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ISOMERIZATION OF PARAFFIN HYDROCARBONS

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This invention relates to an improved process for the isomerization of paraffin hydrocarbons. More particularly, the present invention is directed to a process for the production of commercially valuable branched or more highly branched chain paraffin hydrocarbons from normal or only slightly branched chain hydrocarbons containing at least five carbon atoms per molecule. In one of its more specific aspects, the invention is concerned with a process for the isomerization of normal pentane, normal hexane, and normal heptane and with mixtures consisting essentially of these hydrocarbons.

Paraffin isomerization is of significant commercial importance in that it provides a direct method for the production of isoparaffin hydrocarbons from the more available and less valuable normal paraffin hydrocarbons, such as normal pantane, normal hexane, and normal heptane. The isoparaffins which contain at least 5 carbon atoms are useful as motor fuels and as components of anti-knock motor fuel compositions. In addition, isoparaffins, such as isopentane and the isohexanes, are valuable starting materials in the production of tertiary olefins which, in turn, are valuable in the production by polymerization and hydrogenation procedures of highly branched chain paraffin hydrocarbon motor fuels and motor fuel constituents.

The isomerization of paraffins has heretofore been carried out with the use of a number of catalysts, among which the most commonly used is aluminum chloride. Normal butane has been successfully isomerized in the presence of such catalyst. However, the higher paraffins, for example, normal pentane, normal hexane, and normal heptane, have not been well suited for isomerization in the presence of aluminum chloride since, under such conditions, these hydrocarbons crack quite readily to give degradation products rather than isomerization of the feed material. Thus, the ultimate yield of isoparaffins having at least 5 carbon atoms per molecule obtainable by such process has been relatively low.

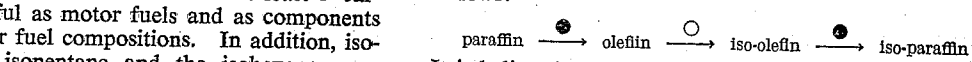
It is an object of this invention to provide an improved process for the catalytic isomerization of paraffin hydrocarbons. Another object is to provide a process for the isomerization of paraffin hydrocarbons containing at least 5 carbon atoms per molecule wherein a high yield of isomerized product with accompanying low yield of cracked products is achieved. A further object is to provide an improved process for the isomerization of normal pentane, normal hexane, normal heptane, and mixtures consisting essentially of these hydrocarbons.

The above and other objects which will be apparent to those skilled in the art are realized by the process of this invention wherein the isomerization of paraffin hydrocarbons is effected in the presence of two chemically distinct catalytic substances which, although not chemically combined, are simultaneously present as mechanical mixtures in the reaction zone and thereby produce a new catalytic activity, different and beyond that obtainable from the simple addition of separate reaction on the two components. It has been discovered, in accordance with the present invention, that a particular mechanical mixture of two types of particles, one containing platinum deposited on alumina and one consisting of a silica-alumina cracking component possesses unusual activity in the isomerization of paraffin hydrocarbons, although this reaction proceeds to a negligible extent on either of these components alone.

It has previously been found, as described in copending application Serial No. 442,975, filed July 13, 1954, of which the present application is a continuation-in-part, that isomerization of paraffin hydrocarbons may be accomplished in the presence of a catalyst having acid and platinum activities residing on separate particles.

In accordance with the present invention, there is provided an improved isomerization process carried out in the presence of a catalyst consisting essentially of a mechanical mixture of finely divided particles of a porous alumina carrier having deposited thereon a small amount of platinum and finely divided particles of a silica-alumina cracking component, the resultant mechanically mixed catalyst having a dehydrogenation activity (DA) in the approximate range of 20 to 2000 and a cracking activity (CAT–A) in the approximate range of 20 to 50, as hereinafter defined.

Without being limited by any theory, it is believed that the success achieved with the mechanical catalyst mixture employed in the present process is attributable to the conversion reactions involved, tending to proceed by way of olefinic intermediates. Thus, isomerization of a normal paraffin is believed to be accomplished as follows:



It is believed that each reaction step marked by ● takes place on a platinum dehydrogenation center, while each step marked by ○ takes place on a silica-alumina acid cracking center. In addition, it is postulated that the two components comprising the instant catalyst mixture, i.e., particles of platinum deposited on alumina and particles of silica-alumina cracking component should present sufficient reaction surface and be sufficiently proximate to one another that the olefinic intermediates formed during the reaction proceed to the desired isomerized end product during the life-time of such intermediate.

Thus, in accordance with the present invention, isomerization of paraffin hydrocarbons having 5 or more carbon atoms has been found to be effected in unexpectedly high yield in the presence of a mechanical catalyst mixture of above defined activity characteristics of platinum dispersed on alumina and silica-alumina cracking component when the particle size of the components making up the instant catalyst is fairly small, specifically less than about 100 microns in diameter and preferably less than 10 microns in diameter.

The dehydrogenation activity (DA) index characterizing the catalyst described herein measures the catalytic efficiency of the dehydrogenation component of the catalyst. In platinum-containing catalysts, it represents the catalytic strength of the platinum in the form contained on the carrier. In evaluating dehydrogenation activity, a small amount of catalyst sample, for example, 15 milligrams deposited on a "boat" as 100–200 mesh powder, is introduced into glass reactor tube. Cyclohexane and hydrogen at a pressure of 350 pounds per square inch gauge are passed over the catalyst at a liquid hourly space velocity of 5000, utilizing a hydrogen to hydrocarbon mole ratio of 4:1. The catalyst temperature is maintained at 750° F. The product liquid is analyzed for benzene by mass spectrometer and from its concentration the rate of formation of benzene in units of 10^{-6} moles/sec. per gram catalyst sample is calculated. This

number is designated as the dehydrogenation activity or DA index.

The cracking activity measures the catalytic strength of the acidic, i.e., the silica-alumina component of the catalyst. Cracking activity is expressed herein in terms of the percent by volume of a standard hydrocarbon charge which is cracked under specific conditions in the "CAT-A" test. The method of such test is described in National Petroleum News, 36, page P.R.-537 (August 2, 1944).

The carrier for the platinum metal component of the instant catalyst is inert with respect to isomerization of paraffin hydrocarbons, i.e., it is not, itself, effective in catalytic isomerization operations under the conditions of the process of this invention. A number of platinum-containing catalysts have heretofore been proposed wherein the platinum metal is impregnated on an alumina base. Such base has been known to impart stability to the platinum in subsequent aging, thereby permitting use of the catalyst over an extended period of time without necessitating regeneration. However, inasmuch as the alumina base itself is not acidic, it has heretofore been the practice to combine the alumina with promoting agents, such as halogens, boria, and the like. It is well known that such promoters are not permanent but may be lost upon contact with water vapor which is inherently or accidently contained in the hydrocarbon feed stock.

Utilizing one embodiment of this invention, it is now possible to combine the advantages of employing alumina as a support or carrier for the platinum component without the attendant disadvantages of the prior art catalysts, since in accordance with the present invention the desired acid centers are located on separate particles distinct from those employed as a carrier for the platinum metal component. It is accordingly a preferred embodiment of this invention to employ as the platinum-bearing component a carrier consisting of alumina having impregnated thereon between about 0.05 and 5 percent by weight and more particularly between about 0.1 and about 2 percent by weight of platinum.

It is contemplated that the alumina employed as a support for the platinum may be any porous inert alumina not adversely affected by the temperature conditions of isomerization. The alumina carrier desirably has a surface area greater than about 10 square meters per gram and preferably in excess of 30 square meters per gram and may extend up to 500 square meters per gram or more. The term "surface area" as used herein designates the surface area of the alumina carrier as determined by the adsorption of nitrogen according to the method of Brunnauer et al. Journal American Chemical Society 60, 309 et. seq. (1938).

The alumina carrier may be in the form of a precipitate or a gel. Various forms of alumina, either singly or in combination, such as eta, chi, gamma, theta, delta, or alpha-alumina, may be suitably employed as the alumina carrier. The above nomenclature used in the present specification and claims with reference to alumina phase designation is that generally employed in the United States and described in "The Aluminum Industry: Aluminum and Its Production" by Edwards, Frary and Jeffries, published by McGraw-Hill (1930). The various above-designated phases of alumina, including occurrence in nature, preparation, phase transitions, crystal structure, and physical properties, are described in detail in "Alumina Properties" by A. S. Russell, Aluminum Company of America, Pittsburgh (1953). A preferred embodiment of the invention is the use of inexpensive, readily available activated alumina as a base for the platinum metal. This form of alumina is obtained by the controlled calcination of alpha alumina trihydrate which occurs naturally and which is also the product of the Bayer process. The decomposition sequence of alpha alumina trihydrate, upon heating 1 hour in dry air, is as follows:

$$\text{Alpha Trihydrate} \xrightarrow[260^\circ\text{ C.}]{140^\circ\text{ C.}} \text{Alpha Monohydrate} \xrightarrow[450^\circ\text{ C.}]{280^\circ\text{ C.}} \text{Chi} \xrightarrow[950^\circ\text{ C.}]{500^\circ\text{ C.}}$$

$$\text{Gamma} \xrightarrow[1050^\circ\text{ C.}]{1020^\circ\text{ C.}} \text{Kappa} \xrightarrow[1120^\circ\text{ C.}]{1080^\circ\text{ C.}} \text{Theta} \xrightarrow[1180^\circ\text{ C.}]{1150^\circ\text{ C.}} \text{Alpha}$$

where the upper numbers show the temperature at which the next phase starts to form and the bottom numbers show the temperature at which transformation is complete. Activated alumina contains, as its principal constituents, chi and gamma aluminas, the relative concentration of each depending on the degree of calcination. The density of the alumina carrier employed, i.e., the bulk density thereof, will usually be within the range of .2 to 2.0 grams/cc. and, more particularly, between about .4 and about 1.2 grams/cc. In contrast to the foregoing preferred use of a carrier of inexpensive activated alumina derived from calcination of alpha alumina trihydrate, is the use of the eta form of alumina which is obtained upon calcining beta alumina trihydrate. The latter does not occur in nature and accordingly is necessarily produced by synthetic means such as by treating aluminum chloride solutions with ammonium hydroxide in the cold followed by syneresis at room temperature, by saturating a solution of sodium aluminate with carbon dioxide at room temperature, or by the action of water on finely divided or amalgamated aluminum. All of these methods for preparing beta alumina trihydrate are relatively expensive. Consequently, the manufacture of eta alumina obtained therefrom is likewise expensive. In previously employed alumina base catalysts impregnated with platinum metal having the acidity characteristic contributed by small amounts of halogen incorporated in the catalyst, the eta form of alumina was necessarily employed in order to maintain halogen retentivity. With the use of the present mechanical catalyst mixture, however, necessary acid activity is divorced from the platinum-containing component, permitting a wide choice of alumina carrier for such metal and making possible use of the readily available activated alumina derived from alpha alumina trihydrate. It is accordingly a particularly preferred embodiment of the invention to employ a carrier of such activated alumina.

The platinum may be deposited on the alumina in any suitable manner. One feasible method is to admix particles of alumina with an aqueous solution of a platinum-containing compound, for example, chloroplatinic acid or of the ammonium salt of said acid, of suitable concentration. The impregnated particles are then dried and treated with hydrogen at elevated temperatures to reduce the platinum chloride to platinum metal and to activate the catalyst.

It is contemplated that the silica-alumina cracking component of the present catalyst may be either a naturally occurring clay or a synthetic composite. The latter may be produced by any of the usual methods, well known in the art, employing cogellation or impregnation techniques. Thus, cogels of silica and alumina may be prepared by intimately admixing an acidic solution of an aluminum salt with sodium silicate to yield a silica-alumina hydrosol which sets after lapse of a suitable period of time, to a hydrogel. The resulting hydrogel is thereafter water-washed, base-exchanged to remove zeolitic sodium, dried, preferably in superheated steam and finally calcined at 900° F. to 1400° F. in air. Alternately, a silica-alumina composite may be produced by separately forming a hydrogel or gelatinous precipitate of silica and a hydrogel or gelatinous precipitate of alumina and ball-milling or otherwise intimately admixing the silica and alumina together to yield a resultant silica-alumina composite. In such instances the silica is suitably prepared by mixing an acid solution, for example, an aqueous sulfuric

acid solution, with sodium silicate. If it is desired to prepare silica initially free of alkali metal ions, such may be accomplished by effecting hydrolysis of alkyl silicates, i.e., ethyl silicate. Alumina is readily prepared by the addition of ammonium or alkali metal hydroxide to an aqueous aluminum salt solution, for example, an aluminum salt of a mineral acid, such as aluminum nitrate, aluminum chloride or aluminum sulfate. As another alternate procedure for preparing the silica-alumina composite, a synthetic silica gel or precipitate may be prepared in accordance with one of the foregoing processes and alumina may be deposited thereon by contacting the silica gel or precipitate with an aqueous aluminum salt solution, followed by the addition of a sufficient amount of ammonium hydroxide to effect precipitation of alumina on the silica. The composite of silica and alumina can further be prepared by contacting a preformed silica gel with an aqueous aluminum salt solution, thereafter removing the impregnated silica gel from the solution and heating to a sufficiently elevated temperature to decompose the aluminum salt laid down by impregnation to alumina so that the resulting product is silica impregnated with the requisite amount of alumina. All of the foregoing methods for preparing composites of alumina and silica are well known in the art and are referred to herein merely as exemplary of suitable preparation procedures.

It is also feasible to produce the silica-alumina cracking component in the form of spheroidal particles such as beads following the teachings of Marisic set forth in U.S. 2,384,946, or in the form of uniformly shaped pellets prepared by casting or extrusion methods. The cracking component may also be prepared as a mass which is thereafter broken up into irregularly shaped pieces. In all of the foregoing procedures, the particles or pieces of produced cracking component are ground to finely divided particles having a requisite particle diameter of less than 100 microns, and preferably less than 10 microns. It is also feasible to initially produce the cracking component in the form of finely divided particles of requisite particle size by employing techniques used in the preparation of fluid catalyst particles, for example, by spraying or rapid agitation of a hydrosol to form minute particles of hydrosol that set to particles of hydrogel which, upon drying, yield discrete gel particles having a diameter or less than 100 microns.

The silica-alumina component may also be prepared in accordance with the method of U.S. 2,469,314, in which case the resulting composite will have an average pore diameter of at least 50 A. and preferably between 55 A. and 75 A., a surface area of at least 400 square meters per gram, a particle density of below 0.95 and preferably between 0.71 and 0.89 gram per cubic centimeter and an alumina content of between 18 and 38 percent and preferably between 20 and 35 percent by weight.

In general, it is preferred to employ as the silica-alumina component of the catalyst utilized in the present isomerization process a synthetic silica-alumina composite having a surface area of at least 300 square meters per gram, a particle density not greater than 1.2 grams per cubic centimeter and an alumina content of at least about 8 percent by weight and generally in the approximate range of 10 to 40 percent by weight. The cracking activity (CAT–A) of the silica-alumina cracking component is within the range of 20 to 50 and preferably between 40 and 50. It will thus be seen that utilization of the present mechanical catalyst mixture wherein the platinum component is divorced from the cracking component permits a wide choice of silica-alumina composites. Accordingly, the present invention makes possible the use of a readily available inexpensive composite of silica-alumina as the cracking component and, indeed, it is a preferred embodiment of the invention to employ such a composite.

The catalyst thus is one consisting essentially of a mechanical mixture of finely divided particles of alumina having platinum deposited thereon and finely divided particles of silica-alumina cracking component. This catalyst may be used in the form of a powdered mixture in a fluidized type reactor. Alternatively, the composite powder may be pelleted, cast, molded, or otherwise formed into pieces of desired size and shape, such as rods, spheres, pellets, etc., it being essential, however, that each of said pieces is composed of particles of both components having a particle diameter of less than about 100 microns and preferably less than 10 microns. It has been conventional practice in obtaining hard pellets to initially mix the material undergoing pelleting with a binder, such as stearic acid, and to subsequently remove such binder from the formed pellets by burning. Since the high temperatures necessarily employed to effect substantially complete removal of the binder from the pellet by combustion may adversely affect the platinum metal, it is preferred to prepare the platinum-containing catalyst pellets of this invention by initially admixing alumina carrier particles having a particle diameter preferably less than 10 microns with silica-alumina particles having a particle diameter preferably less than 10 microns and pelleting the resulting composite with a binder of the conventional type, i.e., one which is capable of being subsequently removed from the pelleted product by combustion. The pellets of alumina and silica-alumina so obtained are then heated in an oxygen-containing atmosphere to a temperature sufficient to burn out the binder. The pellets, after cooling, are then brought into contact with a platinum-containing solution, the time of such contact being sufficient to fill the pores of the pelleted composite with impregnating solution. The impregnated pellets are thereafter removed from the solution and permitted to remain under non-drying conditions for a period of time sufficient to allow the platinum from the solution to reach an adsorption equilibrium between the alumina and silica-alumina surfaces. Such time may extend from about 15 minutes to 30 hours, depending on the size of the particles. The pelleted composite is thereafter dried and the deposited platinum compound is reduced to elemental platinum by treating with hydrogen. By following the foregoing procedure, substantially all of the platinum is deposited on the alumina particles of the composite and very little is deposited on the silica-alumina component of the catalyst. The above procedure takes advantage of the relatively high adsorption constant of alumina for the platinum anion and the comparatively low adsorption constant of the silica-alumina component. Thus, it is estimated that, under the above-outlined conditions of impregnation, less than $\frac{1}{100}$ of the platinum deposited is laid down on the silica-alumina particles.

The process of this invention can be carried out in any equipment suitable for catalytic operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the instant isomerization process is adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst wherein the flow of paraffin hydrocarbon feed may be concurrent or countercurrent to the catalyst flow. A fluid type of operation wherein the catalyst is carried in suspension in the hydrocarbon charge is well adapted for use with the instant catalyst since pelleting or otherwise shaping of the catalyst components is thus rendered unnecessary.

The weight fraction of alumina supporting the platinum component may in accordance with the present invention vary widely, thereby affording desirable flexibility in the catalyst composition which may be varied with the specific paraffin hydrocarbon undergoing isomerization and with the particular reaction conditions under which the isomerization is effected. In general, however, the weight fraction of alumina supporting the platinum component is between about .1 and about .9. Likewise, the weight

fraction of the silica-alumina cracking component is between about .1 and about .9.

The particle size of the two components making up the catalyst mixture employed in the present process may be substantially identical or may vary widely. The particle size of each component, however, is generally within the range of 1–100 microns and preferably in the range of 1–10 microns. For affording a means of ready separation of the catalyst components, it is often desirable to employ a mixture wherein the platinum and silica-alumina components have slightly different particle size. Such difference in particle size is particularly desirable when it is desired to separate the catalyst components prior to separate regeneration thereof or for recovery of the platinum constituent after the same has become catalytically spent. As indicated hereinabove, the catalyst mixture may be in the form of discrete particles or the mixture may be in the form of components which have been finely ground, admixed, and pelleted so that each gross particle contains small particles of both components. In the latter case, the mixture may be separated into its components by initially crushing to a particle size comparable to or below the magnitude of the small constituent particles, and thereafter separating the component particles by flotation, air-blowing, sifting, or by any of various other known means for separating physically and/or chemically different materials. The separated silica-alumina and platinum components may then, if desired, be separately regenerated or platinum may be recovered from the spent platinum-containing component.

The conditions under which paraffin isomerization in the presence of hydrogen is effected in accordance with the present process include a temperature between about 600° F. and about 1000° F. and a pressure in the range of about 50 to about 1000 pounds per square inch gauge and preferably between about 100 and 500 pounds per square inch gauge. The liquid hourly space velocity employed, i.e. the liquid volume of hydrocarbon per hour per volume of catalyst is between about 0.5 and about 40 and preferably between about 2 and about 5. In general, the molar ratio of hydrogen to hydrocarbon charge employed is between about 0.5 and about 20 and preferably between about 1 and about 10. All of the aforementioned variables are interrelated. As a practical matter, the temperature of operation is generally fixed as a result of primary choices with respect to the other variables and the desired conversion level.

The charge stock undergoing conversion in accordance with the present process may be a normal pentane, normal hexane, normal heptane or mixtures consisting essentially of these paraffin hydrocarbons.

Catalyst performance is generally measured by "selectivity" and "activity." Selectivity as utilized herein is the ratio of desired products, i.e., isoparaffin to total products (isoparaffin plus cracked products). Activity as utilized herein is the temperature necessary to produce a standard conversion to all products under otherwise fixed standard test conditions.

The following examples will serve to illustrate the process of the invention without limiting the same:

EXAMPLE 1

A platinum on alumina component was prepared by impregnation of Alcoa F–10 alumina, which is an activated alumina derived from calcination of alpha alumina trihydrate and containing chi and gamma aluminas as principal constituents by contacting with an aqueous solution of chloroplatinic acid to yield a composite containing 1.2 weight percent of platinum.

The above material was mixed with a synthetic silica-alumina cogel containing approximately 10 percent by weight of alumina and having a cracking activity as determined by the CAT–A method of 46.

The two components were ball-milled to a particle size of less than 5 microns average particle diameter and thereafter mixed by ball milling for 16 hours in equal weight portions. The resulting mixture was then formed into ⅛" pellets.

The catalyst so obtained was used for isomerizing a charge of n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 884° F. to produce 60% conversion of n-pentane to all products. The yield of isopentane expressed in mols per 100 mols of charge was 49. The selectivity, i.e., the mols of isopentane per 100 mols of charge converted, was 84.

EXAMPLE 2

A platinum on alumina component was prepared by impregnation of Alcoa F–10 alumina with 2.1 weight percent of platinum. The impregnated alumina, after drying and calcination, was subjected to steam treatment at 950° F. for 3 hours. It was then dry ball-milled until its average particle diameter was less than 5 microns.

The silica-alumina cracking component was a synthetic cogel containing approximately 10 percent by weight of alumina and having a cracking activity as determined by the CAT–A method of 46 and a surface area of 430 square meters per gram. The silica-alumina component was also separately dry ball-milled to less than 5-micron size. The above components of platinum on alumina and silica-alumina in finely divided form and in relative parts by weight of 19 and 81, respectively, were then dry ball-milled together for 16 hours. The resulting mixture was then formed into ⅛" pellets.

The catalyst so obtained was used for isomerizing a charge of n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 867° F. to produce 60% conversion of n-pentane to all products. The yields of isopentane expressed in mols per 100 mols of charge was 53. The selectivity expressed as mols of isopentane per 100 mols of charge converted was 89.

EXAMPLE 3

A platinum on alumina component was prepared by impregnation of Alcoa F–10 alumina with chloroplatinic acid, to give 0.54 weight percent of platinum. The platinum-impregnated alumina, after drying and calcination, was subjected to a steam treatment for 3 hours at 950° F.

The silica-alumina component was a commercial cracking catalyst containing approximately 25 percent by weight of alumina and having an average pore diameter of between 55 A. and 75 A., a particle density of between 0.71 and 0.89, and a surface area exceeding 400 square meters per gram.

The two above components were dry ball-milled together, utilizing 12.5 parts by weight of the platinum on alumina component and 87.5 parts by weight of the silica-alumina component, for 17–18 hours to yield a material having an average particle diameter of less than 10 microns and subsequently pelleted to produce the final catalyst.

The resulting catalyst was employed in isomerizing n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 867° F. to produce 60 percent conversion of n-pentane to all products. The yield of isopentane expressed in mols per 100 mols of charge was 54. The selectivity, i.e., the mols of isopentane per 100 mols of charge converted was 90.

EXAMPLE 4

The platinum on alumina and silica-alumina components employed were identical with those of Example 3. These components, however, were mixed in an amount of 25 parts by weight of the platinum on alumina component with 75 parts by weight of the silica-alumina

component. The activity and selectivity obtained in isomerization of n-pentane were the same as in Example 3.

EXAMPLE 5

The platinum on alumina and silica-alumina components employed were identical with those of Example 3. These components, however, were mixed in amount of 50 parts by weight of the platinum on alumina component with 50 parts by weight of the silica-alumina component. The activity and selectivity obtained in isomerization of n-pentane were the same as in Example 3.

The following comparative examples will serve to point up the criticality of employing as a catalyst in the present isomerization process a mechanical mixture of particles of alumina having platinum impregnated thereon and a silica-alumina cracking component. In the following examples such catalyst was not employed, with the result that the high selectivities obtained with the above catalysts were not realized.

EXAMPLE 6

A platinum on alumina component was prepared by impregnation of Alcoa F–10 alumina with chloroplatinic acid, to give 0.5 weight percent of platinum. This component, after drying and calcination, was subjected to treatment with nitrogen and was thereafter treated with a mixture of steam and oxygen.

The acidic component was eta alumina impregnated with aqueous hydrofluoric acid, to give 1.2 weight percent of fluorine.

The above two components were dry ball-milled together in amounts corresponding to 5 parts by weight of platinum on alumina and 95 parts by weight of alumina containing fluorine for 24 hours and subsequently pelleted to produce the final catalyst.

The resulting catalyst was used for isomerizing n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 940° F. to produce 60% conversion of n-pentane to all products.

EXAMPLE 7

The platinum on alumina and the fluorine-activated alumina components were identical with those employed in Example 6. These components, however, were mixed in amounts corresponding to 25 parts by weight of platinum on alumina and 75 parts by weight of alumina containing fluorine.

The catalyst so obtained was used for isomerizing n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 850° F. to produce 60 percent conversion of n-pentane to all products. The yield of isopentane was 48 and the selectivity was 80.

EXAMPLE 8

The platinum on alumina and the fluorine-activated alumina components were identical with those employed in Example 6. These components, however, were mixed in amounts corresponding to 50 parts by weight of platinum on alumina and 50 parts by weight of alumina containing fluorine.

The catalyst so obtained was used for isomerizing n-pentane at a pressure of 500 p.s.i.g., a hydrogen to hydrocarbon ratio of 10, a liquid hourly space velocity of 2, and required a temperature of 832° F. to produce 60 percent conversion of n-pentane to all products. The yield of isopentane was 43 and the selectivity was 72.

EXAMPLE 9

A component of alumina impregnated with 10 percent by weight of molybdena and a silica-alumina component having a surface area of 430 square meters per gram and an alumina content of about 10 percent by weight were each separately dry ball-milled until the average particle diameters were less than 5 microns. The two components were then dry ball-milled together in amounts corresponding to 33 parts by weight of the alumina containing molybdena and 67 parts by weight of the silica-alumina component for 16 hours and subsequently pelleted to produce the final catalyst.

The resulting catalyst was used for isomerizing n-pentane under the reaction conditions specified in previous examples and required a temperature of 904° F. to produce 60 percent conversion of n-pentane to all products. The yield of isopentane was 30 and the selectivity was 52.

EXAMPLE 10

A silica-alumina component similar to that employed in Example 2 was impregnated with chloroplatinic acid to yield a platinum content of 0.5 weight percent.

This catalyst was used for isomerizing n-pentane at conditions set forth in previous examples and required a temperature of 720° F. to produce 60 percent conversion of n-pentane to all products. The yield of isopentane was 4 and the selectivity was 7.

The results obtained in the foregoing examples are shown in Table I below:

Table I

Example	1	2	3	4	5	6	7	8	9	10
Catalyst Components (pts. wt.):										
0.5 Wt. Percent Pt on F–10 Al_2O_3			12.5	25	50					
0.5 Wt. Percent Pt on F–10 Al_2O_3						5	25	50		
1.2 Wt. Percent Pt on F–10 Al_2O_3	50									
2.1 Wt. Percent Pt on F–10 Al_2O_3		19								
10% MoO_3 on Al_2O_3									33	
46 A.I. SiO_2/Al_2O_3 (25% Al_2O_3)			87.5	75	50					
46 A.I. SiO_2/Al_2O_3 (10% Al_2O_3)	50	81							67	
0.5 Wt. Percent Pt on 46 A.I. SiO_2/Al_2O_3 (10% Al_2O_3)–Al_2O_3—F (1.2% F)										100
Wt. Percent Pt on Catalyst	0.6	0.4	0.07	0.15	0.27	0.03	0.13	0.25	3.3 MoO_3	0.5
Conversion Level	60	60	60	60	60	60	60	60	60	60
Temperature (°F.)	884	867	865	865	865	940	850	832	904	720
i-C_5H_{12} yield (mol per 100 mol of charge)	49	53	54	54	54	34	48	43	30	4
Selectivity (mol i-C_5H_{12} per 100 mol converted)	84	89	90	90	90	57	80	72	52	7

It will be seen from the results of Table I that the mechanical catalyst mixture employed in Example 2 definitely outperformed the platinum-impregnated silica-alumina catalyst used in Example 10. Likewise, the catalysts of Examples 1–5, exemplary of those employed in the process of the invention, afforded an unexpected greater selectivity over catalysts wherein the acidic cracking component was alumina activated with fluorine (Examples 6–8), as well as a catalyst comprising a mechanical mixture of particles of alumina impregnated with molybdena and particles of a silica-alumina component (Example 9).

In accordance with the present invention, it has been found that isomerization of paraffin hydrocarbons can be accomplished with an unusually high yield of isomerized product in the presence of a mechanical catalyst mixture. Such technique affords the combination in one catalyst

of a number of features which are not simultaneously attainable with the use of isomerization catalysts heretofore employed. Thus, the present process is effected in the presence of a catalyst comprising a mechanical mixture consisting essentially of alumina having deposited thereon between about 0.05 and about 5 percent by weight of platinum and a silica-alumina cracking component, the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 20 and about 2000, and preferably between about 50 and about 1200, and an acidic cracking activity of between about 20 and about 50, and preferably between about 40 and about 50. The catalyst employed in the present process accordingly allows the combination of optimum dehydrogenation activity attainable by platinum impregnated on an alumina support but not on a siliceous support with the high acidity which, in itself, is permanent and attainable only on siliceous materials such as a silica-alumina cracking component.

It is accordingly to be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in a diameter of: (1) an alumina carrier having deposited thereon between about 0.05 and about 5 percent by weight of platinum and (2) a silica-alumina cracking component having a cracking activity as determined by the CAT–A method of between about 20 and about 50, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 20 and about 2000, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

2. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 2 and about 5 in the presence of hydrogen under a pressure between about 100 and about 500 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 1 and about 10 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 10 microns in diameter of: (1) an alumina carrier having deposited thereon between about 0.05 and about 5 percent by weight of platinum and (2) a silica-alumina cracking component containing at least 8 percent by weight of alumina and having a cracking activity as determined by the CAT–A method of between about 20 and about 50, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 20 and about 2000, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

3. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of: (1) an alumina carrier having deposited thereon between about 0.05 and about 5 percent by weight of platinum and (2) a synthetic silica-alumina component having a cracking activity as determined by the CAT–A method of between about 20 and about 50, an average pore diameter of at least 50 A., a surface area of at least 300 square meters per gram, a particle density not greater than 1.2 grams per cubic centimeter, and an alumina content in the range of 10 to 40 percent by weight, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 50 and about 1200, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

4. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 10 microns in diameter of: (1) porous activated alumina derived from alpha alumina trihydrate having deposited thereon between about 0.1 and about 2 percent by weight of platinum and (2) a silica-alumina cracking component having a cracking activity as determined by the CAT–A method of between about 20 and about 50, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 20 and about 2000, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

5. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a me-

chanical mixture of particles of less than about 100 microns in diameter of: (1) an alumina carrier having deposited thereon between about 0.05 and about 5 percent by weight of platinum and (2) a synthetic silica-alumina component characterized by a cracking activity as determined by the CAT–A method of between about 20 and about 50, an average pore diameter of between about 55 A. and 75 A., a surface area of at least 400 square meters per gram, a particle density between 0.71 and 0.89 gram per cubic centimeter, and an alumina content of between about 20 and about 35 percent by weight, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 20 and about 2000, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

6. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 10 microns in diameter of: (1) porous activated alumina derived from alpha alumina trihydrate having deposited thereon between about 0.1 and about 2 percent by weight of platinum and (2) a synthetic silica-alumina component having a cracking activity as determined by the CAT–A method of between about 20 and about 50, an average pore diameter of at least 50 A., a surface area of at least 300 square meters per gram, a particle density not greater than 1.2 grams per cubic centimeter, and an alumina content in the range of 10 to 40 percent by weight, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 50 and about 1200, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

7. A process for isomerization of a paraffin hydrocarbon selected from the group consisting of normal pentane, normal hexane, normal heptane, and mixtures of said hydrocarbons, which comprises contacting the same at a temperature between about 600° F. and about 1000° F. at a liquid hourly space velocity between about 0.5 and about 40 in the presence of hydrogen under a pressure between about 50 and about 1000 p.s.i.g. and a molar ratio of hydrogen to hydrocarbon between about 0.5 and about 20 with a catalyst consisting essentially of a mechanical mixture of particles of less than about 100 microns in diameter of: (1) porous activated alumina derived from alpha alumina trihydrate having deposited thereon between about 0.1 and about 2 percent by weight of platinum and (2) a synthetic silica-alumina component characterized by a cracking activity as determined by the CAT–A method of between about 40 and about 50, an average pore diameter of between about 55 A. and 75 A., a surface area of at least 400 square meters per gram, a particle density between 0.71 and 0.89 gram per cubic centimeter, and an alumina content of between about 20 and about 35 percent by weight, the relative weight fractions of the two components being between about 0.1 and about 0.9 and the relationship between said components being such that the resultant mixture is characterized by a dehydrogenation activity of between about 50 and about 1200, where dehydrogenation activity represents the rate of formation of benzene in units of 10^{-6} mols/second per gram of catalyst upon passage of cyclohexane over the catalyst at a temperature of 750° F. and a liquid hourly space velocity of 5000, employing a pressure of 350 p.s.i.g. and hydrogen in a molar ratio of hydrogen to hydrocarbon of 4:1.

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