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ISOMERIZATION OF HYDROCARBONS

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The present invention relates to the catalytic isomerization of hydrocarbons. More particularly, the invention relates to the catalytic conversion of normal or slightly branched saturated hydrocarbons containing at least five carbon atoms to commercially valuable more highly branched isomers. Most particularly, the invention relates to a practical and economical process for the production of isopentane from normal pentane by catalytic isomerization.

As is well known, the various saturated hydrocarbons having at least four carbon atoms can exist in a number of various isomeric modifications. Thus, the paraffinic hydrocarbons from pentane to dodecane can exist in the following number of isomeric forms:

Pentane	3
Hexane	5
Heptane	9
Octane	18
Nonane	35
Decane	159
Undecane	355
Dodecane	802

Notwithstanding the large number of isomeric modifications generally possible, these hydrocarbons, as found in natural sources such as petroleum, occur almost exclusively in the normal or slightly branched modifications.

Although a few of the lower saturated aliphatic hydrocarbons, such as pentane in particular, are used to a certain extent in organic syntheses, etc., by far the most important application of these hydrocarbons, having at least five carbon atoms, is in fuels for internal combustion engines. Studies of the chemical properties and ignition characteristics of a variety of the numerous possible isomers have shown that certain isomeric modifications are vastly superior to others for this purpose and that, in general, the naturally occurring isomers are the least preferred. Normal pentane, for example, is obtained in large quantities from petroleum. It is chemically quite unreactive and, in view of its very poor ignition characteristics, is a poor fuel for internal combustion engines. The branched modification, isopentane, on the other hand, is much more chemically reactive and may be readily condensed with olefinic hydrocarbons by an alkylation process to produce saturated higher molecular weight hydrocarbons having excellent ignition characteristics. Isopentane is, furthermore, a valuable fuel component per se, especially for aviation fuels. It has a high "antiknock rating" (89 vs. 61

for normal pentane) and when blended with aviation spirits, increases both the octane rating and the vapor pressure.

Generally speaking, the relative ignition characteristics and, hence, suitability of the various isomeric modifications, is dependent to a large extent upon the ratio of the number of terminal carbon atoms to the total number of carbon atoms in the hydrocarbon. For lack of a better term, this ratio, which is also an expression of the iso-character of the molecule, may be designated by the coined term "branchedness." The wide variation in the suitability of various isomers for internal combustion engine fuels and the relation between branchedness and ignition characteristics, is illustrated in the following table:

Table I

Compound	Branchedness ratio	Critical compression ratio
Normal heptane	2/7	3
Triethyl methane	3/7	4
2, 4-dimethyl pentane	4/7	5
2, 2, 3-trimethyl butane	5/7	13

In view of the vastly superior properties of isopentane over normal pentane and, in general, hydrocarbons of high branchedness over hydrocarbons of low branchedness, it is apparent that a commercially practical process for the conversion of normal pentane to isopentane and for treating the large available quantities of less desirable hydrocarbons of low branchedness to increase their branchedness, is very desirable and valuable.

It has long been known that certain acid-acting metal halides, such as catalysts of the Friedel-Craft type in particular, exert a strong catalytic influence on hydrocarbon reactions. Aluminum chloride, for example, is one of the most powerful cracking and polymerizing catalysts known and is widely used in the cracking of petroleum hydrocarbons into low boiling hydrocarbons and the polymerization of olefins to synthetic lubricating oils. These catalysts, besides tending to catalyze the rupture of C—C and C—H bonds, when used under certain conditions, also tend to catalyze hydrocarbon isomerization. Although it has long been known that certain saturated hydrocarbons such as normal heptane and normal octane, when treated under certain conditions in the presence of aluminum chloride, are isomerized to a certain extent to branched chain isomers, no commercially practical method for ef-

fecting such isomerization has been developed. At ordinary temperatures the rate of isomerization is too slow to be commercially practical. At higher temperatures the rate of isomerization is more favorable, but in the presence of these catalysts the tendency for the hydrocarbons to undergo splitting or cracking reactions is greatly increased and the isomerized product is largely cracked as soon as it is formed. This is illustrated by the following example showing the results of comparative experiments in which it was attempted to isomerize normal pentane to isopentane with the aid of aluminum chloride at various temperatures.

EXAMPLE I

100 gram portions of normal pentane, 45 grams of aluminum chloride and 10 grams of hydrogen chloride were charged into an iron bomb and the bomb maintained at various constant temperatures for three hours. The percentages of normal pentane converted to lighter cracked products and to isopentane at the various temperatures employed are shown in the following table:

Table II

Temperature	n-Pentane converted to—	
	Lighter cracked products	Isopentane
	Percent	Percent
20° C.	—	3.3
50° C.	22.8	22.5
100° C.	44.1	22.4

An object of the invention is to provide a more practical and economical process for catalytically isomerizing saturated hydrocarbons containing at least five carbon atoms to increase the branchedness thereof. A more particular object is to provide a more practical and economical process for the catalytic conversion of normal saturated aliphatic hydrocarbons having from 5 to about 12 carbon atoms to corresponding branched chain isomers. A still more particular object is to provide a process for the economical production of isopentane from normal pentane by catalytic isomerization. Other objects of the invention are to provide a catalytic isomerization process wherein cracking, polymerization and other undesirable reactions are effectively inhibited; to provide a catalytic isomerization process wherein elevated temperatures affording faster reaction rates may be employed; and to provide a catalytic isomerization process wherein the practical catalytic life of the catalyst is materially increased.

In copending application No. 284,753 filed July 15, 1939 there is described an improved process whereby normal butane may be economically isomerized to isobutane while decomposition reactions are effectively inhibited. It is pointed out in the above-mentioned application that normal butane differs considerably from its higher homologues in that it is considerably less reactive and, consequently, requires the use of higher temperatures in order to effect the isomerization at a practical and economical rate. I have found that a process quite similar to that of the above-mentioned application is effective and most advantageous when applied to the isomer-

ization of normal pentane and higher saturated hydrocarbons since, although these hydrocarbons, in general, undergo isomerization more readily, they are much more susceptible to cracking and decomposition reactions in the presence of isomerization catalysts.

The process of this invention comprises isomerizing the hydrocarbon or mixture of hydrocarbons to be treated with the aid of an acid-acting metal halide in the presence of a hydrogen halide and a metal which acts catalytically to inhibit decomposition and other side reactions.

The process of the invention is generally applicable to the isomerization of saturated hydrocarbons containing at least five carbon atoms such as, for example, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, dimethyl cyclohexane, ethyl cyclohexane, and the like. Of these the paraffinic hydrocarbons containing from 5 to about 12 carbon atoms, and especially normal pentane, are preferred. Normal hydrocarbons containing six or more carbon atoms when treated according to the process of the invention are isomerized to the corresponding branched and multibranched chain isomers. Thus, for example, normal hexane is isomerized to 2-methyl pentane and to dimethyl butane. The process can also be employed, if desired, to increase the branchedness of branched chain hydrocarbons when such further branching is structurally possible. 2-methyl pentane, for example, may be isomerized to dimethyl butane.

The hydrocarbon treated need not necessarily be a pure individual hydrocarbon but may be a mixture of one or more hydrocarbons. Thus, the invention provides a practical process for converting to isopentane the normal pentane content of commercial hydrocarbon mixtures such as are obtained from natural gases, petroleum distillates and from cracking of high molecular weight hydrocarbons. Conveniently treated normal pentane-containing mixtures are the so-called amylene-pentane fractions from which the olefins have been substantially removed. Treatment of such mixtures which contain a certain amount of isopentane, results in very materially increasing their isopentane content and enhancing their value as raw materials in the production of isopentene, alkylation products, etc. Technical pentane fractions, such as those containing from 70% to 98% normal pentane and from 30% to 2% isopentane may be treated in accordance with the process of the invention and their isopentane content increased up to about 90% without appreciable loss of pentanes due to decomposition and while realizing a maximum active life of the catalyst employed. Other mixtures of saturated hydrocarbons such as cuts of "straight run" gasoline which may or may not contain pentane, may also be advantageously treated to produce mixtures of more highly branched saturated hydrocarbons which are more suitable for alkylation with ethylene etc. and have superior ignition characteristics.

The hydrocarbon or mixture of hydrocarbons treated is, however, preferably substantially free of materials which are polymerized by the isomerization catalyst under the reaction conditions. Easily polymerizable materials are more detrimental when the process is executed in the vapor phase. Olefins, when present in any appreciable amount, tend to sludge and materially shorten the life of the catalyst. The detrimental

tal effect of olefins is illustrated by the following example:

EXAMPLE II

100 grams of the commercial pentane fraction containing 85.9% normal pentane and 14.1% isopentane, 1 gram pentene, 9 grams hydrogen chloride and 10 grams of aluminum chloride were reacted for five hours at 40° C. in a one liter V₂A steel rotating autoclave. The catalyst was badly sludged. The analysis of the liquid product is shown in the following table compared with the analysis of the product of a similar experiment made using olefin-free material.

Table III

	Olefin present	Olefin absent
	Percent	Percent
Isopentane.....	27.9	41.6
Normal pentane.....	11.4	12.4
Products of side reactions.....	60.7	46.0

According to a preferred embodiment of the invention, any olefin or other detrimental impurities in the charge stock are removed prior to use by a suitable treatment, such as a treatment with sulfuric acid. Two methods of treating the charging stock prior to use which are especially effective and advantageous to remove detrimental impurities, are by a pretreatment with spent catalyst from the process, and by a hydrogenation treatment. A pretreatment of the charging stock in many cases materially increases the life of the isomerization catalyst even though the amount of detrimental impurities appears to be quite small.

The isomerization is, in general, preferably effected with the aid of the most active isomerization catalysts such as the aluminum halides and, in particular, aluminum chloride or aluminum bromide. Although the aluminum halides are, in general, the most practical and preferred catalysts, such other acid-acting halide catalysts as exert a catalytic influence on the isomerization of hydrocarbons, e. g. the halides of Be, Zn, Zr, Nb, Ta, Sb, B, Cd, and Fe, may also, if desired, be employed. In general, the catalyst is employed in an amount equal to from about 1 to 20% by weight of the hydrocarbon being treated although larger or smaller amounts can be used.

The catalysts are preferably employed in the solid state in any suitable form such as granules, powder, or pellets of the desired size, preferably deposited on or mixed with a suitable solid supporting or carrying material. Particularly effective catalysts are produced when a metal halide catalyst is supported on or intimately mixed with one of the various siliceous and/or aluminous materials of natural or synthetic origin which contains an appreciable amount of firmly-bound water. Suitable materials of this category are, for example, the natural-occurring minerals and clays such as pipe clay, bauxite, fuller's earth, bentonite, kaolin, Florida earth, meerschaum, infusorial earth, kieselguhr, diatomaceous earth, montmorillonite, the permutites, and the like; the various treated clays and clay-like materials such as Tonsil, Celite, Sil-O-Cel, Terrana, and the like; and artificially prepared materials such as Activated Alumina, silica gel, the artificial permutites, and the like. These materials are preferably heated in a dry atmosphere at a temperature somewhat higher than that at which they are to be employed, for instance at

about 300° C., until they substantially cease to give off water. Although these materials produce preferred catalysts when combined with the metal halides, and especially the aluminum halides, other carrier or supporting materials, such as activated charcoal, coke, crushed brick, pumice, porcelain chips, and the like, may also be used, if desired.

While the above-described solid catalysts are preferred, the catalyst may be employed in other forms, if desired. Thus, for example, the metal halide may be simply suspended in the reaction mixture, or it may be employed in the form of a complex double compound with a phenolic, aromatic, or other compound, such, for instance, as the compounds of the types known as "Gustavson's compounds" (C 1903 II 1113) and the "Ansolv acids" (Ann 455 227-253).

Certain catalysts, such as aluminum bromide, may be employed in any of these various ways, or may, if desired, be employed as a liquid or in solution in the reaction mixture. The reaction mixture may or may not contain, besides the hydrocarbon to be treated, varying amounts of solvents, inert diluents, fixed gases, etc.

The process of the present invention is always executed in the presence of at least a small amount of free hydrogen halide. It is known that the catalytic activity of aluminum halides and other Friedel-Craft type catalysts is greatly increased by the presence of a hydrogen halide. Thus, it is found that the rate of isomerization of hydrocarbons, using these catalysts, is, in general, increased appreciably by the presence of a hydrogen halide. The effect of hydrogen halides in isomerization reactions is, however, unusual in that it is more or less proportional to the amount present. This is illustrated, for example, in the following table showing the results of comparative experiments on the isomerization of normal pentane in the presence of 10% by weight of aluminum chloride at 20° C. for 17 hours.

Table IV

Partial pressure of HCl in atmospheres	Isoparaffin in the reaction product
	Percent
1.5.....	11
3.5.....	20
5.5.....	54
7.5.....	66
10.5.....	92

The hydrogen halides, however, likewise tend to promote cracking and decomposition reactions, especially at elevated temperatures, and have, therefore, hitherto been employed only in small amounts. An important feature of this invention is that the beneficial effect of large amounts of hydrogen halide can be utilized while cracking and decomposition reactions are effectively inhibited. In the preferred embodiment of my invention I, therefore, employ a substantial amount of a hydrogen halide such, for example, as a partial pressure of hydrogen chloride, hydrogen bromide or hydrogen fluoride of at least one atmosphere (measured at 20° C.) and, more preferably, from about three to about twenty atmospheres. The hydrogen halide is preferably added directly, in any convenient manner, as a liquid, gas, or solution. The hydrogen halide may, however, be generated in the reaction zone, if desired, by introducing a material which will decompose or react under the prevailing conditions to form the

desired hydrogen halide. Suitable materials which may be added for this purpose are, for example, chlorine, bromine, water, organic halides such as tertiary butyl chloride, organic hydroxy compounds such as ethanol, inorganic salts containing molecular-bound hydrogen halide such as $\text{PbSO}_4 \cdot 2\text{HCl}$, $\text{CuSO}_4 \cdot 2\text{HCl}$, and the like.

When operating in the vapor phase, the hydrocarbon to be treated, may, for example, be bubbled through tertiary butyl chloride or other volatile, readily decomposable halide prior to its passage into the reaction chamber.

The catalytic isomerization, according to the process of the present invention, is executed in the presence of a metal which is capable of reacting with a portion of the hydrogen halide present under the reaction conditions. Examples of such metals which inhibit cracking and other undesirable side reactions are, for instance, aluminum, beryllium, magnesium, calcium, zinc, copper, iron, silver, and the like. Of the available metals aluminum is exceptionally effective and preferred. The aluminum or other metal employed need not necessarily be pure but may be an alloy such, for instance, as an alloy of aluminum and zinc.

The aluminum or other metal is preferably employed in a state offering a large surface such as, for instance, in the form of turnings, shavings, filings, flakes or powder. In some cases it is advantageous to activate the surface of the metal prior or during use. This may be done, for example, by treating it prior to use with a solution of a salt of a less electropositive metal such as Hg, Cu, U, etc., or in some cases, by contacting it with a small amount of mercury.

The metal is preferably employed in intimate admixture with the isomerization catalyst, since the effectiveness is to some extent dependent upon the intimacy of the mixture. Thus, aluminum in the form of a powder may be mixed with the isomerization catalyst and the carrier material prior to forming the mixture into pellets or other suitably shaped pieces, for instance, by pressing. The metal may also, if desired, be incorporated in the catalyst bed or, if the reaction is executed in the liquid phase, suspended in the reaction mixture.

The amount of metal required to produce the optimum results depends upon the fineness of subdivision of the metal, the activation of the metal, if any, the amount of hydrogen halide and/or isomerization catalyst employed; and also upon the temperature at which the reaction is executed. Generally speaking, the amount of metal preferably used is greater the higher the temperature employed and the larger the amount of hydrogen halide and/or isomerization catalyst used. If insufficient metal is employed the decomposition and other side reactions will not be most effectively inhibited. Large, excessive amounts of metal effectively inhibit the side reactions but also tend to inhibit the isomerization to an appreciable extent. The amount of metal preferably employed for any given set of conditions may easily be determined in practice by adding increments of the metal until the decomposition reactions are inhibited to the desired extent.

As will be apparent, the metal will react to a greater or lesser extent with the hydrogen halide present under the reaction conditions to form metal halides which, especially if the metal employed is aluminum, may also exert a

catalytic influence. Care should be taken, therefore, that sufficient metal is added so that there is always free metal in the reaction zone. When aluminum is employed as the metal and the hydrogen halide concentration is properly adjusted, it is possible to generate sufficient aluminum halide in the reaction zone to effect the isomerization without the addition of further quantities of aluminum halide. While this is possible, the results are, in general, not as good as when operating in the presence of added catalyst.

If it is attempted to isomerize the present hydrocarbons with the aid of a metal halide catalyst, such as an aluminum halide in particular, in the presence of a hydrogen halide, but without the presence of an inhibiting metal, it is found that at low temperatures the isomerization takes place very slowly, generally without excessive decomposition. As the temperature is increased, the isomerization takes place at a faster rate but is rapidly overtaken by decomposition reactions. I have found that when executing the isomerization in accordance with the process of the present invention in the presence of aluminum or other suitable metal, the decomposition reactions may be effectively inhibited so that higher temperatures affording more favorable isomerization velocities may be employed. By the use of a sufficient quantity of aluminum according to the present process the decomposition reactions may be effectively inhibited up to temperatures of about 200-250° C., depending upon the hydrocarbon treated, amount of catalyst, amount of hydrogen halide, etc. Since, however, under these strongly inhibited conditions the isomerization is usually somewhat less than can be obtained at lower temperatures, the process is, in general, preferably executed at temperatures below about 200° C. and most preferably between about 30° C. and about 180° C.

The present process may be executed at any pressure from about one atmosphere up to as high as desired. Since the process is, however, usually executed in the presence of at least one atmosphere and preferably between about three and twenty atmospheres pressure of a hydrogen halide (measured at 20° C.), the pressure usually exceeds three atmospheres and is often in the neighborhood of 5-50 atmospheres. The pressure is usually due to the vapor pressure of the hydrocarbon treated and the hydrogen halide, but may also be due to other gases such as H_2 , N_2 , CO_2 , and the like.

The process may be advantageously executed in the liquid phase. Thus, the reaction may be conveniently executed in a suitable continuous reactor of the autoclave type, preferably equipped with suitable heating and agitating means, or the liquid reaction mixture may be circulated through a chamber, reactor, or tower containing the catalyst and maintained at the desired temperature.

According to a preferred embodiment of the invention the hydrocarbon to be treated, for example a commercial pentane fraction, is vaporized and the vapors, along with a suitable quantity of hydrogen halide, passed through a bed of the catalyst metal mixture maintained at the desired temperature.

An important advantage of the present process is that in the presence of even small amounts of aluminum metal the isomerization catalysts

undergo much less alteration during the treatment and remain active for a long time.

The lowest temperature at which it is possible to effect the reaction in the vapor phase depends upon the hydrocarbon or mixture of hydrocarbons treated and upon the pressure employed.

The following examples illustrate suitable applications and aspects of the process of the invention and the advantageous results obtainable thereby.

EXAMPLE III

100 grams of a commercial pentane fraction containing 91.5% normal pentane and 8.5% isopentane were treated for 10 hours at 40° C. with 10 grams of aluminum chloride and 10 grams of hydrogen chloride. The reaction product was found to contain:

	Per cent
Isopentane	22.2
Normal pentane	7.6
Decomposition and polymerization products	70.2

Thus it is seen that although aluminum chloride in the presence of hydrogen chloride does promote isomerization, in the case of the isomerization of normal pentane, considerable decomposition and polymerization products are formed, even at 40° C. When the above experiment was repeated under the same conditions, except that 6 grams of aluminum powder were added, the product was found to contain:

	Experiment	Check experiment
	Percent	Percent
Isopentane	37.4	34.4
Normal pentane	62.4	64.8
Decomposition and polymerization products	0	0.8

Thus it is seen that in the presence of 6 grams of powdered aluminum the formation of undesirable by-products is substantially obviated and the conversion of normal pentane to isopentane is considerably increased.

EXAMPLE IV

100 grams of normal pentane, 1 gram of aluminum powder, 10 grams of hydrogen chloride, and 20 grams of aluminum chloride were charged to a V₂A steel rotating autoclave and the mixture reacted for ten hours at 40° C. The reaction product, after decanting from the catalyst and washing with lye contained:

	Per cent
Isopentane	54.1
Normal pentane	45.3
Decomposition and polymerization products	.6

Thus it is seen that whereas 10 grams of aluminum chloride caused a large amount of decomposition, the decomposition when using 20 grams of aluminum chloride was effectively inhibited by one gram of metallic aluminum.

EXAMPLE V

100 gram portions of a commercial pentane fraction containing 91.5% normal pentane and 8.5% isopentane were reacted in the presence of 10 grams of aluminum chloride, 6 grams of aluminum powder and 10 grams of hydrogen chloride for five hours at various temperatures. The

analyses of the products obtained at the several temperatures are shown in the following table:

Table V

Temperature, ° C.	Isopentane	Normal pentane	Decomposition and polymerization products
	Percent	Percent	Percent
40	34.7	64.8	0.5
60	46.8	52.5	0.7
100	43.4	55.3	1.3
120	37.2	57.7	5.1
140	33.3	63.3	3.4
180	34.2	55.4	10.4

EXAMPLE VI

100 gram portions of a commercial pentane fraction containing 85.9% normal pentane and 14.1% isopentane were treated with 10 grams of aluminum chloride and 6 grams of aluminum powder in a one liter V₂A steel rotating autoclave for five hours at 40° C. under various partial pressures of hydrogen chloride. The percent conversion to isopentane, corresponding to the different pressures of hydrogen chloride used, are shown in the following table:

Table VI

Partial pressure of HCl in atmospheres	Conversion normal to isopentane
	Percent
0	4.9
2.2	12.9
4.6	22.7
14.0	24.4
19.0	49.9
21.0	74.5
24.0	39.4
27.6	30.4

It is seen from this series of experiments that when using 10% of aluminum chloride, 20 atmospheres partial pressure of hydrogen chloride and a temperature of 40° C., the optimum amount of aluminum powder is about 6% by weight of the material treated or about 60% by weight of the amount of aluminum chloride employed.

EXAMPLE VII

100 gram portions of commercial pentane containing a small amount of isopentane were treated in a one liter V₂A steel rotating autoclave in the presence of 20 grams of aluminum chloride, 10 grams of hydrogen chloride and various amounts of aluminum powder for 10 hours at 40° C. The analyses of the products obtained, corresponding to the different amounts of metal used, are shown in the following table:

Table VII

Grams aluminum powder employed	Isopentane	n-Pentane	Decomposition and polymerization products
	Percent	Percent	Percent
0.5	63.9	35.5	0.6
1.0	53.9	45.0	1.1
1.0	54.1	45.3	0.6
3.0	26.4	73.6	0
5.0	37.2	61.6	1.2
8.0	29.2	70.8	0

From this series of experiments it is seen that the optimum amount of aluminum powder under these conditions is about 2% of the amount of the aluminum chloride employed.

EXAMPLE VIII

A series of experiments were made as described in Example VII, except that the temperature was increased to 80° C. The analyses of the products are shown in the following table:

Table VIII

Grams aluminum powder employed	Isopentane	n-Pentane	Decomposition and polymerization products
	Percent	Percent	Percent
2	16.5	8.1	75.4
4	74.1	22.1	3.8
6	70.5	27.7	1.8
8	60.6	38.3	1.1

Thus it is seen that whereas at 40° C. 2% of aluminum powder (based on the amount of aluminum chloride employed) is sufficient to effectively inhibit the undesirable side reactions when using 10% aluminum chloride and 10% hydrogen chloride, at 80° C. the optimum amount of aluminum powder is about 30%. At higher temperatures correspondingly larger amounts of aluminum metal are preferred.

EXAMPLE IX

100 gram portions of a commercial pentane fraction containing 91.5% normal pentane and 8.5% isopentane were treated in a one liter V2A steel rotating autoclave with 10 grams hydrogen chloride and 10 and 20 grams powdered aluminum, respectively, for 10 hours at 40° C. The analyses of the products are shown in the following table:

Table IX

	10 grams Al powder	20 grams Al powder
Isopentane	28.4	24.2
Normal pentane	71.6	73.8
Decomposition products	0.0	2.0
Percent n-pentane converted to isopentane	21.7	17.1

Thus it is seen by comparison with Example III, that the isomerization may be more advantageously effected without the addition of aluminum chloride than with aluminum chloride alone, but less advantageously than with aluminum metal plus added aluminum chloride.

EXAMPLE X

Normal pentane vapors were passed along with hydrogen chloride vapors through a 100 cubic centimeter bed of a catalyst composed of aluminum chloride (10 parts) and aluminum powder (6 parts), held at a temperature of 100° C. The isopentane content of the product varied between 17.4 and 25.4% while the decomposition products varied from 4.2 to 9.8%. Aluminum chloride deposited on aluminum oxide under comparable conditions, gave a product containing 16.2% isopentane and 21.8% decomposition products.

The above examples, which illustrate various aspects of the invention, are not to be considered as limiting the invention. It is to be understood that modifications will be readily apparent to those skilled in the art and that no limitations are intended other than those imposed by the scope of the appended claims.

I claim as my invention:

1. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon con-

taining at least five carbon atoms is contacted with an aluminum chloride isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of an aluminum chloride catalyst containing sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

2. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with an aluminum chloride isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of an aluminum chloride isomerization catalyst containing a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

3. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with a Friedel-Crafts type metal halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

4. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with an aluminum halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of an aluminum halide isomerization catalyst containing a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

5. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with a Friedel-Crafts type metal halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

6. In a process for the production of isopentane from normal pentane wherein normal pentane is contacted with a Friedel-Crafts type metal halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

7. In a process for the production of isopentane from normal pentane wherein normal pentane is contacted with a Friedel-Crafts type metal halide isomerization catalyst and a hydrogen

halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

8. In a process for the production of isopentane from normal pentane wherein normal pentane is contacted with an aluminum halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of an aluminum halide isomerization catalyst containing a metal which

reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

5 9. In a process for the production of isopentane from normal pentane wherein normal pentane is contacted with an aluminum chloride isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization reaction in the presence of an aluminum chloride catalyst containing sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

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