most serious catalyst poisoning. Sulfur levels much in excess of about 50 parts per million should be avoided if satisfactory catalyst life is to be achieved. If possible the sulfur level should be below about 10 parts per million, advantageously even less than about 2 p.p.m. Similarly, hydrogen sulfide in the hydrogen gas supplied to the hydrocracking process should also be low; preferably less than 0.01% at temperatures around 700° F. and, if possible, less than 0.0001% when operating at lower temperatures, e.g., 450° F. Hydrogen sulfide may be removed from a hydrogen containing gas by scrubbing with caustic, monoethanolamine, diethanolamine, or similar alkaline media, desirably followed by contact with suitable dehydrating agent such as ethylene glycol, alumina, or a molecular sieve material.

Nitrogen and oxygen, as components of organic compounds, also appear to be undesirable in a feed stock. Consequently, efforts should be made to reduce or eliminate these materials.

**Process Conditions**

Conditions which are employed in hydrocracking may be selected over a relatively wide range and are normally correlated with the nature of the feed stock to produce either a desired conversion or a desired octane number of product. In general, partial saturation of polyaromatic materials boiling in the gasoline boiling range to cyclalkyl aromatics and cracking of the saturated ring portion thereof are affected by high pressures and moderate temperatures, and an increase in either pressure or temperature has the effect of increasing conversion levels. Excellent results for both virgin and catalytically or thermally cracked feeds may be achieved at pressures in the range of about 500 to 2,000 p.s.i.g. and temperatures in the range of about 400 to 700° F., with optimum results occurring at pressures of about 1,000 to 1,500 p.s.i.g. and temperatures of about 500 to 600° F. For highly refractory stocks, especially those containing lower molecular weight paraffins or aromatics, the pressure may range up to about 3,000 p.s.i.g. or even higher and similarly the temperature may be as high as 900° F. average catalyst temperature or higher. Where only mild conversion per pass is desired, the pressure and/or temperature may be lower than the ranges given above, and may be as little as 300 p.s.i.g. or lower and 200° F. or lower, respectively.

The space velocity, expressed conventionally in terms of volumes of oil feed stock per volume of catalyst per hour, may range from about 0.05 to about 5.0, more suitably from about 0.1 to about 2.0, e.g., 0.2 to 0.5. Reducing the space velocity, or in other words decreasing the charge rate, increases conversion.

Hydrogen to oil ratio, expressed in terms of standard cubic feet of hydrogen gas (60° F., 720 mm. pressure) per barrel of oil feed appears to be a relatively insensitive variable. Major changes in hydrogen/oil ratio do however exert a noticeable alteration of conversion and product quality, and accordingly it is generally desirable to maintain this ratio within the range of about 1,000 to 10,000 s.c.f.b., advantageously about 2,000 to 5,000 s.c.f.b., e.g., 3,000 to 4,000 s.c.f.b.

Naturally, the activity of nickel and heteropoly acid on alumina catalyst is an important variable to be considered when determining optimum process conditions, and consequently this factor must be taken into account in estimating or predicting yields and octane numbers.

It has been found however that over exceedingly wide ranges of conditions, and in fact over all conditions experimentally investigated, the productsobtained boil within the gasoline boiling range. That is, more than 50% by weight of the feed stock which is converted to products boiling below about 400° F. consists of hydrocarbons in the butane and heavier range. Only a minor portion of the product, generally much less than about 5% by weight, consists of methane-ethane-propane hydrocarbons. This product distribution is unique when considering the substantially higher dry gas (methane-ethane-propane) yields from other processes for cracking hydrocarbons such as thermal cracking, or fluid catalytic cracking over a silica-alumina type catalyst.

**Catalyst Preparation**

Numerous techniques are available for preparing the nickel and heteropoly acid on alumina catalyst. In brief, these methods generally involve the preparation of a hydrous alumina which, upon subsequent calcination, will provide either gamma or eta alumina or mixtures of the two. At some stage of alumina production, a heat-decomposable nickel compound and the heteropoly acid are added. Examples of heat decomposable nickel compounds, which decompose to nickel oxide on heating which may be reduced to nickel metal with hydrogen at elevated temperature, include nickel nitrate, nickel (II) acetate, nickel (II) carbonate, nickel formate, nickel (II, III) hydroxide, nickel oxalate, various hydrated forms of the foregoing compounds, nickel carbonate, dicyclopentadienyl nickel, and various nickel chelates such as the ethylene-dimine tetracetic acid, aspartic acid, glutamic acid, and the alanine chelates.
The alumina base may be prepared by any of the methods known to the art for obtaining the desirable form of alumina. For example, gamma alumina is converted by calcining alpha alumina monohydrate, which in turn is obtained by drying alpha alumina trihydrate. The trihydrate, or other form of hydrous alumina which yields gamma alumina, may be obtained by such means as: reacting pure aluminium metal and water above 250°F, reacting aluminum metal with water containing a minor amount of an acid such as dilute HCl; digesting aluminum metal amalgamated with mercury or a mercuric compound such as the oxide with water containing a dilute organic acid such as acetic acid; or by reacting aluminum metal with an aqueous strong acid. In each case, the hydrous alumina may be modified by adjusting the pH to within the range of about 6.8-7.8 with a base, preferably a nitrogen base such as ammonia or ethanolamine.

Alumina which contains at least a substantial proportion, e.g., 5% or more ranging up to 95% or more, of the eta form may also be prepared by any of several well known means. Each of the following methods affords a hydrous alumina which, upon drying, transforms to beta alumina trihydrate, which in turn is converted to ceria through the alpha alumina monohydrate stage and yields eta alumina. By way of example, an alumina hydrosol or other form of hydrous alumina which would ordinarily be converted to gamma alumina may be aged at a pH in excess of around 8 for from 1 to 48 or more hours, after which the resultant alumina may be dried and calcined to eta alumina. Other methods of preparing eta alumina, or an alumina containing a substantial proportion of the eta phase, include: reacting water on finely divided or amalgamated aluminum metal at a temperature below 104°F; hydrolyzing an aluminum alkoxide at room temperature or below; alkalinizing an aqueous solution of an acid-acting water-soluble aluminum salt such as the nitrate or chloride; acidification or neutralization of a basic aluminum salt as sodium aluminate; or by hydrolyzing a neutral aluminum salt such as aluminum acetate.

According to the preferred method of preparing the alumina support, whether gamma or eta, alumina metal in the form of sheets, granules, turnings, shot, or other high surface area forms is subjected to amalgamation by contact with mercury or with an aqueous solution of a mercuric salt. The amalgamated alumina is then digested in water. The precipitate containing anhydrous or partially dehydrated (suitably about 0.5-7 percent by weight) of acetic acid or other weak organic carboxylic acid is a peptizing agent. The reaction goes forward readily at ordinarily or autogenous pressures and at temperatures above about 100°F, preferably about 125-210°F. Thick viscous hydrosols are obtained at temperatures above 160°F, while relatively thin hydrosols are obtained at temperatures below 160°F. The alumina concentration ordinarily varies from about 2 to about 8% Al₂O₃. The mixture of amalgamated aluminum and acidulated water is preferably agitated in order to improve the contact of the reacting materials and to assist in breaking the layer of froth which is ordinarily formed by hydrogen liberated in the reaction. A reflux condenser is advantageously employed to condense water and acid vapors from the emerging hydrogen stream and to return the resulting condensate to the reaction vessel. The reaction gradually slows down after about 24 hours and ultimately ceases for practical purposes after about 40 hours. The resultant hydrosol product is a syrupy liquid of opalescent, nearly transparent appearance, and may be further clarified by settling, centrifugation, filtration, or the like to remove any suspended solids, including particles of metallic impurities. For gamma alumina, the hydrosol may be dried at 200-400°F, for 6-24 hours to afford alpha alumina trihydrate. Upon calcination at 800-1200°F, for 1-6 hours the alpha trihydrate forms gamma alumina.

The method described immediately above may also be employed, according to the preferred embodiment of this invention, to manufacture eta alumina. To obtain the eta modification, the hydrosol is agitated and commingled with an alkaline substance, preferably a nitrogen base such as ammonia, in a quantity sufficient to raise the pH to about above 8.5, but insufficient to convert any considerable portion of the alumina into an ammine salt. The pH is ordinarily maintained below about 12, and preferably in the range of about 10-11. The alkalized hydrosol is aged for about 1 to 48 hours or more at about 50-250°F, preferably around 100-180°F, for 24 hours, the shorter aging periods corresponding generally to the higher pH levels and (in lesser degree) to the higher temperatures. During this operation, white, finely divided hydrous alumina forms in the liquid phase as a filterable slurry. After completion of the desired alkali aging the slurry may be filtered to separate the hydrous alumina, suitably at about 150-200°F, in order to ensure rapid filtration rates. The filter cake is then dried at 150-400°F to beta alumina trihydrate, i.e., to a water content less than about 50%, wet basis, preferably between 15 and 40%; it may be calcined at 800-1200°F to material which contains at least a substantial portion, i.e., 5% or more of eta alumina.

The heat decomposable nickel compound is advantageously incorporated into the alumina as an aqueous solution of such compound, and similarly the heteropoly acid may be incorporated. In particular circumstances however it may be desirable to employ organic solvents for each substance. Incorporation of either or both of the heat decomposable nickel compound and the heteropoly acid may illustratively take place by cobbling with an alumina sol or gel, either before or after alkali aging; by impregnation onto a solid alumina; by addition to the hydrous alumina which has been aged to the hydrosol; by impregnation onto dried or calcined alumina; or by impregnation onto calcined and pelletized alumina.

Once the alumina is formed, one or more finishing operations may be needed to prepare the catalyst in a physical form suitable for employment. A fixed, fluidized, or moving bed hydrocracking unit. These finishing operations depend not only on the previous method of making the catalyst and on the type of processing for which it is to be used, but on the choice of fabricating procedures adapted to provide catalysts of desirable particle size and shape. Accordingly, the finishing operations, generally in accordance with considerations well known to the art, may be relied upon to provide the final catalyst. After drying an alumina hydrosol or hydrogen the product is ordinarily in the form of a solid cake. This cake may be comminuted as by grinding and the ground alumina may then be calcined. At this stage, it may or may not have the heteropoly acid and/or the nickel incorporated therein. Where alumina is prepared by a precipitation technique, ordinarily no commination is necessary.

A comminuted alumina which has either been dried or calcined and which has already lost alkali aging and heteropoly acid incorporation therein may be formed into suitable shapes by, for example, admixing with a lubricant such as Sterotex (hydrogenated coconut oil) formed into shaped particles such as pills, pellets, extrudates, and the like prior to the high temperature calcination. Alternatively, if a dried and crushed alumina has not yet been treated with either nickel or heteropoly acid, these materials may be added in solution form to the dried alumina, which after it may be redried and then formed into shapes, or else extruded in moist form and subsequently redried and calcined. Another variation is to extrude an alumina hydrosol, preferably a thicker hydrosol, into a bath of hot oil to form the alumina into bead-like spheres; the hot oil effects partial drying and solidifi-
cation, and may be employed either with pure alumina or with alumina containing either or both of the metal and heteropoly acid constituent.

Alumina, nickel and heteropoly acid on alumina has been formed into suitable shapes and calcined at a temperature of from about 800 to about 1,200°F. (or up to the onset of alpha alumina transition) It is preferable to reduce the catalyst in hydrogen prior to employment in a hydrocracking process. Reduction effects conversion of nickel oxide resulting from decomposition of the heat decomposable nickel compound during calcination, to nickel metal. Reduction is best effected in a stream of flowing hydrogen gas at atmospheric pressure until about at least the stoichiometric requirement for converting nickel oxide to the metal has been met. Temperature for hydrogen reduction are advantageous in the range of about 500–900°F, preferably from about 600 to about 800°F. The hydrogen flow rate, in units of standard cubic feet per hour per ton of catalyst, is advantageously in the range of about 30 to 150, preferably from about 30 to 90. Efficient reduction conditions include a temperature of about 700–750°F and a hydrogen gas flow rate of about 50–70 standard cubic feet per hour per ton of catalyst. Hydrogen reduction may take place shortly after calcination, or may be reserved until the calcined catalyst is placed in the hydrocracking reactor and before any processing of hydrocarbons occurs. This latter procedure is most advantageous as it avoids problems associated with the pyrolyticity of catalysts containing finely divided nickel.

The final catalyst will advantageously contain from about 0.1 to about 24 weight percent nickel metal and from about 1 to about 60 weight percent heteropoly acid, the balance being essentially alumina. The preferred catalyst contains from about 5 to about 30% heteropoly acid and from about 1 to about 10 weight percent nickel metal, all figures being on total basis.

By way of illustration, but not by way of limitation, the following specific embodiments showing the preparation and use of the inventive catalysts are furnished.

Example I

In this example a nickel and silicotungstic acid on alumina catalyst is prepared by impregnation of nickel silicotungstic acid on a calcined Heard-type hydrocracking.

The alumina hydrocracking is prepared by reacting amalgamated aluminum with 2% aqueous acetic acid at 160–170°F for 24 hours. At the end of which time the reaction proceeds and the reaction product is allowed to settle for 12 hours and the hydrocracking decanted from the reaction vessel. The hydrocracking contains 5.5% weight percent alumina (water free basis) and is treated with 10% aqueous ammonia to a pH of about 6–6.5 and then dried at 255°F and calcined at 500°F. The resultant gamma alumina is ground to 20–48 mesh.

To 35 grams of the ground gamma alumina is added a solution consisting of 32 grams silicotungstic acid and 40 cc. distilled water. The material is allowed to soak with occasional mixing for one hour and then dried at 400°F. The dried material is calcined at 1100°F. for 4 hours.

The calcined material is then mixed with 40 cc. of a nickel acetate solution having a nickel concentration of 0.9 mol per liter. After soaking with occasional mixing for one hour, the catalyst is dried at 400°F. and calcined at 1100°F. for 4 hours. The catalyst is tested for its hydrocracking properties by employing the catalyst to hydrocrack a light catalytic cycle oil, boiling within the range of about 420–620°F and containing 3 parts per million sulfur, at 1000 p.s.i.g. 650°F., a liquid hourly space velocity of 1.0, and 7000 standard cubic feet of hydrogen per barrel of oil.

The test procedure involves reduction of 15 cc. of catalyst in situ with hydrogen at 750°F. and atmospheric pressure for 90 minutes. Oil is then processed under the above test conditions for 3 hours before samples are taken. Two consecutive one hour samples are then collected, and the liquid product is analyzed for 15-ppm asphaltenes by gas chromatography.

The hydrocracking is conducted at 48.6 weight percent of C2–C6 paraffins by gas chromatography.

The fourth hour sample produces 48.6 weight percent of C2–C6 paraffins, and the fifth hour sample contains 44.3 weight percent paraffins. By comparison, a catalyst containing only 5% nickel on gamma alumina, without heteropoly acid, and prepared according to the same procedure produces no detectable yield of C2–C6 paraffins.

Example II

In this example the procedure is identical with that employed for preparing and testing the catalyst in Example I, except that the quantity of silicotungstic acid is reduced to 8 grams. C2–C6 paraffins yields are 16.5 and 14.3 weight percent for the first and fifth hour respectively.

Example III

In this example, nickel and silicotungstic acid are impregnated on one-eighth inch diameter pellets of gamma alumina, and the resultant catalyst is tested for hydrocracking activity.

Ground and calcined gamma alumina, prepared as in the manner of Example I, is mixed with 2% Sterotex, pelleted, and calcined for 4 hours at 1100°F.

To 200 grams of the pelleted gamma alumina is added 200 cc. of a solution containing 120 grams of silicotungstic acid in distilled water. The pellets are allowed to soak with occasional stirring for one hour and then dried at 400°F. and calcined at 1100°F for 4 hours. This calcined material is then impregnated with 140 cc. of a nickel acetate solution containing 0.9 mol per liter of nickel. After soaking for one hour, with occasional stirring, the catalyst is dried at 400°F. and calcined at 1100°F for 4 hours.

The test conditions are 1000 p.s.i.g., about 565°F, average catalyst temperature, 0.25 liquid hourly space velocity, and 3900 s.c.f.b. of hydrogen. The catalyst is reduced with hydrogen for 4 hours at 750°F. and atmospheric pressure prior to introduction of the light catalytic cycle oil feed.

Oil is passed over the catalyst for 6 hours, the product of the last five hours being collected for analysis. Essentially 100% of the catalytic cycle oil is converted to gasoline and lower boiling products. The methane yield is 0.04 weight percent of product, ethane is 0.27, propane is 4.95, isobutane is 17.40, normal butane is 5.13, pentane-180°F is 31.02 weight percent of product, and 180–400°F is 41.18 weight percent.

Example IV

In this example nickel and silicotungstic acid are impregnated onto an eta alumina composition.

A hydrocracking containing 5.51 percent by weight of AlO2, and prepared as in Example I, is adjusted to a pH of approximately 10 by addition of the required quantity of aqueous 29% ammonium hydroxide. The mixture is thereafter allowed to stand at room temperature for a total period of 48 hours and the resulting slurry is filtered. A portion of the filter cake weighing 35 grams is comilled with a solution consisting of 32 grams of silicotungstic acid and 40 cc. of distilled water and the entire mixture is dried at 250°F. The dried material is calcined for 3 hours at 900°F and then ground to about 30 mesh.

The calcined material is then mixed with 40 cc. of a nickel acetate solution having a nickel concentration of 0.9 mol per liter. After soaking with occasional mixing for one hour, the catalyst is dried at 400°F. and calcined at 1100°F. for 4 hours.
To a hydrosol containing 5.51% by weight of Al₂O₃ and prepared as in Example I, a 65 weight percent aqueous silicotungstic acid solution and a 0.9 molar aqueous nickel acetate solution are simultaneously added in quantities sufficient to produce a final catalyst composition containing 2% nickel and 10% silicotungstic acid. Gelation occurs rapidly, and the resultant slurry is dried on a hot plate at about 250° F. for 4 hours. The dried material is calcined for 3 hours at 900° F., ground, mixed with 2% Sterotex, pelleted, and recalcined for 4 hours at 1100° F.

Example VI

In this example a nickel and phosphostungstic acid on gamma alumina is prepared, following the exact procedure set forth for Example I except that 32 grams of phosphostungstic acid is used.

Upon testing according to the procedure of Example I, the fourth and fifth hour samples indicate that 48.7 and 41.8 weight percent, respectively, product is C₅-C₉ paraffins.

Example VII

In this example a nickel and phosphostungstic acid on gamma alumina catalyst is prepared in precisely the manner described for Example II, except that 8 grams of phosphostungstic acid is employed.

The fourth and fifth hour product samples contain 20.6 and 14.2 weight percent C₅-C₉ paraffins, respectively.

Example VIII

In this example the procedure and catalyst of Example III are employed, except that the space velocity is increased to 1.0 and the temperature raised to 630° F. Under these conditions, weight percent conversion is 85. The C₅-180° F. fraction, representing 27.8% on product, has an octane number, research method with 3 cc. TEL per gallon, of 96.7. Heavy naphtha having a 180°-300° F. boiling range and recovered in a 40.6 weight percent yield on product has an octane number research plus 3 cc. of 87.8.

While the invention has been described with reference to certain specific embodiments thereof, it is to be understood that these are illustrative only and not by way of limitation. Numerous modifications and equivalents of our invention will be apparent from the foregoing description to those skilled in the art.

We claim:

1. A process for hydrocracking substantially sulfur-free hydrocarbons to obtain predominantly gasoline-boiling-range products of high octane number, said process being characterized by the conversion of a polynuclear aromatic compounds to an alkyl-substituted benzene and an iso-paraffin, which comprises contacting said hydrocarbons with hydrogen gas under hydrocracking conditions in the presence of a catalyst essentially comprising nickel metal and a heteropoly acid on alumina.

2. Process of claim 1 wherein said hydrocarbons are virgin gas oil.

3. Process of claim 1 wherein said hydrocarbons are catalytic cycle oil.

4. Process of claim 1 wherein said heteropoly acid is phosphostungstic acid.

5. Process of claim 1 wherein said heteropoly acid is silicotungstic acid.

6. Process of claim 1 wherein said alumina is chiefly gamma alumina.

7. Process of claim 1 wherein said alumina is chiefly eta alumina.

8. Process of claim 1 wherein said hydrocracking conditions include a pressure in the range of about 500–3000 p.s.i.g., a temperature in the range of about 400–900° F., a hydrogen to hydrocarbon ratio in the range of about 1,000–10,000 s.c.f.b., and a liquid hourly space velocity in the range of about 0.05 to about 5.0.

9. Process of claim 1 wherein said hydrocracking conditions include a pressure in the range of about 500–2,000 p.s.i.g., a temperature in the range of about 400–700° F., a hydrogen to hydrocarbon ratio in the range of about 2,000–5,000 s.c.f.b., and a liquid hourly space velocity in the range of about 0.1–2.

10. Process of claim 1 wherein said catalyst essentially comprises from about 0.1 to about 24 weight percent nickel metal, for about 1–60 weight percent heteropoly acid, the balance essentially comprising alumina.

11. A catalyst composition suitable for hydrocracking substantially sulfur-free hydrocarbons to obtain predominantly gasoline-boiling-range products of high octane number, which essentially comprises nickel metal and a heteropoly acid on alumina.

12. Composition of claim 11 wherein said heteropoly acid is phosphostungstic acid.

13. Composition of claim 11 wherein said heteropoly acid is silicotungstic acid.

14. Composition of claim 11 wherein said alumina is chiefly gamma alumina.

15. Composition of claim 11 wherein said alumina contains at least a substantial proportion of eta alumina.

16. Composition of claim 11 wherein said catalyst essentially comprises from about 0.1 to about 24 weight percent nickel metal and from about 1 to 60 weight percent heteropoly acid, the balance essentially comprising alumina.

References Cited in the file of this patent

UNITED STATES PATENTS