

UNITED STATES PATENT OFFICE

2,327,593

CATALYTIC ISOMERIZATION OF SATURATED HYDROCARBONS

Martin de Simó, Piedmont, and Frank Matthew McMillan, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application January 21, 1941,
Serial No. 375,260

9 Claims. (Cl. 260—683.5)

The present invention relates to a process for the catalytic isomerization of hydrocarbons. More particularly, the invention relates to the catalytic isomerization of saturated hydrocarbons having from four to about nine carbon atoms. Particular aspects of the invention are the catalytic conversion of normal butane and normal pentane to isobutane and isopentane, respectively, and the conversion of methyl cyclopentane and dimethyl cyclopentane to cyclohexane and methyl cyclohexane, respectively.

The normal paraffin hydrocarbons may be obtained in a relatively pure state in large quantities from petroleum and natural gas. These hydrocarbons are chemically quite unreactive and have poor ignition characteristics. Their corresponding branched chain isomers, on the other hand, are chemically much more reactive and have excellent ignition characteristics but occur naturally only to very limited extents. The branched chain isomers may be readily alkylated with olefines, for example, to produce saturated hydrocarbons which are especially desired for premium and aviation gasoline, and they may be readily dehydrogenated to the respective tertiary olefines which, in turn, are excellent starting materials for the synthesis of a wide variety of useful and valuable products. In view of the abundance of these normal hydrocarbons and the ever increasing demand for their branched chain isomers, a commercially practical process for the conversion of the normal isomers to their branched chain isomers is in demand.

An object of the invention is to provide an improved, practical and economical process for the catalytic isomerization of saturated hydrocarbon to their more highly branched isomers. A particular object is to provide a more advantageous process whereby normal butane and normal pentane may be converted with improved yields and more practical catalyst life to isobutane and isopentane, respectively. Another particular object is to provide an improved method for the isomerization of saturated cycloparaffins such as cyclohexane, methyl cyclohexane, methyl cyclopentane and dimethyl cyclopentane.

Another particular object of the invention is to provide a process whereby lower boiling saturated distillates of the nature of gasoline may be isomerized efficiently and more advantageously to increase their ignition properties. Other objects of the invention will be apparent from the following description of the process.

In its more general aspect the process of the invention comprises isomerizing saturated hydro-

carbons or mixture of saturated hydrocarbons by treating them under isomerizing conditions with improved catalysts.

While the process is generally applicable to the isomerization of saturated hydrocarbons, it is especially advantageous for the isomerization of normal butane, normal pentane, methyl cyclopentane and dimethyl cyclopentane. These hydrocarbons may be obtained in large quantities as individual compounds in a relatively pure state. The hydrocarbon treated need not necessarily be a pure individual hydrocarbon, however, but may be a mixture of one or more hydrocarbons. Thus, the invention provides a practical process for converting the normal butane and normal pentane contents of commercial hydrocarbon mixtures such as are obtained from natural gas, petroleum distillates, cracked distillates, etc. to the more valuable branched chain isomers. Especially suitable mixtures of hydrocarbons are the so-called butane-butylene fractions and pentane-amylenes fractions from which unsaturated hydrocarbons have been substantially removed. Treatment of such mixtures, such as obtained for instance as a by-product in the sulfuric acid alkylation of isoparaffins, results in very materially increasing their content of branched chain isomers and converting them to suitable raw materials for reuse in the alkylation process. Technical butane and pentane fractions, such as those containing from 70% to 90% of the normal isomer and from 2% to 30% of the branched chain isomer, may be conveniently treated in accordance with the process of the invention and their content of branched chain isomers materially increased without loss due to decomposition and side reactions, and while realizing a maximum active life of the catalyst employed. Other mixtures of saturated hydrocarbons, such as those of straight run gasoline, casinghead gasoline, etc. containing appreciable quantities of normal butane, normal pentane, cyclohexane, methyl cyclohexane or other lower boiling non-branched saturated hydrocarbons, may be advantageously treated to produce products which are suitable for alkylation, dehydrogenation and/or have superior ignition characteristics.

The hydrocarbon or mixture of hydrocarbons treated is preferably substantially free of materials which are polymerized by aluminum chloride under the reaction conditions. According to the preferred embodiment of the invention, any olefines, diolefines or other detrimental impurities in the hydrocarbon or hydrocarbon mixture to be treated are removed prior to the isomeriza-

tion by a suitable treatment, such as with a mineral acid, hydrogenation or with a portion of spent catalyst from the process.

The isomerization of these various saturated hydrocarbons is effected, according to the process of the invention, with the aid of certain solid promoted aluminum halide catalysts found to be particularly adapted for the purpose. Thus, the isomerization is effected by contacting the saturated hydrocarbon under isomerizing conditions with isomerization catalysts comprising an anhydrous aluminum halide promoted by an alumina.

It has been found that alumina has the peculiar property of promoting the isomerizing activity and selectivity of aluminum halides. The effect of the alumina when in combination with an anhydrous aluminum halide is unique, very pronounced, and not approached by any of the many other carrier and supporting materials which we have tried. The promoting action to which we refer is, however, not manifest to an equal degree with all of the many forms of alumina, but is particularly pronounced with aluminas of the specific type more fully described below.

The type of alumina which we have found to produce exceptionally desirable isomerization catalysts when combined with anhydrous aluminum halide usually consists largely of α alumina monohydrate and γ alumina in various proportions and is characterized by its highly active adsorptive properties. A particular example of this type of alumina is the "activated alumina of commerce."

The "activated alumina of commerce" is a well-known and readily available adsorptive alumina widely used for the adsorption of gases and vapors from gaseous mixtures. It is a specially prepared, hard, stony, crystalline, nonfriable, highly adsorptive, partially hydrated form of aluminum trioxide discovered about ten years ago and designated "activated alumina" because of its active adsorptive properties. Thus, when contacted with moist gases such as air it removes water vapor with 100% efficiency until it has taken up between about 10% and 15% of its dry weight. Beyond this point it continues to adsorb at decreasing efficiencies until it contains 20% to 25% adsorbed water. It is a special and distinct type of alumina and should not be confused with various aluminas which have been made active catalytically and are thus said to have been "activated."

The "activated alumina of commerce" is at present produced from the hard crystalline scale which forms in the precipitation tanks and discharge pipes in the Fickes-Sherwin modification of the Bayer process. In this process sodium alumina liquors containing particles of hydrates of alumina in suspension are agitated in large tanks with the result that the sodium aluminate is decomposed and the aluminum precipitated as a hydrated alumina. During the process, which is cyclic and continuous, deposits of a particularly hard form of a hydrated alumina form on the tank walls. These deposits are removed from time to time with pneumatic drills, broken up into pieces of the desired size and partially dehydrated by heating at a temperature between about 300° C. and 800° C., preferably in a current of inert gas or in vacuo. The preparation of this material is more fully described and claimed in U. S. Patent Nos. 1,868,869 and 2,015,593.

While the above-described commercial product known and sold under the name "activated alumina," is particularly suitable, it is, of course, understood that the alumina employed in the preparation of the catalysts used in the process of the present invention is not restricted to this particular product and that any partially hydrated alumina of this type having the characteristics of the "activated alumina of commerce" is applicable regardless of its method of preparation. Thus, for example, a suitable material having nearly the same characteristics as the "activated alumina of commerce" may be prepared by very slow precipitation of aluminum trihydrate from an aqueous solution of sodium aluminate by passing therethrough a very slow stream of gaseous carbon dioxide and, subsequently, carefully drying and heating the crystalline precipitate in air at about 600° C. or by the method described in German Patent No. 405,238. A suitable material may also be prepared from hydrargillite by acid washing and careful heating. Hydrargillite is a crustaceous or stalactitic crystalline form of hydrated alumina which occurs in small quantities as grains, nodules and irregular pockets in limestone and dolomite. A suitable material may also be prepared by treating aluminum amalgam under water and calcining the resulting fibrous precipitate. The term, "activated alumina," as used hereinafter and in the claims, embraces all such partially hydrated aluminas possessing the physical structure and surface characteristics of the above-described products. The term "activated alumina of commerce," refers to that material produced under U. S. Patents 1,868,869 and/or 2,015,593.

"Activated alumina" differs from other forms of alumina commonly employed as catalyst carriers in several respects. The "activated alumina of commerce," for instance, is a hard crystalline material and in this respect is quite distinct from the common alumina gels prepared by precipitating aluminum hydroxide and calcining in the usual manner. Furthermore, it is totally different in character and properties from bauxite and diaspore. A characteristic property of "activated alumina" which is not usually possessed by other forms of alumina is the ability to catalyze certain dehydrogenation reactions. "Activated alumina" has recently been found to be an excellent catalyst *per se* for the dehydrogenation of hydrocarbons at temperatures of about 600° C. Other aluminas, such as those produced from gels by the usual methods, on the other hand, are almost entirely inactive. "Activated alumina" is not only quite different from the more common aluminas for the present purpose, but also from other common carriers and supporting materials. Thus, such materials as pumice, porcelain chips, majolica chips, silica gel, activated charcoal, diatomaceous earth, pipe clay, and the like, when combined with aluminum halides do not yield catalysts having comparable promoted and selective activity for hydrocarbon isomerizations.

The superiority of the present catalysts comprising anhydrous aluminum halides in combination with "activated alumina" is due largely to the particular structure of the surface of this form of alumina and is not simply due to the increased surface area. Thus, although silica gel has an exceedingly large "inner surface" (2.5×10^8 cm.²/gm.) and possesses a very large adsorptive capacity, the catalysts prepared with this material are much inferior. This is clearly shown in Example V below.

Although any substantially anhydrous aluminum halide may be employed, aluminum chloride is by far the most practical and preferred. Any substantially anhydrous aluminum chloride, such as the powdered commercial product, is suitable.

The anhydrous aluminum halides may be combined with the "activated alumina," according to the present invention in any of the conventional ways. Thus, the "activated alumina" may be finely ground, intimately mixed with the anhydrous powdered aluminum halide, and the resulting mixture pilled, either with or without a binder or other material. The "activated alumina" may also, if desired, be employed in the form of granules or pieces of the desired size and impregnated by mixing with finely powdered aluminum halide or by soaking in a non-aqueous solution of the anhydrous aluminum halide.

While the anhydrous aluminum halide may be combined with the "activated alumina" in these conventional ways, the combination may also be effected in still other ways. Thus, the "activated alumina," in the form of a coarse powder or pieces up to about one inch in diameter, may be placed in a suitable container and allowed to adsorb vapors of the anhydrous aluminum halide. A suitable catalyst may also be prepared by heating a mixture of "activated alumina" and an aluminum halide at a temperature somewhat above the melting point of the aluminum halide, cooling and crushing the resulting cake. Also, the "activated alumina" in the form of granules or pieces of the desired size may be dipped into molten aluminum halide. The catalysts prepared by these "hot methods" show exceptionally high activity.

The amount of aluminum halide which is combined with the "activated alumina" may vary within wide limits depending upon the method of preparation, the degree of subdivision of the "activated alumina," etc. By pilling or by fusing, active catalysts may be prepared containing over 90% aluminum chloride. On the other hand, by allowing the "activated alumina" to adsorb vapors of aluminum chloride, catalysts may be prepared which contain as little as 5% aluminum chloride. Catalysts prepared by dipping pieces of "activated alumina" ranging from about $\frac{1}{8}$ inch to 1 inch in diameter into molten aluminum chloride, usually contain from about 15% to about 40% aluminum chloride, depending upon the temperature employed, the viscosity of the molten aluminum chloride, the time allowed for impregnation, the size of the particles, etc. Generally speaking, catalysts comprising a minor amount (10-40%) of the aluminum halide and a major amount of alumina are the most active. Catalysts of the above type are described and claimed in our copending application, Serial No. 292,295, filed August 28, 1939, which matured into Patent No. 2,277,512 on March 24, 1942, of which application the present application is a continuation-in-part.

The isomerization, according to the present invention, may be executed in either the vapor phase, liquid phase or mixed phase. Treatment of the lower boiling hydrocarbons, such as normal butane, is preferably, but not necessarily, executed in the vapor phase. Higher boiling hydrocarbons, on the other hand, are usually more preferably isomerized in the liquid or mixed phase. In operation in the vapor phase the catalyst is preferably suspended as a fixed bed in a suitable reactor such as a tubular reactor or a catalytic case provided with means of establish-

ing and maintaining the desired temperature, and the material to be isomerized is passed in the vapor phase at a suitable space velocity there-through. In operation in the liquid phase the catalyst may be conveniently suspended as a fixed bed in an elongated tower through which the liquid hydrocarbon to be isomerized is percolated.

In order to realize the full activity of the catalyst it is most desirable to execute the isomerization in the presence of a hydrogen halide. The desired hydrogen halide may be added directly to the reaction zone of the feed or may be produced in the reaction zone by the addition of a small quantity of a substance which will react or decompose under the reaction conditions to liberate the desired hydrogen halide. Suitable materials of this latter category are, for example, water, alcohols, alkyl halides, etc. The amount of hydrogen halide preferably employed depends somewhat upon the particular circumstances. When executing the isomerization in the vapor phase a small amount of hydrogen halide, for example, 0.1% to 3%, may be added to the feed and removed from the product by a suitable washing treatment. It is preferable, however, when it is economically feasible, to recover the hydrogen halide from the product, for example, by fractional distillation, and to recycle the same through the reaction zone. In this way much higher concentrations of hydrogen halide, for example, 3% to 40%, may be economically employed.

The isomerization process is usually executed at atmospheric pressure or somewhat elevated pressures, for example, 3 to 50 atmospheres. The prevailing pressure will depend somewhat upon the treating temperature but may also be influenced by the deliberate addition of non-condensable gases, such in particular as the hydrogen halide promoter, hydrogen, lower boiling saturated hydrocarbons, etc. In general, the isomerization is effected at moderately elevated temperatures such, for example, as from about 50° C. to about 150° C. Lower or higher temperatures such, for example, as from room temperature, up to about 300° C. may, however, be employed, if desired. Since, however, the object of the process is to isomerize saturated hydrocarbons or to improve the ignition characteristics of saturated hydrocarbon fractions through isomerization, and since side reactions considerably decrease the efficiency and shorten the life of the catalyst, the temperatures or other conditions are not allowed to become so severe as to cause substantial degradation or other side reactions to take place.

The isomerization reaction is, in general, mildly exothermic. When employing catalytic reactors of comparatively large cross section such as can be employed with the present catalysts, and particularly when the reaction temperature is adjusted not far below that at which appreciable side reactions begin, localized zones of higher temperature may be caused by the exothermic heat of reaction. This condition may be avoided by supplying the fresh feed at a plurality of points along the length of the catalyst bed.

EXAMPLE I

A catalyst containing 25% anhydrous aluminum chloride, 10% "activated alumina" and 65% pumice was prepared by applying a mixture of anhydrous aluminum chloride powder and 80 mesh "activated alumina" to 8 to 10 mesh pumice. Normal butane vapor was passed at the rate

of 3400 cc. per hour along with 280 cc. per hour of hydrogen chloride at atmospheric pressure and a temperature of 135° C. to 140° C. over 240 cc. of this catalyst.

The conversion of normal butane to isobutane was 46.2% and the yield of isobutane (based on the normal butane reacting) was 90%. While this particular catalyst is not especially advantageous due to the poor bond between the catalyst and the pumice, it illustrates the effect of the "activated alumina." By applying an equivalent amount of aluminum chloride directly to the pumice without the "activated alumina" the conversion, under these conditions, is much lower (less than 20%).

EXAMPLE II

Two parts by weight of powdered anhydrous aluminum chloride were mixed with one part by weight of 150 to 200 mesh "activated alumina." The mixture was placed in a pressure vessel, subject to 40 lbs./in. of nitrogen pressure, and heated to about 210° C. The heating was discontinued and the pressure released while cooling whereupon the molten mass expanded and froze to a hard, porous cake. The cake was removed and broken up into pieces of the desired size in a dry atmosphere.

Normal butane was passed over this catalyst with a small amount of hydrogen chloride at a temperature of 135° C. and at a contact time of about 1.75 minutes. The product was found to contain 52.7% isobutane.

When normal butane containing 2 mol percent hydrogen chloride was passed over this catalyst at a temperature of only 100° C., at a space velocity of 4.6 mol/liter/hr. and at a pressure of 11 atmospheres, the conversions of normal to isobutane was 54% and the yield (based on the butane reacted) was 96%.

EXAMPLE III

A catalyst was prepared as described in Example II. Normal butane was isomerized with the aid of this catalyst under the following conditions:

Temperature 100° C.
Pressure 150 lbs./in.²
Space velocity 5.4 mol/liter/hr.
Hydrogen chloride percent 2 mol per cent

The isomerization was continued for a total of 318 hours. Although the per cent conversion fluctuated somewhat, it did not fall below 40% at any time and averaged 46% for the entire run. Since the average conversion of 46% was still prevailing at the end of 318 hours of continuous operation and there was no indication that the catalyst was near exhaustion, the catalyst consumption in this process is very low (3% maximum) when using the catalyst. The catalyst, after 318 hours of operation, was still active, unchanged in appearance (except for a small amount of a tarry deposit near the butane inlet) and still contained at least 85% of the original aluminum chloride.

EXAMPLE IV

"Activated alumina" (6 to 8 mesh) was soaked in molten anhydrous alumina chloride for 2 hours at 225° C. under pressure and then drained for 15 minutes under pressure. The catalyst contained 30% aluminum chloride.

Normal butane was isomerized with the aid of this catalyst under the following conditions:

Temperature 100° C.
Pressure 11 atmospheres
Space velocity 6 mol/liter/hr.
Hydrogen chloride percent 2 per cent

During 126 hours of continuous operation the average isobutane content of the product was 60%. Furthermore, in proportion to the amount of isomerization obtained, the amount of the side reaction products normally present was unusually small.

EXAMPLE V

The remarkable efficiency of the present catalyst for paraffin isomerization is clearly apparent when the results obtained therewith are compared with the results obtained with catalysts prepared in the same way with various common carrier materials and employed under the same conditions. Such experimental results are tabulated in the following table. The catalysts were all made and applied for the isomerization of normal butane under the conditions shown in Example IV.

Table I

Carrier material employed	AlCl ₃	Per cent isobutane in product	
		After	Per cent isobutane
	Per cent	Hrs.	
"Activated Alumina".....	30	2	66
Do.....	30	22	65
Do.....	30	162	48
Do.....	30	270	40
Pumice.....	40	2	9
Do.....	40	27	7
Silica gel.....	23	4	4
Activated charcoal.....	46	13	27
Sil-O-Cel (a diatomaceous earth).....	33	13	43
Bauxite.....	39	5	25
Majolica chips.....	11	4	19

EXAMPLE VI

A catalyst prepared as described in Example IV and containing 25.7% aluminum chloride was used for the isomerization of normal butane to isobutane under the following conditions:

Temperature..... 103-110° C.
Pressure 12 atmospheres
Amount of catalyst..... 6.1 kgs.=5.7 liter
Amount of Hydrogen chloride in feed..... 2.3 mol per cent
Feed rate in kgs. N-butane/liter catalyst/hr 0.32

In 553 hours of continuous operation a total of 520 kgs. of isobutane or 138 kgs. of isobutane per pound of aluminum chloride was produced (average conversion of 47%). The catalyst at the end of 553 hours of operation was substantially unchanged in appearance and still quite active. In this experiment a liter of "activated alumina" was placed in the line of flow just beyond the catalyst. This "activated alumina" adsorbed substantially all of the aluminum chloride vapors from the exit gas; consequently, when the experiment was stopped at the end of 553 hours of continuous operation, substantially all of the original aluminum chloride was found to have remained in the reaction chamber.

EXAMPLE VII

"Activated alumina" in the form of pieces of 6 to 8 mesh was impregnated at 220° C. and under

pressure by means of vapors of anhydrous aluminum chloride, to substantial saturation.

When this catalyst was used in the isomerization of normal butane under conditions shown in Example IV, the isobutane content of the product after four hours of operation was 65% and was still 44% after 361 hours of continuous operation.

EXAMPLE VIII

"Activated alumina" in the form of pieces of 6 to 8 mesh was heated to 220° C. to 250° C. in a suitable container while passing vapors of anhydrous aluminum chloride therethrough at atmospheric pressure. The impregnated "activated alumina" contained 15% aluminum chloride.

When this catalyst was used in the isomerization of normal butane under the conditions shown in Example IV, the isobutane content in the product was 66% after four hours, 50% after 119 hours and 44% after 181 hours of continuous use.

The conversions of normal butane to isobutane obtained by the present process, as shown in the above examples, are exceptionally high and, in fact, very near to the maximum conversion possible at these temperatures. Thus, substantially the same product is obtained when starting with either normal butane or isobutane. This is illustrated in the following example:

EXAMPLE IX

Normal butane and isobutane were each passed separately over "activated alumina" catalysts containing 30% aluminum chloride under the conditions shown in Example IV. The results were as follows:

Product	Starting with N-butane	Starting with isobutane
Mol per cent isobutane.....	65. (3)	65. (0)
Mol per cent N-butane.....	26. (1)	25. (8)
Ratio isobutane N-butane.....	2.5 (0)	25. (2)

The catalysts, as can be seen from the examples, not only possess outstanding isomerizing activity but maintain their activity for long periods of time. When, after a long period of use, the catalytic activity of the catalyst finally becomes too low for practical use, the "activated alumina" which is the more costly ingredient may be recovered and reused, or in some cases the catalyst may be regenerated. Thus, for example, the degenerated catalyst may be treated with a suitable solvent to remove the aluminum halide and impurities. The recovered "activated alumina" may then be recombined with fresh aluminum halide.

The above examples illustrate the excellent results obtainable in the vapor phase isomerization of butane. It is to be particularly pointed out, however, that this isomerization is one of the most difficult to effect and that although isomerization in the vapor phase and the isomerization of butane represent preferred embodiments of the invention, the various other saturated hydrocarbons mentioned above may also be advantageously isomerized according to the process in the vapor, mixed and liquid phases. The foregoing examples are therefore solely illustrative and are not to be construed as limiting the invention.

We claim as our invention:

1. In a process for the isomerization of butane

with an aluminum halide catalyst, the improvement which comprises contacting butane under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum chloride and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

2. In a process for the isomerization of pentane with an aluminum halide catalyst, the improvement which comprises contacting pentane under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum chloride and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

3. In a process for the isomerization of an isomerizable saturated hydrocarbon with an aluminum halide catalyst, the improvement which comprises contacting the hydrocarbon under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum chloride and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

4. In a process for the isomerization of butane with an aluminum halide catalyst, the improvement which comprises contacting butane under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum halide and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

5. In a process for the isomerization of pentane with an aluminum halide catalyst, the improvement which comprises contacting pentane under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum halide and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

6. In a process for the isomerization of an isomerizable saturated hydrocarbon with an aluminum halide catalyst, the improvement which comprises contacting the hydrocarbon under isomerization conditions with a catalyst consisting essentially of an effective amount of anhydrous aluminum halide and an adsorptive alumina, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

7. In a process for the isomerization of butane with an aluminum halide catalyst, the improvement which comprises contacting butane under isomerization conditions with a catalyst consisting essentially of an adsorptive alumina impregnated with from about 15% to 40% by weight of aluminum chloride, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

8. In a process for the isomerization of pentane with an aluminum halide catalyst, the im-

provement which comprises contacting pentane under isomerization conditions with a catalyst consisting essentially of an adsorptive alumina impregnated with from about 15% to 40% by weight of aluminum chloride, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

9. In a process for the isomerization of an isomerizable saturated hydrocarbon with an aluminum halide catalyst, the improvement which com-

prises contacting the hydrocarbon under isomerization conditions with a catalyst consisting essentially of an adsorptive alumina impregnated with from about 15% to 40% by weight of aluminum chloride, said adsorptive alumina having been prepared by partially dehydrating a crystalline alumina alpha trihydrate formed by precipitation from a solution of sodium aluminate.

MARTIN DE SIMÓ.
FRANK MATTHEW McMILLAN.