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HYDROTREATING OF LIGHT CYCLE OILS

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ABSTRACT OF THE DISCLOSURE

A light cycle oil is treated in admixture with hydrogen at about 500–850° F. and about 400–2000 p.s.i.g. in the presence of a Group VI–B metal and a Group VIII metal on a silica-alumina composite containing about 35–65% silica to convert refractory polynuclear aromatic hydrocarbons contained therein to aromatic hydrocarbons wherein the only unsaturation is in a single benzene nucleus.

RELATED APPLICATION

This application is a continuation-in-part of a copending application Ser. No. 595,331, filed Nov. 18, 1966, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the hydrotreating of light cycle oils. This invention further relates to a catalyst uniquely adapted thereto, and to a novel method of preparing said catalyst. It has been known for many years that heavy petroleum fractions such as gas oils, vacuum gas oils, coker gas oils, and the like, are advantageously cracked in the presence of a catalyst to produce lower boiling petroleum fractions including a high octane gasoline fraction. Most catalytic cracking units are operated at conditions whereby higher boiling materials are also recovered from the reaction zone. The gasoline and lower boiling materials are separated from the higher boiling materials by means of a fractionator. Typically, high octane gasoline and lower boiling materials are recovered as an overhead fraction, a cycle oil as an intermediate fraction, and a slurry oil as a bottom fraction. The cycle oil is normally recovered as an upper side cut, or light cycle oil, and a lower side cut, or heavy cycle oil. Usually, the heavy cycle oil is recycled to the reaction zone while the slurry oil is clarified and thereafter recycled or recovered as a fuel oil. However, the light cycle oil comprises the bulk of refractory aromatic hydrocarbons produced in the catalytic process and is therefore not susceptible to further cracking.

Catalytic cracking, although resulting in a higher liquid yield per pass, is relatively deficient in total yield since the refractory light cycle oil fraction cannot be economically recycled. The refractory nature of the light cycle oil has been attributed to the polynuclear aromatic content thereof, the light cycle oil being more aromatic in nature than the virgin gas oil from which it is derived.

It has been proposed to effect a selective hydrogenation of the refractory light cycle oil to improve its susceptibility to catalytic cracking. In the selective hydrogenation process it is of considerable importance to retain in the cycle oil those aromatic hydrocarbons wherein the only unsaturation is in a single benzene nucleus while at the same time selectively hydrogenating the more unsaturated aromatic hydrocarbons, such as naphthalene, to the first mentioned aromatic hydrocarbons, such as Tetralin. Cycle stocks containing aromatics such as the described selectively hydrogenated aromatics are substantially less refractory than would otherwise be the case and

yield a gasoline product of improved octane level when subjected to catalytic cracking.

It is an object of this invention to present a novel process for effecting the selective hydrogenation of a light cycle oil. Another object is to effect said selective hydrogenation of said cycle oil while retaining those aromatics therein which are conducive to increased octane levels in cracked gasolines produced therefrom. It is a further object to present a novel catalyst uniquely adapted to the selective hydrogenation of said cycle oils, and a still further object to present a novel method of preparing said catalyst which is a contributing factor to its activity.

SUMMARY OF THE INVENTION

In one of its broad aspects, the present invention embodies a process for converting refractory polynuclear aromatic hydrocarbons contained in a light cycle oil which comprises passing said cycle oil in contact with a catalyst in the presence of hydrogen at a temperature of from about 500° F. to about 850° F. and at a pressure of from about 400 p.s.i.g. to about 2000 p.s.i.g., and selectively hydrogenating the aromatic hydrocarbons contained therein to form aromatic hydrocarbons wherein the only unsaturation is in a single benzene nucleus, said catalyst comprising a metal of Group VI–B and a metal of Group VIII deposited on a silica-alumina composite, said composite comprising from about 35 to about 65% silica.

Other objects and embodiments of this invention will become apparent in the following detailed specification.

The process of this invention can be effected at reaction conditions hereinafter set forth, and in contact with the catalyst herein described, in any conventional or otherwise convenient manner. For example, a light cycle oil can be preheated and charged to a high pressure vessel utilized as a hydrotreater. The cycle oil can be commingled with hydrogen prior to charging the same to the hydrotreater, or the cycle oil and hydrogen can be charged thereto in individual and separate streams. Preferably, the catalyst is disposed in one or more fixed beds within a reaction zone of the hydrotreater, the cycle oil and hydrogen being charged upflow or downflow in contact therewith. The hydrotreater effluent is preferably cooled and passed to a high pressure separator wherein it is separated into a normally liquid hydrotreated product and a normally gaseous stream. The normally gaseous stream, comprising principally hydrogen, is suitably recycled to the hydrotreater as a portion of the hydrogen charge thereto. If desired, a portion of the gaseous stream may be vented to maintain hydrogen purity although this is not essential to the process of this invention. While the normally liquid product stream may be flashed or stripped to remove dissolved gases, such as hydrogen sulfide, this step may be omitted in view of the sulphur resistant catalyst employed.

The catalyst of this invention comprises a metal of Group VI–B and a metal of Group VIII deposited on a silica-alumina composite comprising from about 35 weight percent to about 65 weight percent silica. Thus, the catalyst comprises chromium, molybdenum and/or tungsten in combination with one or more metals of Group VIII, i.e., iron, nickel, cobalt, platinum, palladium, ruthenium, rhodium, osmium, and iridium. Of the Group VI–B metals, tungsten is preferred. The Group VI–B metal is suitably employed in an amount to comprise from about 0.5 to about 20 weight percent of the final catalyst composite. The Group VIII metal, which is preferably nickel, is suitably effective in amounts to comprise from about 0.1 to about 10 weight percent of the final catalyst composite.

The silica-alumina composite utilized herein is synthetically prepared and is considered to function as a catalytic element of the final catalyst composite as well

as the carrier for the metallic components thereof to give a final catalyst composite of improved properties with respect to hydrotreating as herein contemplated, particularly when prepared in accordance with the preferred method of this invention.

The silica-alumina composite is suitably prepared as spheroidal particles by the well-known oil-drop method. For example, an alumina sol, utilized as an alumina source, is commingled with an acidified water glass solution as a silica source, and the mixture further commingled with a suitable gelling agent, for example, urea. The mixture is discharged while still below gelation temperature, and by means of a nozzle or rotating disc into a hot oil bath maintained at gelation temperature. The mixture is dispersed into the oil bath as droplets which form into spheroidal gel particles during passage therethrough. The alumina sol is generally prepared by conventional methods. For example, aluminum pellets are commingled with a quantity of treated or deionized water, with hydrochloric acid being added thereto in sufficient amount to digest a portion of the aluminum metal and form the desired sol. A suitable reaction rate is effected at about reflux temperature of the mixture—usually from about 175° F. to about 220° F., depending upon the particle size and purity of the aluminum. Another method commonly employed consists in the addition of aluminum metal to an aqueous aluminum chloride solution and treating the mixture at about reflux temperature.

The acidified water glass solution is conveniently prepared by acidifying the water glass in aqueous solution with a small amount of mineral acid, usually hydrochloric or sulphuric acid, effecting hydrolysis of the water glass and conversion to a silicic acid or silica hydrosol. In the process, the temperature is maintained at below about 60° F. to obviate polymerization of the silicic acid and premature gelation.

The spheroidal gel particles prepared by the oil-drop method are aged, usually in the oil bath, for a period of at least 10 hours, and then in a suitable alkaline or basic medium for at least another 10 hours, and finally water-washed. Proper gelation of the mixture in the oil bath, as well as subsequent aging of the gel spheres, is not readily accomplished below about 120° F., and above 210° F. the rapid evolution of the gases tends to rupture and otherwise weaken the spheres. By maintaining sufficient superatmospheric pressure during the forming and aging steps in order to maintain water in the liquid phase, a high temperature can be employed, frequently with improved results.

The spheres are suitably water-washed by percolation, either with an upward or downward flow of water, and preferably with water containing a small amount of ammonium hydroxide and/or ammonium nitrate. After washing, the spheres are dried at a temperature of from about 200° F. to about 600° F. for a period of from about 6 hours to about 24 hours or more, and then calcined at a temperature of from about 800° F. to about 1400° F. for a period of from about 2 hours to about 12 hours or more.

In a preferred embodiment of this invention, an aluminum sulphate rather than an alumina sol is utilized as an alumina source. In the method herein contemplated, ammonium hydroxide and aluminum sulphate are commingled in aqueous solution in a ratio to effect a pH of from about 3.8 to about 4.1 and thereafter admixed with an acidified water glass solution. The resulting mixture is then discharged by means of a nozzle or rotating disc into a hot oil bath in the manner and at the conditions hereinbefore set forth. In some cases, the inclusion of a small amount of alumina sol in the dropping mixture will facilitate gelation of the spheres, although this is considered merely an expedient.

The Group VI–B and the Group VIII metal component can be composited with the silica-alumina in any suitable manner, for example, the silica-alumina particles can be soaked, dipped, suspended or otherwise immersed in a common solution comprising a suitable compound of a Group VI–B metal and a suitable Group VIII metal compound. Alternatively, the group VI–B and the Group VIII metals can be composited with the silica-alumina utilizing individual solutions thereof and in any convenient sequence. Suitable compounds of Group VI–B metals include ammonium molybdate, ammonium paramolybdate, molybdic acid, molybdenum trioxide, ammonium chromate, ammonium peroxychromate, chromium acetate, chromous chloride, chromium nitrate, ammonium metatungstate, tungstic acid, etc. Compounds of metals of Group VIII which are suitable include nickel nitrate, nickel sulphate, nickel chloride, nickel bromide, nickel fluoride, nickel iodide, nickel acetate, nickel formate, cobaltous nitrate, cobaltous sulphate, cobaltous fluoride, ferric chloride, ferric bromide, ferric fluoride, ferric nitate, ferric sulphate, ferric formate, ferric acetate, platinum chloride, chloroplatinic acid, chloropalladic acid, palladium chloride, etc.

The final catalyst composite after all of the catalytic components are present therein, is dried for a period of from about 2 to about 8 hours or more in a steam drier, and subsequently oxidized in an oxygen-containing atmosphere, such as air, at an elevated temperature of from about 1100° F. to about 1700° F. for a period of from about 1 to about 8 hours or more. Following this high temperature oxidation procedure, the catalyst may be reduced for a period ranging from about ½ hour to about 1 hour at a temperature within the range of from about 700° F. to about 1000° F. in the presence of hydrogen.

The reaction conditions employed in the hydrotreating of cycle oils as herein contemplated, such as temperature, pressure, liquid hourly space velocity (LHSV), hydrogen/oil ratio, etc., are selected to effect optimum conversion of the refractory cycle oil to a product having as the major aromatic component a benzene hydrocarbon wherein the only unsaturation occurs in the single benzene nucleus. It is desirable to maintain pressure, LHSV, and the hydrogen/oil ratio constant and vary the temperature to maximize conversion of the aromatics to benzene hydrocarbons as aforesaid. Reaction conditions may be selected initially on the basis of the particular cycle stock to be treated. A reactor pressure in the range of about 400 p.s.i.g. to about 2000 p.s.i.g. is suitable, a pressure of from about 800 p.s.i.g. to about 1200 p.s.i.g. being preferred. The LHSV is suitably from about 0.5 to about 20 although a LHVS of from about 2 to about 6 is preferred. A hydrogen/oil ratio of from about 2 to about 20, preferably from about 5 to about 15, is suitable. Preferably, the temperature is adjusted upon selection of the aforesaid variables to a temperature of from about 500° F. to about 850° F., and preferably from about 600° F. to about 700° F. The most straight forward way to attain proper operating condition is to select the independent variables, conduct a product analysis, and adjust the temperature, within the aforementioned limitations, to attain optimum selective hydrogenation. If the hydrotreating conditions are too severe for the particular charge stock, the aromatics will become overly saturated. This results in an undue consumption of hydrogen and, more important, a reduction in the octane level of the gasoline product resulting from catalytic cracking of the hydrotreated cycle oil. If the hydrotreating conditions are not sufficiently severe, there will be little if any improvement in the refractory character of the cycle oil. When properly hydrotreated, a cycle oil is readily catalytically cracked yielding high quality gasoline at conversions of about 100%.

The following example is presented in illustration of one preferred embodiment of this invention and is not intended as a limitation of the generally broad scope of the invention as set out in the appended claims.

EXAMPLE I

Silica-alumina spheroidal particles comprising 60 weight percent silica and 40 weight percent alumina were prepared by the oil drop method. An alumina hydrosol (143 cc.) comprising 14.18% alumina and 10.7% chloride was mixed together with an aqueous aluminum sulphate solution (1876 cc.) comprising 26% aluminum sulphate, and a 28% aqueous ammonia solution (462 cc.). This mixture was pumped in a stream to a mixer where it was rapidly and thoroughly admixed with a stream of acidified water glass solution containing 18.41% silica. The resulting mixture was immediately dispersed as droplets into a hot (210° F.) oil bath and formed into spherical gel particles. The spheres were recovered, washed to 203° F. over a 4 hour period with a 1% aqueous ammonium nitrate solution. The washed spheres were then dried at 212° F. for 3 hours and calcined for another 3 hours at 1200° F.

137 grams of the spheroidal silica-alumina (1/16" spheres) was immersed in an aqueous solution (155 cc.) containing 34.3 grams of ammonium metatungstate and 14.35 grams of nickelous nitrate, the solution being thereafter evaporated to dryness in a rotary steam drier. After impregnation and drying, the catalyst was calcined for 1 hour at 1100° F. 168 grams of catalyst was recovered.

39 grams of the catalyst (50 cc.) was placed in a fixed bed in a vertical tubular reactor. The reactor was immersed in a fused salt bath whereby the reaction temperature was maintained at about 600° F., the pressure being maintained at about 1000 p.s.i.g. A refractory light cycle oil, hereinafter described, was charged to the reactor in a once-through type of operation at a LHSV of about 4 together with recycle hydrogen charged thereto at a rate of about 5000 s.c.f./b.b.l. The charge traveled downflow through the reactor, the reactor effluent being recovered in a high pressure separator. Recycle hydrogen was recovered overhead from the separator, scrubbed with water and recycled. The hydrotreated cycle oil was recovered from the separator, charged to a stripper and the stripped product recovered. The product was analyzed periodically by mass spectrometer to determine the aromatic content and nature thereof.

The refractory light cycle oil charge stock boiled in the 445–655° F. range and contained 89 p.p.m. nitrogen and 1.7% sulfur. Mass spectrometer analysis showed the charge stock to contain 63% aromatics of which 13.8% were represented by the general formula $C_nH_{2n}-x$ where $x=8$ (Tetralin, indane, etc.), and 47.8% were represented by said formula where $x=10$ or 12 (naphthalene, indene, etc.). The described cycle oil was converted to a substantially less refractory cycle oil comprising 59.6% aromatics of which 71% were represented by said general formula where $x=8$, and 6.1% were represented by said formula where $x=10$ or 12.

It will be observed that while the cycle oil suffers little change in the total aromatics content thereof (59.6% as opposed to 63%), there is a significant and substantial increase in those desirable aromatics such as Tetralin, etc., (71% as opposed to 13.8%) which are conductive to improved octane levels of cracked gasolines prepared therefrom, and the refractory aromatics, such as naphthalene etc., have been reduced to a level of only 6.1%.

We claim as our invention:

1. A process for converting refractory polynuclear aromatic hydrocarbons contained in a light cycle oil which comprises passing said cycle oil in contact with a catalyst in the presence of hydrogen at a temperature of from about 500° F. to about 850° F. and at a pressure of from about 400 p.s.i.g. to about 2000 p.s.i.g. and selectively hydrogenating the aromatic hydrocarbons contained therein to form aromatic hydrocarbons wherein the only unsaturation is in a single benzene nucleus, said catalyst comprising a metal of Group VI–B and a metal of Group VIII deposited on a silica-alumina composite, said composite comprising from about 35 to about 65% silica, the total aromatics content of said light cycle oil being substantially unchanged by said conversion.

2. The process of claim 1 further characterized in that said Group VI–B metal is tungsten and said Group VIII metal is nickel.

3. The process of claim 2 further characterized in that said tungsten comprises from about 0.5 to about 20 wt. percent of the catalyst and said nickel comprises from about 0.1 to about 10 wt. percent thereof.

4. The process of claim 1 further characterized in that said pressure is from about 800 p.s.i.g. to about 1200 p.s.i.g. and said temperature is from about 600° F. to about 700° F.

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