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CATALYTIC CONVERSION OF HYDROCARBONS

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This application is a continuation-in-part of the application Serial No. 104,014, filed April 19, 1961, now abandoned.

This invention relates to the catalytic conversion of hydrocarbons, and more particularly to a process for the catalytic conversion of petroleum distillates to products of a lower boiling range. Still more particularly, the invention concerns the catalytic hydrocracking of petroleum distillates to obtain predominantly gasoline boiling range products.

This conversion process involves a multiple combination of reactions, in which hydrogenation, isomerization and cracking predominate, whereby higher boiling hydrocarbon fractions are converted to lower boiling hydrocarbon products which are rich in isoparaffins and/or aromatics. In a preferred embodiment of the invention higher boiling hydrocarbons are converted to products which predominantly boil in the gasoline boiling range, i.e., butanes through about 400° F.

In accordance with this invention, it has now been discovered that high boiling hydrocarbons such as petroleum distillates boiling above about 300° F. may be catalytically cracked in the presence of hydrogen, or "hydrocracked," to obtain lower boiling hydrocarbons by contacting the high boiling hydrocarbons under hydrocracking conditions at elevated temperature and pressure and in the presence of hydrogen-containing gas with a catalyst comprising a metallic hydrogenation component, a solid acidic cracking component and a normally solid element of Group VA of the Periodic Table. With feed stocks containing polynuclear aromatics, the process variables can be controlled to provide a product rich in alkylbenzenes and isoparaffins both of which are desirable components of high octane gasolines. Further, normal paraffins are converted to products having greater than equilibrium concentrations of isoparaffins. The invention advantageously provides such a process wherein the gas make is low, i.e., only a very small portion of the feed stock is converted into undesirable light gases, and the product predominantly boils in the gasoline boiling range.

In a preferred embodiment of the invention the conversion process is carried out by contacting a hydrocarbon distillate boiling between about 300° F. and 850° F. in the presence of hydrogen at a temperature between about 500° F. and about 700° F., a pressure between about 200 p.s.i.g. and about 2000 p.s.i.g., and a liquid hourly space velocity between about .1 and 10 volumes of oil per hour per volume of catalyst with a catalyst comprising: a hydrogenation component selected from the metals of Group VIII of the Periodic Table, particularly nickel, platinum, cobalt and palladium; a solid acidic cracking component, particularly silica-alumina; and arsenic. Preferably, fluorine is incorporated into the catalyst to provide an exceptionally high catalyst activity.

In the operation of the process, a selected feed stock is introduced into a reaction zone containing catalyst along with a hydrogen containing gas such as hydrogen gas, catalytic reformer make-gas or a recycled hydrogen-rich gas from the present process. The process may be operated in the liquid phase, the vapor phase or mixed vapor-liquid phase. The catalyst system may be of the fixed bed type, as well as a fluidized bed or other appropriate

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type of system. The feed stocks employed may be derived from petroleum, shale, gilsonite or other such sources. Also, it may be desirable to recycle a portion of the effluent to the reaction zone.

The feed stocks which may be satisfactorily hydrocracked in the present process may have compositions ranging from essentially all saturates to all aromatics. Saturates are hydrocracked to gasoline-boiling-range paraffins containing a greater than equilibrium concentration of isoparaffins in the product, while in the case of polynuclear aromatics these are partially hydrogenated and the hydrogenated ring portion is hydrocracked to afford an alkyl substituted benzene and an isoparaffin.

High boiling fractions of crude oil constitute advantageous feed stocks for the process of the invention. Most generally the feed stock will range from naphtha and kerosene through the light and heavy gas oils. The feed stock will normally boil above about 300° F. and may boil up to about 1000° F. Advantageously, the boiling range of the feed stock is about 300° F. to about 850° F. Examples of desirable feed stocks are light catalytic cycle oil having a boiling range of from about 350° F. to 650° F., heavy catalytic cycle oil boiling in the range of about 500° F. to 850° F., virgin gas oil boiling from about 400° F. to 1000° F. and coker gas oil boiling in the range of about 350° F. to 800° F.

Product yields are especially dependent upon the nature of the feed stock, the process conditions and the catalyst employed in the process. In each instance it is necessary to correlate the aforementioned factors according to the desired product.

In previous hydrocracking processes sulfur in the system has been regarded as a catalyst poison, i.e., in that it undesirably reduces catalyst activity. Furthermore, the deposition of sulfidic deposits on the catalyst has presented problems in the regeneration of a deactivated catalyst due to the tendency to form sulfates on the catalyst and thereby further reduce catalyst activity. It has been found that the normal amounts of sulfur which are found in the above-described feed stocks do not adversely affect the catalyst employed in the present invention, either during the on-oil period, or during the regeneration of the catalyst. While the catalysts employed in the process of the invention have been found to have suitable cycle life, over a prolonged period of use the catalysts may become deactivated due to the build up of carbonaceous deposits thereon, and the catalyst may be regenerated by the technique described hereinafter.

Desirably, nitrogen and oxygen as components of compounds in the feed stock are kept as low as possible in order to maintain a desirably long cycle life; i.e., the period of time for which the catalyst remains effective in producing the desired product. With higher nitrogen contents in the feed stock more frequent regenerations and/or higher temperatures are required to maintain a suitable cycle life. Typically, the feed may contain less than about 0.01 weight percent nitrogen and when operating at temperatures of about 700° F. or lower it is desirable to maintain the nitrogen level at about 10–15 parts per million, and advantageously at about 1 part per million.

The process conditions which are employed in the present invention can be selected over a relatively wide range and are correlated, according to the nature of the feed stock and of the particular catalyst employed, so as to produce either a desired conversion; i.e., as the percentage of feed stock converted to product or a product of a desired octane number. The formation of alkylbenzenes from polynuclear aromatics is favored by higher pressures and moderate temperatures, and an increase in both of these variables has the effect of increasing the degree of conversion. Satisfactory conversions are ob-

tained with the above described feed stocks at pressures in the range of about 200 to 2000 p.s.i.g. and temperatures in the range of about 400° F. to 1000° F., although pressures and temperatures outside of these ranges may be employed when utilizing certain feed stocks, particularly highly refractory feeds. Advantageously, pressures in the range of about 750 to 1500 p.s.i.g. and temperatures between about 500° F. to 700° F. are employed. It may be desirable during the course of a run to increase the temperature within the reaction zone as the catalyst deactivates in order to compensate for a drop in catalyst activity. Thus, with a fresh or newly regenerated catalyst it may be desirable to come on stream at a temperature of about 500° F. and to gradually increase the operating temperature towards about 700° F. during the course of a run. In most instances it is desirable to maintain a low operating temperature, since higher temperatures have been found to result in increased coking and increased amounts of gas formation.

The space velocity, expressed herein as liquid hourly space velocity (LHSV), in terms of volumes of oil charged to the reaction zone per hour per volume of catalyst, may range from about .1 to 10, normally from about 0.2 to 5, and preferably from about 0.25 to 2 LHSV. Lower space velocities tend to increase the degree of conversion.

Hydrogen is consumed in the process and it is necessary to maintain an excess of hydrogen in the reaction zone. However, the process is relatively unaffected by changes in the hydrogen to oil ratio within the general range of operations. The hydrogen to oil ratio employed desirably is in the range of about 1000 to 20,000 standard cubic feet of hydrogen gas per barrel of feed (s.c.f.b.) and advantageously about 2000 to 10,000 s.c.f.b. is employed.

It has been found that over wide ranges of operating conditions the products of the hydrocracking process predominantly boil within the gasoline boiling range. The dry gas make; i.e., methane through propane, generally is less than about 5 weight percent and typically is in the order of about 2 to 3 weight percent. The butane-pentane fraction of the product also is low, with the amount produced being more dependent upon operating conditions and the nature of the feed stock. When employing a feed stock such as light catalytic cycle oil the pentane-plus to 400° F. fraction of the product generally will range upwardly from about 50 weight percent of the total converted product.

The catalyst employed in the present process comprises a hydrogenation component, a solid acidic component and a normally solid element of Group VA of the Periodic Table (from College Chemistry, 2nd edition, by Paul R. Frey, Prentice-Hall, Inc., 1958); i.e., phosphorus, arsenic, antimony and bismuth. Heretofore, it has been thought that elements such as arsenic, antimony, etc. would act to destroy the effectiveness of catalysts used in petroleum processes especially those containing platinum, nickel and the like. It has now been found, however, that the incorporation of such elements in the catalysts employed in the present invention results in improved results in the process described herein. Among the benefits obtained from employing these catalysts in the present process are the increased production of branched chain paraffins, more favorable control of catalyst activity and the simplification of catalyst reactivation techniques whereby a readily regenerable catalyst can be employed in the process.

The acidic cracking component of the catalyst may comprise one or more solid acidic components such as silica-alumina (naturally occurring and/or synthetic) silica-magnesia, silica-alumina-zirconia, and the like. Also, acid-treated-aluminas, with or without halogens, such as fluorided alumina, boria-alumina, and the heteropoly-acid-treated aluminas, i.e. treated with phosphotungstic acid, phosphovanadic acid, silicotungstic acid, silicomolybdo-

vanadic acid and the like, may be employed. However, it is critical that such materials possess substantial cracking activity in the finished catalyst composite. A preferred acidic component of the present catalyst composition is one of the commercially available synthetic silica-alumina cracking catalysts which may contain about 5 to 40 weight percent alumina. Preferably, the acidic component of the catalyst is employed as a support and it is highly porous, having a surface area of between about 100 and 500 square meters per gram. The preparation and properties of the acidic cracking components are well-known in the art and they need not be described further herein for the purpose of the present invention. For example, see the series entitled "Catalysis" by Emmett (Reinhold Publishing Corporation), particularly volume VII, pp. 1-91.

Any of the well-known metallic hydrogenation catalysts may be incorporated in the present catalyst, but preferably, the metallic constituent of this component is selected from the metals of Group VIII of the Periodic Table which are known to possess satisfactory hydrogenation activities, especially nickel, platinum, cobalt and palladium. The hydrogenation component of the catalyst advantageously can be incorporated into the catalyst by impregnating a porous acidic cracking component with a heat-decomposable compound of the hydrogenation metal, followed by calcining to provide a composite. Typically, a silica-alumina cracking catalyst or an acid-treated alumina base is impregnated with a solution of nickel acetate, chloroplatinic acid or the like, and then dried; followed by pelleting and calcining at an elevated temperature (about 1000° F.).

However, it is contemplated that the finished catalyst may also be produced by various methods such as by co-gelling the various components and by other well-known variations in catalyst preparation techniques to produce a finished catalyst having the desired properties.

The amount of the hydrogenation component incorporated in the catalyst can vary over a wide range, with the amount being selected to provide the desired catalyst activity. For example, large amounts of nickel, e.g., up to about 30 weight percent can be employed, and relatively small amounts of nickel, e.g., as little as about 0.1 weight percent is also effective, with about 0.5 to 10 weight percent nickel being preferred. Typically, about 0.1 to 2 weight percent platinum is effective in the catalyst and preferably about 0.1 to 1 weight percent platinum is employed. The amount of the hydrogenation component employed in the catalyst thus will depend upon the catalytic ability and economic factors.

The Group VA component of the catalyst composition, for example, may be incorporated during the catalyst manufacture by impregnating a nickel/silica-alumina composite of the type described above with a solution of an organic compound of the Group VA element, including aryl or alkyl substituted organo-metallics, such as triphenyl arsine, triphenyl stibine, etc., with the subsequent evaporation of the solvent to leave a deposit on the base. Also, the catalyst base can be impregnated with inorganic compounds, including the acids, ammonium salts, nitrates, halides, etc., of the normally solid Group VA elements, e.g., arsenic trioxide in an ammoniacal solution, followed by drying. Prior to use, the catalyst is treated with hydrogen at elevated temperature (ca. 850° F.). However, it is also contemplated that such elements may be introduced into the reaction zone as during the on-oil period or the regeneration to contact the catalyst base in situ so that these elements are incorporated in the catalyst. Typically, an organic compound or arsenic may be introduced into the reaction zone with the hydrocracking feed so that the catalyst base is arsenided in situ.

Normally only a small amount of the Group VA element is required in the catalyst. The total amount employed will most often be governed by the amount of

hydrogenation metal incorporated in the catalyst and upon the chemical form, i.e., arsenic may be present as either the arsenide or sub-arsenide. Generally speaking, no more than one atom of the normally solid Group VA element per atom of the hydrogenation metal is required in the catalyst, although greater amounts may be employed as long as the desired catalyst activity is maintained. Typically, arsenic may be employed in a ratio up to about 2 atoms per atom of hydrogenation metal in the catalyst. Advantageously, however, about 0.01 to 1 atom of such elements per atom of hydrogenation metal is employed, while a ratio of from about 0.1 to 0.5 is preferred.

The preferred catalyst, which has been found to have an exceptionally high activity, consists essentially of a Group VIII hydrogenation metal component, especially nickel; a normally solid element of Group VA, especially arsenic; fluorine; and a silica-alumina catalyst base. The silica-alumina preferably is a silica-alumina cracking catalyst, and either the so-called "high alumina" (about 20-30% Al_2O_3) or the "low alumina" (about 10-15% Al_2O_3) may be used. The amount of the hydrogenation metal employed in the catalyst will vary according to the desired activity. Typically, about 0.5 to 5 weight percent nickel is supported on the catalyst base, although up to about 10 weight percent nickel may be used in some instances. About 0.5-6 weight percent, and preferably about 2-4 weight percent, halide is incorporated in the catalyst by impregnating the catalyst base, either with or without the hydrogenation metal, with an organic or inorganic halide compound which reacts therewith. Fluorine is the preferred halide since it has been found to impart an exceptionally high activity to the catalyst. The various components may be combined with the catalyst base either simultaneously or in a stepwise manner, followed by drying and calcining. In the latter case, exceptionally good results have been obtained by impregnating silica-alumina containing nickel with an inorganic fluoride solution, such as ammonium fluoride. However, the catalyst base may be impregnated with a single solution containing a nickel compound, an arsenic compound and the halide, and for example, nickel fluoride may be used advantageously.

In the preparation of the above-described catalyst exceptionally high catalyst activity resulted when the catalyst was pre-reduced in a hydrogen atmosphere at 700° F. to 900° F., calcined at 900° F. to 1100° F., and then reduced again in hydrogen at 700° F. to 900° F.

Various halogen compounds may be used in preparing the preferred catalyst. These include inorganic compounds and alkyl or aryl organic compounds such as hydrogen fluoride, ammonium fluoride, fluoro benzene, benzyl trifluoride, benzyl fluoride, etc., although all are not necessarily equivalent in their effect upon the catalyst.

As used herein, the terms "arsenided," "antimonided," "bismuthided," "fluorided," etc. refer to the incorporation of arsenic, antimony, bismuth, fluorine, etc. in the catalyst composition in any manner suitable to provide a hydrocarbon conversion catalyst of the type described herein.

After operating for a period of time the catalyst described herein may decline in activity with carbonaceous deposits being accumulated on the catalyst. The activity decline is indicated by a lower level of conversion in the effluent from the reaction zone, or by a decline in the octane number of the converted product. As previously mentioned, the catalyst activity decline may be offset by increasing the operating severity, e.g., by operating at increased temperature, to maintain the desired product quality. When the catalyst activity has declined to the point where it is unsatisfactory, the catalyst can be re-activated to a satisfactory level.

The following sequence of steps has been found to be very satisfactory for restoring the activity of the de-activated catalyst:

(1) The catalyst bed and reaction zone are purged

of combustible materials such as hydrocarbons and hydrogen, by passing an inert gas such as nitrogen, carbon dioxide, flue gas, etc., through the catalyst bed. Advantageously, this inert gas purge is carried out at atmospheric pressure, but a higher pressure may be employed. Preferably, the temperature of the catalyst bed is adjusted to the "burn-off" temperature during the period of purging by externally heating the catalyst bed or by passing a heated inert gas into the bed. Typically, a 500° F. to 700° F. on-oil operating temperature is employed and while purging, the catalyst bed temperature is raised to a temperature in the range of about 750° F. to 1000° F., preferably about 850° F., sufficient to burn off the carbonaceous deposits on the catalyst.

(2) After the combustibles are purged from the catalyst bed and the reactor to a sufficiently low level, an oxygen-containing gas is contacted with the catalyst at a controlled rate to oxidize the carbonaceous deposits, mainly coke, on the catalyst. The burnoff rate is limited by the oxygen supplied, and the catalyst bed during the burnoff period must not be permitted to overheat so as to cause permanent catalyst damage by sintering any of the catalyst components, reducing the surface area or causing harmful crystalline phase changes. A maximum temperature of about 1000° F. is permissible with a nickel-containing catalyst, although with other metals such as a platinum, higher temperatures may be employed. However, the burnoff has been carried out very satisfactorily by employing, first, a diluted oxygen-containing gas such as about 2-20% oxygen in nitrogen and preferably a 2% oxygen in nitrogen gas at 750° F. to 1000° F. to burn off most of the coke, followed by contacting the catalyst with atmospheric air at 850° F. to oxidize any remaining carbonaceous deposits.

(3) Following the burnoff, it is preferred to again purge the catalyst bed, as with an inert gas such as described above, to remove any remaining oxygen, and the catalyst bed temperature preferably is reduced to the process operating temperature during this period.

(4) Then, the catalyst is contacted with a hydrogen-containing gas. Metal oxides resulting from contact with the oxygen-containing gas during the burnoff period are reduced by the hydrogen. In this step, hydrogen, hydrogen-rich recycle gas from the present process or other processes such as catalytic reforming, and similar gas streams containing sufficient available hydrogen may be utilized. Preferably, the hydrogen contacting step is carried out at approximately the process operating temperature and pressure, but other conditions operative for the reduction may be employed.

After regenerating the catalyst as described above, the reactivated catalyst was found to be fully capable of producing a hydrocracked product according to the present invention. To off-set any loss of fluorine during regeneration, the catalyst may be contacted with a substance containing available fluorine. For example, a small amount, e.g., up to about 100 p.p.m., and preferably 10 p.p.m. or less, of HF may be included in the above hydrogen contacting step. The following example is given as being illustrative of the operation of the process of the invention. However, it is to be understood that the example is given by way of illustration only, and does not serve in any way to limit the scope of the present invention.

EXAMPLE I

A catalyst was prepared comprising 5 weight percent nickel and 2.5 weight percent arsenic on a silica-alumina support containing about 25 weight percent alumina. In preparing the catalyst, a commercial high alumina silica-alumina cracking catalyst was impregnated with an aqueous solution of nickel acetate. The impregnated composite was dried at about 400° F., mixed with 4 percent Sterotex (hydrogenated coconut oil), pelleted to 1/8" size and calcined for 6 hours at 1000° F. The calcined catalyst was then crushed to 20-48 mesh and impregnated

with a solution of triphenyl-arsine in normal heptane. The heptane was evaporated and the arsenic-treated catalyst was then placed in a reactor where it was treated with flowing hydrogen at atmospheric pressure and 750° F. to decompose the arsine, resulting in an arsenided nickel on silica-alumina catalyst.

During the first period of operation approximately 90 ccs. of the finished catalyst was contacted in the presence of hydrogen with a light catalytic cycle oil boiling in the range of about 400° F. to 600° F.

The light catalyst cycle oil feed stock had previously been hydrodesulfurized over a cobalt-molybdena catalyst. The aromatic content of the hydrodesulfurized light catalytic cycle oil had previously been reduced to a level

ing the first period of the run. Results obtained from this third period are as shown in the following table, indicating that the reactivated catalyst possesses a high level of activity after previous exposure to a feed high in sulfur and nitrogen.

During the fourth period of the run, the feed was changed again to the light raw catalytic cycle oil employed previously. Results from this fourth period of the run was shown in the following table.

Octane ratings of the C₅ to 180° F. hydrocracked gasoline range material produced with the fresh catalyst were found to be in the range of 98–100 F–1 + 3 cc. TEL, and with reactivated catalyst the octane rating were found to be in the same range as with the fresh catalyst.

HYDROCRACKING RUN DATA RESULTS

Catalyst: 5% Ni + 2.5% As on high alumina silica-alumina
Conditions: 1000 p.s.i.g.; 0.25 V_o/hr./V_c; H₂/hc.=3000 s.c.f.b.

Period	Hours	Temp. (° F.)	Normalized Weight Balance				Conversion Wt. Percent
			C ₁ -C ₃	C ₄ -C ₅ gas	C ₅ -180° F.	180°-400° F.	
I ¹	4-18	504	4.8	20.2	31.0	43.0	99.0
	112-136	506	4.2	16.8	30.2	41.3	92.5
	208-232	558	1.3	5.8	6.9	29.3	43.4
	328-352	589	0.3	6.9	20.6	41.8	69.5
II ²	452-476	634	1.0	.5	.7	10.2	12.4
	Regenerated catalyst at 850° F., 1 atm.: 14.5 s.c.f. 2% O ₂ in N ₂ , then 18.2 s.c.f. air Catalyst hydrogen treated at 600° F. and 1 atm. with 5.5 s.c.f. H ₂ before going on oil						
III ¹	476-500	500	3.7	16.3	37.2	35.2	92.4
IV ²	528-552	588	2.0	6.2	9.9	40.3	58.4
	672-696	684	3.0	0.5	3.1	16.2	22.8

¹ Hydrodesulfurized LCCO Feed—38.9° API; 20 p.p.m. S; 12 p.p.m. N.

² Raw LCCO Feed—29.2° API; 1.23 wt. % S; 240 p.p.m. N.

which was lower than the level normally found in this type refinery stream, but the aromatic content of the feed was substantial. The feed stock contained about 20 p.p.m. sulfur, 12 p.p.m. nitrogen and had an API gravity of 38.9°. The catalyst was contacted with the feed stock at 1000 p.s.i.g., a liquid hourly space velocity of 0.25 volume of oil per hour per volume of catalyst and a hydrogen to oil ratio of about 3000 s.c.f.b. The catalyst bed temperature was varied during the various periods of the run as shown in the table.

Subsequently, during the second period of the run the feed stock was changed to a raw light catalytic cycle oil having an API gravity of 29.2° and containing 1.23 weight percent sulfur and 240 p.p.m. of nitrogen. The results from this run are shown in the following table.

From the above it is seen that the cycle life of the catalyst employed in the present invention is shortened with a feed stock such as high nitrogen raw light catalytic cycle oil. However, it is apparent that the catalyst is capable of hydrocracking such feed stocks for a significant time.

Following the above-mentioned second period, the flow of the feed and the hydrogen to the reactor was stopped, and the catalyst bed and the reactor were purged with nitrogen at atmospheric pressure while the catalyst bed temperature was raised to 850° F. This purging was continued until the reactor was rid of hydrocarbons and hydrogen. The nitrogen purge was then followed by a burnoff with 2 percent oxygen in nitrogen at 850° F. and atmospheric pressure, whereby carbonaceous deposits on the catalyst were oxidized. Following the dilute oxygen burnoff, the catalyst was contacted with air at 850° F. and atmospheric pressure to complete the oxidation of the deposits on the catalyst. Next, the reactor was purged with nitrogen while the catalyst bed temperature was lowered to about the operating temperature. Finally, the catalyst was contacted with flowing hydrogen at 600° F. and at one atmosphere, prior to resuming operations during the next period of the run.

During the third period of the run, the reactivated catalyst was contacted with the same feed employed dur-

EXAMPLE II

25 grams of 20–48 mesh high alumina silica-alumina cracking catalyst (about 25 weight percent alumina) was impregnated with an ammoniacal solution of nickel acetate tetrahydrate (10 grams) by allowing the catalyst to soak therein for about an hour, followed by drying at 400° F. and calcining for four hours at 1000° F. The nickel-containing composite then was impregnated with a mixture of As₂O₃ (0.8 gram) in 30 percent H₂O₂ and NH₄F (1.5 grams) in water, followed by drying and calcining as described above. The completed catalyst contained approximately 9.4 weight percent nickel, 2.4 weight percent arsenic and 3.0 weight percent fluorine. Prior to contact with the hydrocarbon feed, the catalyst was pretreated with flowing hydrogen for one hour at 750° F. and 1 atmosphere pressure.

A light catalytic cycle oil which had been hydrogen treated over a cobalt molybdena catalyst was employed as the feed stock. The feed stock contained about 3 p.p.m. sulfur, 13 p.p.m. nitrogen and had an API gravity of 31.8 degrees API. Feed inspection (simulated distillation) showed an initial boiling point of 402° F.; 50 percent 538° F.; and 100 percent, 744° F.

The above catalyst was placed in a reactor and contacted with the above-described feed stock at a temperature of 591° F., a pressure of 1,000 p.s.i.g., a weight hourly space velocity of 2.6 and a hydrogen to oil ratio of 7,000 standard cubic feet of hydrogen per barrel of oil.

Liquid product from the reactor was analyzed by gas chromatography using the simulated distillation technique and the tail gas was analyzed by mass spectrometry. The product distribution was as follows.

Product distribution, wt. percent:

C ₁	-----	.1
C-156° F.	-----	41.0
C ₂ -385° F.	-----	92.9
C ₂ -421° F.	-----	94.5

The C₅ iso to normal paraffin ratio was 5.3.

The above-described nickel-arsenic-fluorine on silica-alumina catalyst was found to be about 200–235% more

active than a silica-alumina base catalyst containing 7.2 weight percent Ni, 2.4 weight percent As and 0% F on Si/Al and about 300-400% more active than a silica-alumina base catalyst containing about 5% Ni, 0% As and 0% F on Si/Al.

EXAMPLE III

25 grams of 20-48 mesh high alumina silica-alumina cracking catalyst was impregnated with an ammoniacal solution of nickel acetate tetrahydrate (5 grams), arsenic trioxide (0.8 gram) in H_2O_2 and ammonium fluoride (1.5 grams) in water, followed by drying at 400° F. and calcining for 4 hours at 1000° F. The completed catalyst contained approximately 4.7 weight percent nickel, 2.4 weight percent arsenic and 3.0 weight percent fluorine. Prior to contact with the hydrocarbon feed the catalyst was pretreated in flowing hydrogen for one hour at 750° F. and one atmospheric pressure.

10 grams of the above catalyst was placed in a reactor and contacted with the feed stock as described in Example II at a temperature of 604° F., a pressure of 1000 p.s.i.g., a weight hourly space velocity of 1.3 and a hydrogen to oil ratio of 7000 standard cubic feet of hydrogen per barrel of oil.

Products from the reactor were analyzed as described in Example II. The product distribution was as follows.

Product distribution, wt. percent:

C ₁ -----	4
C ₂ -156° F. -----	54.8
C ₂ -385° F. -----	98.0
C ₂ -421° F. -----	98.2

The C₅ oil to normal paraffin ratio was 7.9.

EXAMPLE IV

The catalyst was prepared in the manner described in Example II except a 5-gram solution of nickel acetate tetrahydrate was employed. The completed catalyst contained approximately 4.7 weight percent nickel, 2.4 weight percent arsenic and 3.0 weight percent fluorine.

10 grams of this catalyst was contacted in a reactor with the feed stock described in Example II at a temperature of 592° F., a pressure of 1000 p.s.i.g., a weight hourly space velocity of 2.6 and a hydrogen oil ratio of 7000 standard cubic feet of hydrogen per barrel of oil.

Products from the reactor were analyzed as described in Example II. The product distribution was as follows:

Product distribution, wt. percent:

C ₁ -----	0
C ₂ -156° F. -----	15
C ₂ -385° F. -----	60.8
C ₂ -421° F. -----	69.3

The C₅ iso to normal paraffin ratio was 7.6.

A fluorine free catalyst was prepared for reference purposes and tested in the same manner as the catalysts of Examples II, III and IV. This catalyst was prepared by impregnating 20-48 mesh high alumina silica-alumina cracking catalyst with an aqueous solution of nickel acetate tetrahydrate, drying at 250° F., pelleting into 1/8" pills and calcining for 6 hours at 1000° F. After calcination a portion was impregnated with triphenylarsine in normal hexane and dried at 250° F. The finished catalyst contained approximately 7.2 weight percent nickel, 2.4 weight percent arsenic and 0 weight percent fluorine. Varying pretreatments were employed prior to contacting the catalyst with oil. In the first case, the catalyst was reduced in flowing hydrogen overnight at 750° F. and one atmosphere pressure, and in the second case the reduced catalyst was calcinated for 4 hours at 1000° F. and then pretreated in flowing hydrogen for one hour at 750° F. and one atmosphere pressure. Each of the above catalysts were subsequently contacted with the feed stock described in Example II at 592° F. to 595° F., 1000 p.s.i.g., a weight hourly space velocity of 1.3 and a hy-

drogen to oil ratio of 7000 standard cubic feet of hydrogen per barrel of oil.

Products were analyzed as described in Example II and the product distribution was as follows:

C ₁	C ₂ -156° F.	C ₂ -385° F.	C ₂ -321° F.
0	28.0	72.2	78.2
0	31.5	82.5	85.8

For the first catalyst the C₅ iso to normal paraffin ratio was 13.9; and for the second, 13.8.

From the foregoing, it is readily seen that the process of the present invention is very suitable for the hydrocracking of a higher boiling hydrocarbon distillate such as light catalytic cycle oil to lower the boiling hydrocarbons. It is also seen that the products of the process predominantly boil within the gasoline boiling range and have very satisfactory octane ratings. It is further apparent that the process provides a readily regenerable catalyst which can be reactivated by a simple technique to restore its catalytic properties.

While the present invention has been described with particular reference to the feed stocks and preferred methods of operation given above, it would be understood that variations in the method of practicing the invention will become apparent to the skilled artisan from the foregoing description. It is to be understood that such variations fall within the spirit and scope of the present invention.

What is claimed is:

1. A process for the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons, which process comprises contacting said higher boiling hydrocarbons under hydrocracking conditions and in the presence of hydrogen-containing gas with a catalyst comprising a metallic hydrogenation component comprising a metal selected from the group consisting of cobalt, nickel, platinum, rhodium and palladium in an amount from about 0.1 to about 30 percent by weight together with an element selected from the group consisting of arsenic, antimony, bismuth and phosphorus, wherein said element is present in an amount from about 0.01 to about 2 atomic weights per atomic weight of said metal, and a porous solid acidic cracking catalyst base.

2. The process of claim 1 wherein said catalyst also contains from about 0.5 to about 6 percent by weight of fluorine.

3. The process of claim 1 wherein said catalyst is arsenided nickel on a silica-alumina cracking catalyst base.

4. The process of claim 1 wherein said catalyst is antimonided nickel on a silica-alumina cracking catalyst base.

5. The process of claim 1 wherein said catalyst is arsenided platinum on a silica-alumina cracking catalyst base.

6. The process of claim 1 wherein said catalyst is antimonided platinum on a silica-alumina cracking catalyst base.

7. The process of claim 1 wherein said hydrocracking conditions include a temperature of about 500° F. to 700° F., a pressure of about 200 to 2000 p.s.i.g., a liquid hourly space velocity between about 0.1 and 10 volumes of oil per hour per volume of catalyst and a hydrogen-to-oil ratio of about 1000 to 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon feed.

8. The process of claim 1 wherein the feedstock is a catalytic cycle oil.

9. The process of claim 1 wherein said catalyst comprises about 0.5 to 10 weight percent nickel and from about 0.01 to 1 atomic weight of arsenic per atomic weight of said nickel supported on silica-alumina cracking catalyst.

10. The process of claim 1 wherein said catalyst comprises from about 0.01 to 1 atomic weight of said element per atomic weight of said metal, from about 0.5 to 6 weight percent fluorine and a silica-alumina cracking base.

11. The process of claim 1 wherein said catalyst comprises about 0.5 to 10 weight percent nickel, from about 0.1 to 0.5 atomic weight of arsenic per atomic weight of nickel, from about 2 to 4 weight percent fluorine and a silica-alumina cracking base.

12. The process of claim 11 wherein said catalyst is prepared by impregnating said silica-alumina base with compounds of nickel, arsenic and fluorine, drying and calcining.

13. A process for the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons, which process comprises contacting said higher boiling hydrocarbons with a catalyst containing about 0.5 to 10 weight percent nickel and from about 0.01 to 1 atomic weight of arsenic per atomic weight of said nickel supported on silica-alumina cracking catalyst, at a temperature of about 500° F. to 700° F., a pressure of about 750 to 1500 p.s.i.g., a liquid hourly space velocity between about 0.2 and 5 volumes of oil per hour per volume of catalyst and in the presence of about 1000 to 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon feed.

14. The process of claim 13 wherein the catalyst further comprises about 2 to 4 weight percent fluorine.

15. A process for the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons, which process comprises contacting said higher boiling hydrocarbons under hydrocracking conditions and in the presence of hydrogen-containing gas with a catalyst comprising a metallic hydrogenation component comprising a metal selected from the group consisting of nickel, platinum, rhodium, cobalt and palladium together with an element selected from the group consisting of arsenic, antimony, bismuth and phosphorus, and a porous solid acidic cracking component, for a time sufficient for the catalytic activity of said catalyst to decline; subsequently, purging said hydrocarbon-contacted catalyst of combustibles, oxidizing accumulated carbonaceous deposits on said catalyst, reducing the metallic oxides resulting from the oxidizing treatment of said catalyst, whereby the catalytic activity of said catalyst is restored to a suitable level; and again contacting said reactivated catalyst with said higher boiling hydrocarbons under hydrocracking conditions and in the presence of said hydrogen-containing gas.

16. A process for the conversion of higher boiling hydrocarbons to lower boiling hydrocarbons, which process comprises contacting said higher boiling hydrocarbons with a catalyst containing about 0.5 to 10 weight percent nickel and from about 0.01 to 1 atomic weight of arsenic per atomic weight of said nickel supported on silica-alumina cracking catalyst at a temperature of about 500° F. to 700° F., a pressure of about 750 to 1500 p.s.i.g., a liquid hourly space velocity between about 0.2 and 5 volumes of oil per hour per volume of catalyst and in the presence of about 2000 to 10,000 standard

cubic feet of hydrogen per barrel of hydrocarbon feed; subsequently, purging said hydrocarbon-contacted catalyst of combustibles, contacting said purged catalyst with an oxygen-containing gas at a temperature between about 750° F. and 1000° F., purging said oxygen-contacted catalyst of oxygen, contacting said oxygen-purged catalyst with hydrogen-containing gas at elevated temperature to reduce the metallic oxides resulting from contact with said oxygen-containing gas; and again contacting said catalyst with said higher boiling hydrocarbons under hydrocracking conditions and in the presence of said hydrogen-containing gas.

17. The process of claim 16 wherein said catalyst further comprises about 2 to 4 weight percent fluorine and wherein after said oxygen contacting step said catalyst is contacted with a substance containing available fluorine.

18. A hydrocarbon conversion catalyst which comprises a metallic hydrogenation component comprising a metal selected from the group consisting of cobalt, nickel, platinum, rhodium and palladium in an amount from about 0.1 to about 30 percent by weight together with an element selected from the group consisting of arsenic, antimony, bismuth and phosphorus present in an amount from about 0.1 to about 2 atomic weights per atomic weight of said metal, a silica-alumina cracking catalyst base and fluorine present in an amount from about 0.5 to about 6 percent by weight.

19. The catalyst of claim 18 wherein said metal is nickel and said element is arsenic.

20. A hydrocarbon conversion catalyst which comprises a metallic hydrogenation component comprising a metal selected from the group consisting of cobalt, nickel, platinum, rhodium and palladium in an amount from about 0.5 to about 10 percent by weight together with an element selected from the group consisting of arsenic, antimony, bismuth and phosphorus present in an amount from about 0.1 to about 0.5 atomic weights per atomic weight of said metal, a silica-alumina cracking catalyst base and fluorine present in an amount from about 2 to about 4 percent by weight.

21. The catalyst of claim 20 wherein said metal is nickel and said element is arsenic.

22. A hydrocarbon conversion catalyst which comprises about 0.5 to 10 weight percent nickel, about 2 to 4 percent by weight arsenic, about 2 to 3 percent by weight fluorine, and a silica-alumina cracking catalyst base.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,206,391

September 14, 1965

Louis C. Gutberlet et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 20, for "ismerization" read -- isomerization --; column 3, line 74, for "phostungstic" read -- phosphotungstic --; column 4, line 70, for "or" read -- of --; column 6, line 18, for "depostis" read -- deposits --; column 7, line 52, for "catalystic" read -- catalytic --; column 8, line 69, for "C-156° F." read -- C₂-156° F. --; column 10, lines 5 to 10, insert the following as a centered heading above the table:

Product distribution, wt. percent

Signed and sealed this 15th day of March 1966.

SEAL)

Testing Officer

RNEST W. SWIDER

Testing Officer

EDWARD J. BRENNER

Commissioner of Patents