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HYDROISOMERIZATION OF OLEFINS TO ISOPARAFFINS

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ABSTRACT OF THE DISCLOSURE

Light aliphatic olefins, admixed with hydrogen, are contacted with a catalytic composite of an active metallic component and a carrier material having an acidity factor greater than about 40 at 400° C. Contacting conditions include a temperature of 350° F. to 900° F. and a pressure of 200 to 1,000 p.s.i.g. The carrier material may be a crystalline alumino-silicate, a porous refractory inorganic oxide, mixtures thereof, and may contain halogen. The process yields a product rich in branched-chain paraffins boiling within the gaseoline boiling range.

RELATED APPLICATIONS

The present application is a continuation-in-part of my copending application, Ser. No. 598,214, filed Dec. 1, 1966, now abandoned, all the teachings of which are incorporated herein by specific reference thereto.

APPLICABILITY OF INVENTION

The invention herein described is directed toward a process for producing isoparaffins boiling within the gasoline boiling range. More specifically, the present invention relates to an improved process which utilizes a dual function catalyst comprising a support, or carrier material, having an acidity factor greater than about 40 at 400° C. and at least one hydrogenation promoter thereon to increase the octane number of the charge stock. It has been found that such a process will increase the octane number and especially the motor octane number of an olefinic hydrocarbon fraction such as that resulting from a catalytic cracking unit.

There are many stocks available in refineries which contain appreciable amounts of olefins, particularly in the C_4 to C_9 carbon number boiling range. Most commonly these streams are obtained from catalytic cracking and thermal cracking operations. These gasoline boiling range olefins have high research octane numbers but relatively low motor octane number ratings. The motor octane number rating of a gasoline is becoming increasingly importion in commercial operations especially in the light of producing lead-free gasolines.

Examination of the research and motor octane ratings, or numbers, of gasoline boiling range olefins and paraffins reveals certain interesting facts. For example, on a leaded basis 1-pentene has a ASTM research octane rating of 96.1 (87.9 clear) whereas its corresponding hydrogenated paraffin (normal pentane) has a research octane number of 84.8 (61.8 clear). On the motor octane number scale these numbers are 82.9 (77.1 clear) and 84.8 (63.2 clear), respectively. In the case of 2-methyl-1-butene the research octane numbers before and after hydrogenation are 103.5 (98.3 clear) and 104.9 (93.0 clear), whereas the corresponding motor octane numbers are 84.2 (81.9 clear) and 107.3 (89.7 clear). For 2-heptene the research octane numbers before and after hydrogenation are 89.5 (73.4 clear) and 41.9 (0 clear), whereas the corresponding motor octane numbers are 78.9 (68.8 clear) and

48.1 (0 clear). With 2,3-dimethyl-1-pentene, the research octane numbers before and after hydrogenation are 102.1 (99.3 clear) and 103.5 (91.1 clear), whereas the motor octane numbers before and after hydrogenation are 86.4 (84.2 clear) and 103.4 (88.5 clear). It is apparent from these examples, that hydrogenation of the light olefin to the corresponding saturated paraffin lowers the clear research octane number in all cases but the direction of this change in the case of the motor octane number is not fixed as, for example, in the case of the 2-heptene, the hydrogenation has decreased the motor octane number whereas, in the case of the 2,3-dimethyl-1-pentene, the hydrogenation has increased the octane number. It becomes clear that the conversion of olefins to isoparaffins will increase the motor octane number markedly. Furthermore, if lead-free gasoline is to be commercially utilized, it is apparent that the composition of the gasoline will have to be predominantly aromatics and isoparaffins.

OBJECTS AND EMBODIMENTS

A principal object of my invention is to produce isoparaffinic hydrocarbons from light aliphatic olefins boiling in the gasoline boiling range. A related object is to improve the motor octane rating of aliphatic olefins by conversion thereof to isoparaffins.

Another object is to provide an isoparaffin producing process utilizing a dual-function catalytic composite of a Group VIII metallic component and a carrier material having an acidity factor greater than about 40.

In one embodiment, the present invention affords a catalytic process for producing isoparaffins, boiling within the gasoline boiling range, from aliphatic olefins, which process comprises reacting said olefins with hydrogen at reaction conditions including a pressure of from about 200 to about 1,000 p.s.i.g. and a temperature within the range of about 350° F. to about 900° F., and in contact with a catalytic composite of at least one metallic component from Groups VI and VIII of the Periodic Table and a carrier material having an acidity factor, at a temperature of 400° C., greater than about 40.

A more limited embodiment encompasses a process for producing isoparaffins, boiling within the gasoline boiling range, from aliphatic olefins, which process comprises contacting said olefins, in admixture with hydrogen, with a catalytic composite of a carrier material having n acidity factor greater than about 40 at 400° C. and at least one metallic component from Group VIII noble metals; said carrier material being further characterized in that it is a porous inorganic oxide matrix having finely divided crystalline aluminosilicate particles dispersed therein, a major proportion of said particles being below about 60 microns in size and the concentration of said crystalline aluminosilicate being from about 0.1% to about 50.0% by weight of said carrier material.

SUMMARY OF INVENTION

Hydrocarbon fractions and/or distillates well-suited as charge stocks, in the process of my invention, are gasoline boiling range (end point of 400° F. or lower) mixtures containing significant quantities of olefins. Preferred charge stocks are those containing more than 50.0% by volume of olefinic hydrocarbons. Specific examples of preferable charge stocks are light catalytically-cracked naphtha, thermally-cracked naphtha, the naphtha product from a vis-breaking operation, pyrolysis naphtha and fluid coker naphthas. In general, it is desirable that the stock contain at least about 5.0% by volume of olefinic hydrocarbons, although feed stocks having above about 20.0% to 25.0% olefins are preferred. Feeds containing from about 50.0% to about 90.0% by volume of olefins are very satisfactory for the process of this invention.

The catalysts for use in the present invention are characterized as being dual-functional catalysts; that is, possessing both acid-acting activity and hydrogenation activity. Among the suitable catalysts are those which have a support, or carrier material, which possess acid activity such as silica-alumina, fluorided alumina, pure crystalline aluminosilicate, crystalline aluminosilicate dispersed in an inorganic oxide matrix, aluminum chloride, BF_3 modified alumina, etc. Especially preferable supports are those either composed entirely of crystalline aluminosilicates or crystalline aluminosilicates dispersed in an organic oxide matrix such as an alumina matrix or a silica or silica metal oxide co-gel matrix. The crystalline aluminosilicate should be prepared in its most active acid form; that is, either in the hydrogen form, or in the polyvalent cation form. The hydrogen form of the crystalline aluminosilicate may be prepared by ion-exchanging the sodium form of the crystalline aluminosilicate (which is the most common form of synthetic crystalline aluminosilicates) with ammonium ions followed by thermal treatment to decompose the ammonium ions, thereby evolving ammonia and leaving the hydrogen form of the crystalline aluminosilicate. The polyvalent form may be prepared by ion-exchange of suitable polyvalent cations such as calcium, magnesium, rare earths, etc. with the sodium form of the crystalline aluminosilicate. Subsequent drying will render the polyvalent crystalline aluminosilicate catalytically active for the process of the present invention. The preferable crystalline aluminosilicates employed in the present invention are those having pore entrances above about 5 Angstroms, and especially faujasite and mordenite. In each case, the synthetic variety of faujasite (especially the higher silica content faujasite, having from about three to about six moles of silica per mole of alumina) and mordenite are preferred. Especially preferred for use as an integral part of the catalyst are the hydrogen forms of faujasite and mordenite. In many instances, it is preferable to disperse this crystalline material in a suitable inorganic oxide matrix. One preferable matrix is alumina either in the bayerite or the boehmite form. Another preferable matrix is a siliceous matrix such as silica, silica-alumina, silica-magnesia, silica-zirconia, silica-alumina-zirconia, etc. The concentration of crystalline aluminosilicate in the matrix is preferably from about 0.1% to about 50.0% by weight of the support.

When a non-crystalline refractory inorganic oxide (sometimes referred to as an "amorphous" material) is utilized as the carrier material, or support, it is generally preferable that the same be siliceous in nature, or be made more "acid-acting" by the incorporation of fluorine and/or chlorine. As hereinafter indicated in a specific example, when a non-crystalline carrier material of silica and alumina is utilized, there appears to be a requirement the aluminum/silicon atomic ratio be in the range of 0.8 to about 2.0. Carriers having a composition in this range possess acidity factors of at least about 90. Non-crystalline alumina-silica material having a composition outside this range are suitable, provided the acidity factor is greater than 40, but do not appear capable of functioning in an acceptable manner for as long a period of time. Of further interest is the observation that crystalline aluminosilicate material can have a lower acidity factor than the non-crystalline material, and will be more capable of effecting the desired reactions.

Suitable catalytically active hydrogenation promoters are the metals of Groups VI and VIII of the Periodic Table and compounds thereof. Particularly preferred metals are chromium, molybdenum, tungsten, cobalt, nickel and the Group VIII noble metals, especially palladium, and platinum. In some instances, it is preferred to incorporate both a Group VI and a Group VIII metal onto the support such as cobalt or nickel and chromium, molybdenum, or tungsten. When noble metals such as platinum and palladium are used, the preferable concentration ranges from about 0.1% to about 1.5% by weight. These catalysts may be further modified by the incorporation of additional catalytic ingredients. For example, a halogen such a fluorine or chlorine can be incorporated to modify the acid activity; the halogen is generally utilized in an amount of from 0.1% to about 8.0% by weight, and usually from 0.1 % to about 5.0%.

An especially preferred catalyst, for use in the process of the present invention, is a composite of a carrier comprising an alumina matrix having from about 2.0% to about 10.0% by weight of mordenite (the hydrogen form) dispersed therein, and from 0.2% to about 1.5% by weight of platinum and 0.1% to about 1.5% by weight of chloride, calculated as the elements. One such catalyst consists essentially of 5.0% by weight of mordenite dispersed in an alumina matrix, with which 0.6% platinum and 0.85% chloride are combined.

Another preferred catalyst comprises substantially pure synthetic faujasite, in the hydrogen form, divalent form, or mixtures, having at least one Group VIII metallic component composited therewith. When non-noble Group VIII metals, such as nickel, are used, concentrations of from about 2.0% to about 15.0% by weight are preferred, whereas, when noble Group VIII metals are employed, concentration ranges of from about 0.2% to about 1.0% by weight are preferred. The state concentrations are computed on the basis of the elemental metal, regardless of the state thereof in the finished catalyst.

Still another suitable catalyst comprises fluorided alumina having at least one Group VIII metal or metal compound deposited thereon. Fluorided alumina is readily prepared by adding hydrofluoric acid to an alumina sol prior to gelation of the sol to produced hydrogel particles. Alternately, the fluorided alumina particles can be formed by mixing an alumina sol with a gelling agent, as hereinafter described in Example I, dropping the mixture into a forming oil to produce hydrogel particles which are subsequently aged, washed, dried and calcined. These resulting alumina particles are contacted with an ammonium fluoride solution and thermally treated to drive off ammonia leaving fluorided alumina particles. The fluoride content is suitably from about 0.1% to about 8.0% by weight of the finished catalyst, and preferably from about 2.0% to about 5.0% by weight. The Group VIII metal is combined with the fluorided alumina (nickel in concentrations of from about 3.0% to 8.0%, or platinum or palladium in concentrations of from about 0.2% to about 1.0% by weight) to produce the finished catalyst.

Operating conditions under which the process of the present invention are carried out will vary widely since these variables are interrelated and also dependent on the particular catalyst employed. Suitable pressures are from about atmospheric up to about 2,000 p.s.i.g., temperatures from about 250° F. to about 1200° F., liquid hourly space velocities of from about 0.1 to about 10.0 and hydrogen to oil mole ratios of from about 0.5 to about 20.0. Preferable operation conditions include pressures of from about 200 to about 1,000 p.s.i.g., temperatures of from about 350° F. to about 900° F., space velocities of from about 0.4 to about 2.5 and hydrogen to oil mole ratios of from about 2.0 to about 10.0.

It should be recognized that the preferable catalyst disclosed herein are dual-function catalysts; that is, they contain a hydrogenation promoting agent and an acid-acting agent. There occurs on the catalyst, competition between the hydrogenation reactions and those reactions which require the acid acting function. If the acid activity is too low relative to the hydrogenation activity, too many normal paraffins will be produced in the normally liquid product, thereby suppressing the octane number of said product (either on the motor or research scale). Therefore, it is of importance that a proper balance be maintained between the hydrogenation activity and the acid activity. To a certain extent process operating variables may be employed to bring about a proper balance between the hydrogenation activity and the acid activity. The preferable variable to control hydrogenation to acidi-

ty balance is pressure, higher pressures being used with low hydrogenation-high acid strength catalysts and lower pressures being used with high hydrogenation-low acid strength catalysts. Temperature is also a significant variable since in many catalyst supports the acidity of the catalyst is a function of the temperature employed. In general, acidity of catalyst supports tend to decrease as temperature increases although in some cases the acidity stays relatively constant over wide temperature ranges.

A preferable, convenient method with which to characterize acidity is an ammonia adsorption technique. Briefly, this method consists of the following steps: A one gram sample of the carrier material is pretreated by outgassing at 600° C. for one-half hour under high vacuum (about 10^{-6} mm. mercury); after outgassing, the sample is contacted with ammonia gas for 10 minutes at the temperature level at which the acidity is to be measured (preferably 400° C.); this sample is then outgassed at high vacuum (about 10^{-6} mm. mercury) for one-half hour; the sample is thereafter cooled to room temperature and the quantity of ammonia remaining on the sample is determined by oxidization with a 2.0% oxygen in helium blend. This is accomplished by passing the blend over the sample and analyzing the effluent gas with a quantitive oxygen analyzer; the temperatures are increased up to 600° C. over a ten minute period and maintained there for an additional fifteen minutes with the effluent gas being continually analyzed for disappearance of oxygen. The oxygen consumed is calculated by the area under the read-out curve on the oxygen analyzer and is taken as an arbitrary measure of acidity. The actual acidity factors referred to herein represent micromoles of oxygen reacted with the sample. The carrier materials utilized in preparing catalysts for use in the present process are characterized by an acidity factor greater than about 40 when measured at 400° C. in accordance with the above-described ammonia adsorption technique. When the non-crystalline alumina-silica composites are intended for use as the carrier material, the acidity factor is preferably at least 90, and the aluminum/silicon atomic ratio is within the range of 0.8 to 2.0. When a catalyst possesses this desired acidity support, then non-noble Group VI and VIII metals in concentrations of from about 0.1% to about 1.5% by weight may be incorporated on the support with the process being operated at pressures of from about 200 to 1,000 p.s.i.g., hydrogen to oil mole ratios of from 2.0 to 10.0 and temperatures of from 350° F. to about 900° F. These conditions in conjunction with the above catalysts constitute the preferred manner for effecting the process of the present invention.

When using catalysts wherein a crystalline aluminosilicate is dispersed in an inorganic oxide gel, it is preferred that the solid crystalline aluminosilicate be added to the inorganic hydrosol, prior to forming the gel, in order to thoroughly disperse the crystalline aluminosilicate. This permits reactions to occur between the crystalline aluminosilicate and the inorganic oxide matrix to give stronger acid properties than that exhibited by either of the components alone. For example, in the preparation of mordenite-in-alumina carrier material, it is preferred to add fine particles of synthetic mordenite to an alumina hydrosol and a solution of hexamethylenetetramine and then drop the resulting mixture into a forming oil to form hydrogel particles having mordenite dispersed therein. Subsequent aging, washing, drying and calcining to produce a catalyst carrier material having enhanced acid-acting properties as compared to a physical mixture of alumina and mordenite.

EXAMPLES

These examples are presented herein for the purpose of further illustrating the process of the present invention, and of indicating various catalytic composites suitable for use in the process. It is not intended that the examples be construed as necessarily limiting the present invention, the scope and spirit of which is defined by the appended claims.

Example I

As hereinbefore set forth, one particularly preferred catalytic composite for use in the process encompassed by my invention makes use of a carrier material of alumina having dispersed therein finely-divided mordenite particles. This carrier material may be prepared by initially digesting high purity aluminum metal (99.99%) in hydrochloric acid to produce a hydrosol having an aluminum to chloride weight ratio of about 1:15, the specific gravity being about 1.3450.

An aqueous solution containing 28.0% by weight of HMT (hexamethylenetetramine), in an amount of 700 cc. is added to 700 cc. of the alumina hydrosol and thoroughly mixed to form a dropping solution. About 10 grams of hydrogen form mordenite, as a finely-divided powder is added to the dropping solution and thoroughly admixed therein. Another portion of the mordenite is analyzed for particle size distribution. The results show that 57.6% by weight of the powder is between 0 and 20 microns in size, 69.5% is between 0 and 40 microns in size and 82.1% is between 0 and 60 microns in size.

The alumina sol, containing the dispersed mordenite, is passed through a vibrating dropping head and dropped in discrete particles into a forming oil maintained at 95° C. The rate of vibration and volumetric flow of dropping solution is set to produce finished spherical particles of about 1/16 of an inch in diameter. The dropped spheres are aged in oil for a period of about 16 hours, separated from the oil and aged in an ammonia solution at 95° C. to about 3 hours. The aged spherical particles are then water washed to remove neutralization salts, and subsequently dried. The particles are thereupon calcined at 600° C. for four hours in dry air to yield a catalyst support having an ABD of between 0.4 and 0.5. A portion of the particles are analyzed for acidity using the ammonia adsorption technique previously described. The results show an acidity factor of 135 at 400° C.

About 350 cc. of the catalyst support is placed in a steam jacketed rotating vessel and 250 cc. of an impregnation solution containing chloroplatinic acid and HCl is added thereto. The impregnation solution contains 131.2 cc. of 10 milligram per milliliter of platinum and 8.4 cc. of concentrated HCl. The vessel is rotated until all the liquid solution is evaporated. The catalyst particles are then oxidized to produce a finished catalyst containing about 0.75% by weight of platinum and about 0.75% by weight of chloride, with about 5.0% by weight of mordenite in the alumina matrix.

Example II

Another catalyst is prepared in a manner similar to that set forth in Example I, except faujasite, having a silica to alumina mole ratio of about 4:5, is employed as the crystalline aluminosilicate instead of the mordenite. The finished catalyst contains about 0.75% platinum, 0.75% chloride and 5.0% faujasite dispersed in the alumina matrix.

Example III

A series of non-crystalline ("amorphous") alumina-silica composites of varying alumina to silica ratios were prepared. All preparations followed the co-precipitation technique (with the exception, obviously, of the substantially pure silica carrier) utilizing a hydrosol of water glass, hydrochloric acid and an aqueous solution of aluminum sulfate, to which ammonium hydroxide was added to bring about the formation of the hydrogel precipitate. Following a series of washing-filtration steps, drying and calcination, the alumina-silica composite was formed into 1/8-inch by 1/8-inch cylindrical pills. In view of the fact that this and other methods of manufacturing alumina-silica are well-known and well-defined in the literature, and since the precise manufacturing technique forms no essential

part of the present invention, in the interest of brevity, the details of any given method of preparation are not presented herein.

Five carriers were prepared having the following silica concentrations: 12.0% by weight, 37.0% by weight, 60.0% by weight, 75.0% by weight and 100.0% by weight. Respectively, therefore, the aluminum/silicone atomic ratios are: 8:7, 2:0, 0:8, 0:4 and zero. All these carriers were subjected to the ammonia adsorption technique hereinabove described; the results indicated the following respective acidity factors at 400° C.: 57, 98, 119, 79 and zero. A graphical correlation of acidity factor vs. aluminum/silicon atomic ratio presents a parabolic-type curve which indicates an apparent requirements of an aluminum/silicon atomic ratio of from about 0.8 to about 2.0.

Example IV

Silica spheres, having a nominal diameter of 1/16-inch, in an amount of about 1.125 pounds, are placed into a dry, pressurized vessel. A solution containing 0.695 pound of water glass, 0.700 pound of sodium aluminate (said sodium aluminate containing 46.0% by weight of alumina and 31.0% by weight of Na_2O), 0.773 pound of sodium hydroxide (98 wt. percent NaOH pellets) and 8.165 pounds of water is added to the vessel. The mixture is aged at room temperature (about 70° F.) and 50 p.s.i.g. for about four hours. The temperature of the mixture is thereafter increased up to about 305° F., and the pressure raised to about 100 p.s.i.g. over a six-hour period. The pressurized vessel is maintained at 305° F. and 100 p.s.ig. for an additional six-hour period. The vessel is then cooled to room temperature and depressured, and the mother liquor is decanted off the solids. Water is added to the vessel and the crystals and water are poured onto a filter. The crystals on the filter are water washed until 10 volumes of water per volume of crystals have passed therethrough. The water washed crystals are reslurried in water to a solids concentration of about 10.0% by weight. This reslurried mixture is pressured through an orifice into a hot chamber at conditions to produce spray dried particles of about 65 microns in average diameter. The spray dried particles are introduced into a pilling machine where they are pilled into 1/8-inch cylinders having from about 5 to about 10 pound crushing strength. These pills are analyzed and shown to be substantially pure faujasite. The pills are converted to the hydrogen form by ion exchange with solutions of ammonium chloride in repeated batch washing steps until there is no further removal of sodium ions from the pills. The ion exchanged pills are heated in an oven to a temperature of about 150° C. The pills are subjected to the ammonia adsorption technique, the results thereof indicating an acidity factor of 70 at 400° C. These hydrogen form pills are impregnated with an aqueous solution of nickel nitrate hexahydrate to incorporate therein about 5.0% by weight of nickel. The impregnated pills are dried and oxidized to produce the finished catalyst.

Example V

A series of fluorided alumina carriers were prepared by the hydrogen fluoride technique. Of the six carriers, five contained varying quantities of fluoride, the sixth being substantially pure alumina. The concentrations of fluoride were as follows: zero, 0.97% by weight, 1.83%, 4.45%, 1.87% and 3.05%. The ammonia adsorption test method indicated the following respective acidity factors at 400° C.: 30.0, 88.5, 116.0, 130, 121 and 165. The hydrogenation component is incorporated into the fluorided aluminas by way of an impregnation technique utilizing sufficient chloroplatinic acid to produce final catalysts containing 0.6% by weight of platinum, computed as the element.

Example VI

Alumina particles are prepared by the technique of Example I with the ommission of mordenite. These particles contain some chloride ion (about 0.12% by weight), but the ammonia adsorption method shows the acidity number to be about 29.7 at 400° C. Platinum in concentrations of about 1.0% by weight is impregnated on the support using a platinum diamino-dinitrite solution.

Example VII

The preceding catalysts are evaluated under an activity test in an appropriate apparatus. About 100 cc. of the catalyst of Example I is loaded into a fixed bed reactor and the reactor and associated equipment pressured to a level of 500 p.s.i.g. with hydrogen. A light naphtha derived from a catalytic cracking operation, having a leaded research octane number of about 94 and a leaded motor octane number of about 80, an end point (Engler distillation) of about 200° F. and an olefin content of about 65% by volume, charged into the reactor containing the fixed bed. A recycle compressor is employed to maintain a hydrogen to oil mole ratio of about 6:0 and the temperatures are maintained at about 400° F. The normally liquid product is analyzed and found to contain less than 10% olefins, a leaded research octane number of about 99 and a leaded motor octane rating of about 94. It is expected that a catalyst not having an acid function which is supplied in the Example I catalyst by the mordenite and the chloride would produce only a saturated product having a significantly lower octane rating.

Example VII

A similar evaluation of the foregoing catalysts is made on a 1-hexane feed stock in a similar apparatus as that of Example VI using the catalyst of Example I. The reactor pressure is maintained at 300 p.s.i.g. and the temperature is maintained at about 600° F. The product shows significant amounts of iso-C_4's, iso-C_5's and highly branched C_6+ with only small amounts of straight chain C_6's. The motor octane number of the product has been significantly increased over that of the 1-hexene feed.

Example IX

Another experiment is performed in the hydroisomerization apparatus using a feed stock containing normal pentene and a small amount (about 2%) of normal pentane, with the catalyst of Example I. The operating conditions are 1,000 p.s.i.g., 610° F., and a hydrogen to oil mole ratio of about 8. Analysis of the total product reveals that the predominant product is isopentane.

The faujasite-alumina composite of Example II indicates results similar to those obtained with the mordenite-alumina composite of Example I. The octane ratings of the three products are, however, from 1.0 to about 1.5 numbers lower. With respect to Example III, the two catalysts having aluminum to silicon atomic ratios of 8:7 and 0:4 result in improved octane ratings, but not to the extent as the composite of Example I.

With the exception of the non-fluorided alumina of Example V and the alumina particles of Example VI, all the catalytic composites yield improved results comparing favorably with the catalyst of Example I.

I claim as my invention:

1. A catalytic process for producing isoparaffins, boiling within the gasoline boiling range, from aliphatic olefins, which process comprises reacting said olefins with hydrogen at reaction conditions including a pressure of from about 200 to about 1,000 p.s.i.g. and a temperature within the range of about 350° F. to about 900° F., and in contact with a catalytic composite of at least one metallic component from Groups VI and VIII of the Periodic Table and a porous inorganic oxide carrier material having an acidity factor, at a temperature of 400° C., greater than about 40 and having finely divided zeolitic crystalline aluminosilicate particles dispersed therein, said catalytic composite having been prepared by mixing said finely divided crystalline aluminosilicate particles with a hydrosol of said inorganic oxide to disperse said particles

in the hydrosol, gelling the resultant dispersion to form said carrier, calcining the carrier and thereafter impregnating the calcined carrier with said metallic component.

2. The process of claim 1 further characterized in that said carrier material is at amorphous silica-alumina composite having an aluminum/silicon atomic ratio of from 0.8 to 2.0.

3. The process of claim 1 further characterized in that said carrier material is fluorided alumina.

4. A process for producing isoparaffins, boiling within the gasoline boiling range, from aliphatic olefins, which process comprises contacting said olefins, in admixture with hydrogen, with a catalytic composite of a carrier material having an acidity factor greater than about 40 at 400° C. and at least one metallic component from Group VIII noble metals; said carrier material being further characterized in that it is a porous inorganic oxide matrix having finely divided zeolitic crystalline aluminosilicate particles dispersed therein, a major proportion of said particles being below about 60 microns in size and the concentration of said crystalline aluminosilicate being from about 0.1% to about 50.0% by weight of said carrier material, said catalytic composite having been prepared by mixing said finely divided crystalline aluminosilicate particles with a hydrosol of said inorganic oxide to disperse said particles in the hydrosol, gelling the resultant dispersion to form said carrier, calcining the carrier and thereafter impregnating the calcined carrier with said metallic component.

5. The process of claim 4 further characterized in that said crystalline aluminosilicate is mordenite.

6. The process of claim 4 further characterized in that said crystalline aluminosilicate is faujasite.

7. The process of claim 4 further characterized in that said carrier material is an alumina matrix having dispersed therein from about 2.0% to about 10.0% by weight of hydrogen form mordenite.

References Cited

UNITED STATES PATENTS

2,478,916	8/1949	Haensel et al.	208—138
3,116,232	12/1963	Nager et al.	208—64
3,140,253	7/1964	Plank et al.	208—120
3,182,097	5/1965	Brennan et al.	260—683.65
3,301,917	1/1967	Wise	260—683.65
3,463,744	8/1969	Mitsche	252—442

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