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ISOMERIZATION OF HYDROCARBONS

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The present invention relates to a process for the catalytic isomerization of hydrocarbons. More particularly, the invention relates to the catalytic conversion of normal butane and normal pentane to isobutane and isopentane respectively.

Normal butane and normal pentane are 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. Isobutane and isopentane, on the other hand, are chemically much more reactive but occur naturally only to a very limited extent. They may be readily alkyllated 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 olefins which, in turn, are excellent starting materials for the syntheses of a wide variety of useful and valuable products. In view of the abundance of normal butane and normal pentane and the ever-increasing demand for isobutane and isopentane, a commercially-practical process for the conversion of the normal isomers to the branched chain isomers is of great value.

An object of the invention is to provide a more practical and economical process for the production of isobutane and/or isopentane by the catalytic isomerization of normal butane and/or normal pentane. A more particular object is to provide a process whereby normal butane and/or normal pentane may be catalytically isomerized at a practical rate with a minimum formation of undesirable products due to side reactions. Another object of the invention is to provide a process for the catalytic isomerization of normal butane and/or normal pentane wherein the active life of the catalyst is materially increased. Other objects of the invention will be apparent in the following description of the process.

In its more general aspect, the process of the invention comprises isomerizing the hydrocarbon or mixture of hydrocarbons to be treated with the aid of an acid-acting metal halide catalyst under a substantial pressure of hydrogen.

While the process is generally applicable to the isomerization of saturated hydrocarbons, it is especially advantageous for the isomerization of normal butane and/or normal pentane. These two hydrocarbons are obtained in large quantities as individual compounds in a relatively pure state. They are, moreover, chemically quite unreactive and do not undergo isomerization at a practical rate except at quite high temperatures. Butane, which is particularly unreactive, requires over two months, for example, to reach equilibrium at room temperature in the presence of 5 mol.% of aluminum bromide.

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 the normal butane and normal pentane contents of commercial hydrocarbon mixtures, such as are obtained from natural gases, 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-amylene fractions from which the unsaturated hydrocarbons have been substantially removed. Treatment of such mixtures which contain a certain amount of normal butane and/or normal pentane, results in very materially increasing their content of branched chain isomers and enhancing their value as raw materials for use in alkylation, production of tertiary olefins, etc. Technical butane or pentane fractions, such as those containing from 70% to 98% 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 cuts of "straight run" gasoline, casinghead gasoline, etc., containing appreciable quantities of normal butane and/or normal pentane, may also be advantageously treated to produce products which are more suitable for alkylation with olefins and have superior ignition characteristics.

The hydrocarbon or mixture of hydrocarbons treated is preferably substantially free of materials which are polymerized by the isomerization catalyst under the reaction conditions. According to a preferred embodiment of the invention, any olefins, diolefins, or other detrimental impurities in the hydrocarbon or hydrocarbon mixture to be treated are removed prior to use by a suitable treatment, such as with a mineral acid or with a portion of spent catalyst from the process.

The isomerization is preferably effected with the aid of an aluminum halide such as aluminum chloride or aluminum bromide. Although the aluminum halides are, in general, the most practical and efficient 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, and B, may also, if desired, be employed. Exceptionally suitable catalyst combinations are mixtures of an aluminum halide with a free metal of the group consisting of Al, Be, Mg, Zn, Cu, and Fe.

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 material. Particularly effective catalysts are produced when aluminum chloride is supported in or intimately mixed with one of the various siliceous and/or aluminous materials of natural or synthetic origin which contain an appreciable amount of firmly-bound water. Suitable materials of the category are, for example, the naturally-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. The aluminum halide may, moreover, be simply suspended in the liquid reaction mixture, or it may be employed in the form of a complex double compound such, for instance, as those known as "Gustavson's compounds" (C 1903 II 1113) and the "Ansolvo Acids" (Ann 455 227–253).

The isomerization is executed, according to the process of the present invention, under a pressure of hydrogen. It is found that hydrogen exerts a remarkable and unexpected influence in the isomerization reaction and that an appreciable pressure of hydrogen is, in general, very beneficial. By the use of suitable pressure of hydrogen, higher temperatures affording more practical reaction rates may be employed, undesirable side reactions are repressed, and the active life of the catalyst is materially increased.

It is also found that moderate hydrogen pressures, i. e. from about one to about five atmospheres (measured at 20° C.), tend to a certain extent to promote the isomerizing activity of the catalyst. Thus, whereas unpromoted aluminum halides are known not to catalyze isomerization to any appreciable extent, it is found that, in the case of the isomerization of normal butane and normal pentane, the isomerization may be effected even in the absence of a hydrogen halide if a suitable pressure of hydrogen is applied. This is illustrated by the following examples:

Example I

100 parts by weight of a commercial pentane fraction containing 85.9% normal pentane and 14.1% isopentane were charged, along with 10 parts of aluminum bromide and sufficient hydrogen to create a partial pressure of five atmospheres (measured at 20° C.), into a rotating autoclave. After heating the mixture for ten hours at 80° C. the product was found to contain 31.7% normal pentane and 67.8% isopentane.

Example II

80 parts of a butane fraction containing 96% normal butane and 4% isobutane were charged, along with 40 parts of aluminum chloride and sufficient hydrogen to create a partial pressure of five atmospheres (measured at 20° C.), into a rotating autoclave. After heating the mixture for ten hours at 140° C., the reaction product was found to contain 30.3% isobutane and 69.3% normal butane.

While, in the case of normal butane and normal pentane, the isomerization may be executed, according to the present process, in the absence of a hydrogen halide promoter, the process is much more efficient and the beneficial effect of hydrogen pressure is even more pronounced when the catalyst is promoted by a hydrogen halide. The hydrogen halides exert a strong promoting action on acid halide catalysts. The promotion of the isomerizating action of aluminum halides by hydrogen halides 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 12 hours:

Table I

Partial pressure of HCl in atmospheres	Per cent isoparaffin in the reaction product
1.5	11
3.5	20
5.5	54
7.5	66
10.5	92

Since, however, the halogen halides promote cracking and other undesirable side reactions, especially at elevated temperatures where practical rates of isomerization prevail, it has hitherto been considered necessary to limit the amount of hydrogen halide employed to about 0.2 to 2% and not more than 5% by weight of the hydrocarbon undergoing treatment, and the full benefit of these promoters has not been utilized.

An important feature of the present invention is that the beneficial effect of much larger concentrations of hydrogen halides may be employed while the side reactions, which usually accompany their use, are substantially obviated. This is illustrated in the following examples:

Example III

80 parts of normal butane were treated with 40 parts of aluminum chloride and 8 parts of hydrogen chloride for four hours at 120° C. In the absence of hydrogen, 75% of the normal butane was isomerized to isobutane while 89% of the normal butane was consumed by undesirable side reactions. Upon repeating the experiment using substantial pressures of hydrogen, it was found that the conversion to isobutane increased and the side reactions decreased. When employing a partial pressure of hydrogen of only three atmospheres (measured at 20° C.), for example, the conversion to isobutane increased to about 50%, and the consumption of normal butane by side reactions was already decreased to about 9%.

Example IV

100 parts of normal pentane were treated with 10 parts of aluminum chloride and 10 parts of hydrogen chloride for five hours at 40° C. In the absence of hydrogen 53% of the normal pentane was consumed by undesirable side reactions. When, however, the experiment was repeated under a partial pressure of hydrogen of three atmospheres (measured at 20° C.) the undesirable side reactions were substantially completely obviated.

Example V

154 parts of normal pentane and 15.4 parts of technical aluminum chloride were introduced into an iron autoclave of suitable capacity, whereupon gaseous hydrogen chloride was pressed in until the partial pressure of the hy-

drogen chloride was 17 atmospheres at 20° C. Subsequently, hydrogen was pressed in until its partial pressure was 33 atmospheres at 20° C. The autoclave was then heated and kept at 80° C. for 17 hours. After removal of aluminum chloride, hydrogen chloride and hydrogen, the product obtained consisted of 60.5% by weight of isopentane, 37.2% by weight of normal pentane and 2.3% by weight of products formed by side reactions. Upon repeating the experiment in the absence of hydrogen but under otherwise identical conditions, the pentane was practically entirely consumed by undesirable side reactions and no appreciable quantity of isopentane was detected.

EXAMPLE VI

A series of experiments was made wherein the aluminum chloride catalyst was generated in the reaction system by reaction between metallic aluminum and hydrogen chloride. In each experiment 80 parts of a butane fraction containing 4% isobutane were heated to 120° C. for ten hours with metallic aluminum and hydrogen chloride and with or without added hydrogen in a V_2A steel rotating autoclave. The results of the respective experiments are tabulated in the following table:

Table II

Al (parts)	HCl (parts)	H_2 added (atm.)	Reaction product		
			Per cent decomp. prod.	Per cent isobutane	Per cent N-butane
4	33	0	59.3	27.6	13.1
4	35	0	60.8	25.8	13.4
4	62	5	17.9	53.7	28.4
4	53	5	10.6	57.8	31.6

Although the process of the present invention is applicable and advantageous when executed in the total absence of a hydrogen halide and also in the presence of less than 5% by weight of a hydrogen halide, it is, in general, most advantageous when the partial pressure is greater than one atmosphere and preferably at least three atmospheres (measured at 20° C.) The hydrogen halide may be added directly in any convenient manner, as a liquid, gas or solution. Furthermore, the hydrogen halide may, if desired, be generated in the reaction zone 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, water, organic hydroxy compounds, inorganic salts, such as $PbSO_4 \cdot 2HCl$, $CuSO_4 \cdot 2HCl$, containing molecular-bound hydrogen halide, alkyl halides, and the like.

This promoting action of hydrogen, when used under suitable pressures, is also noticed when the catalyst is promoted with a hydrogen halide. This is illustrated by the following example:

EXAMPLE VII

100 parts of normal pentane were reacted with 10 parts of aluminum chloride and 10 parts of hydrogen chloride in a V_2A steel rotating autoclave at 40° C. for five hours. The conversion to isopentane amounted to 32%. Upon repeating the above experiment under three atmospheres pressure of hydrogen (measured at 20° C.) the conversion to isopentane amounted to 37%. This represents an increase in conversion of about 5% and an increase in efficiency of about 15%.

As the hydrogen pressure is increased, this promoting action disappears and further increase of the hydrogen pressure gradually decreases the isomerizing activity of the catalyst until at very high hydrogen pressures the isomerization is entirely inhibited. Thus, for example, in the isomerization of pentane at a temperature of 40° C. the isomerization was completely inhibited when a hydrogen pressure of 200 atmospheres was employed.

Since the optimum pressure of hydrogen (measured at 20° C.) according to the process of the invention depends upon the hydrocarbon or hydrocarbon mixture being treated, the temperature, the kind and amount of catalyst, the amount of hydrogen halide, and possibly also upon the type of apparatus and the reaction time, applicable hydrogen pressures may vary from a fraction of an atmosphere up to several hundred atmospheres. In general, under the more usual conditions, excellent results may be obtained using hydrogen pressures in the range of from about 1 to about 50 atmospheres and usually from about 2 to about 20 atmospheres.

An other and important advantage of the present process is that higher temperatures affording more favorable isomerization rates may be employed. By the use of suitable pressures of hydrogen, the decomposition and other side reactions which normally consume an appreciable portion of the initial hydrocarbon and isomerized reaction product at elevated temperatures, may be effectively inhibited in the case of butane up to about 300° C. and in the case of pentane up to about 250° C. Since, however, under the strongly inhibited conditions necessary when using these temperatures, the isomerization itself is somewhat retarded by the hydrogen pressure, there is usually no advantage to be gained in executing the process at temperatures higher than about 200° C. and temperatures ranging from about 30° C. to about 180° C. are usually most practical.

The process according to the present invention may be carried out in the gaseous phase as well as in the liquid phase and either batchwise or continuously.

When the isomerization is carried out in the gaseous or vaporous phase, the presence of even very small amounts of hydrogen, such as for example 1% or even less, is mostly sufficient for its exerting a very marked favorable influence on the course of the reaction. This is illustrated by the following examples.

Example VIII

A mixture of about 85.6 mol. % normal butane, 14 mol. % isobutane and 0.4% hydrogen was passed, in the presence of 6% by weight of dry HCl, over a catalyst prepared by converting into tablets a mixture of 70 parts by weight technical $AlCl_3$ and 30 parts by weight kaolin under an excess pressure of 15 atm. at a temperature of 100° C. The velocity with which the gas mixture was passed over the catalyst amounted to 0.8 kg. per litre catalyst per hour, whilst the partial pressure of the HCl amounted to about 1.5 atm. and that of the hydrogen to about 0.08 atm. During the first 200 hours of continuous operation the isobutane content of the reaction product exceeded 40%. Upon the operation being continued the average isobutane content slowly decreased and after 500 hours it amounted

to about 30%. The total quantity of isobutane produced amounted to 90 kg. per litre of catalyst. In a comparative run carried out under identical conditions, but in the absence of hydrogen, the average isobutane content of the reaction product after 500 hours' operation had dropped to 23%, whilst the total quantity of isobutane produced was 75 kg. per litre of catalyst.

EXAMPLE IX

A gas mixture consisting of about 10 mol. % isobutane, about 89 mol. % normal butane and about 1 mol. % hydrogen, which mixture had been obtained by hydrogenation of a mixture of butanes and butenes, was introduced at the bottom of a reaction tower filled with a catalyst consisting of a mixture of 70% by weight technical aluminium chloride (with an iron content below 0.3% by weight) and 30% by weight kaolin (which had been dried to about 300° C.), which mixture had been compressed to pills of about 5 mm. diameter. The throughput of the gas mixture amounted to 0.65 kg. per litre catalyst per hour. The gas mixture was previously dried by contacting it with silicagel or solid potassium hydroxide and was freed of any further impurities by passing it over technical aluminium chloride and then over common salt at normal temperature.

Together with the gas mixture about 8 mol. % hydrogen chloride was introduced into the reaction tower. The temperature in the reaction tower amounted to 90–95° C. and the pressure to about 15 atm.

At the bottom the tower was equipped with a device for collecting the sludge formed, thus making possible the continuous withdrawal thereof.

The reaction product leaving the tower at the top was first led into a cooled space, in order to separate entrained aluminium chloride, in which space a mechanical device was provided for returning the aluminium chloride to the reaction tower. Subsequently a separation of the hydrogen was effected by further cooling, whilst in a following fractionating apparatus the reaction product was separated from hydrogen chloride. Finally any traces of hydrogen chloride remaining in the product were removed by washing with lye.

The purified reaction product contained about 40 mol. % isobutane. Only about 1% by-product had been formed.

After 500 hours' operation the activity of the catalyst had practically not decreased.

The several examples herein submitted to 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 normal pentane with an aluminum halide catalyst, the step of executing the isomerization reaction at a temperature below 200° C. in the presence of at least 1 atmosphere pressure of a hydrogen halide promoter as measured at 20° C. and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

2. In a process for the isomerization of normal butane with an aluminum halide catalyst, the step of executing the isomerization reaction in the presence of at least 1 atmosphere pressure of a hydrogen halide promoter as measured at 20° C. and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

3. In a process for the isomerization of normal pentane with an aluminum halide catalyst, the step of executing the isomerization reaction at a temperature below 200° C. in the presence of a hydrogen halide promoter and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

4. In a process for the isomerization of normal butane with an aluminum halide catalyst, the step of executing the isomerization reaction in the presence of a hydrogen halide promoter and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

5. In a process for the isomerization of normal pentane with an aluminum halide catalyst, the step of executing the isomerization reaction under between 0.08 and 33 atmospheres pressure of hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

6. In a process for the isomerization of normal butane with an aluminum halide catalyst, the step of executing the isomerization reaction under between 0.08 and 33 atmospheres pressure of hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

7. In a process for the isomerization of a saturated aliphatic hydrocarbon containing more than 3 and less than 6 carbon atoms with an aluminum halide catalyst, the step of executing the isomerization reaction under between 0.08 and 33 atmospheres pressure of hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

8. In a process for the isomerization of normal pentane with an aluminum chloride catalyst, the step of executing the isomerization reaction at a temperature below 200° C. in the presence of a hydrogen chloride promoter and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

9. In a process for the isomerization of normal butane with an aluminum chloride catalyst, the step of executing the isomerization reaction in the presence of a hydrogen chloride promoter and between 0.08 and 33 atmospheres pressure of added hydrogen, the partial pressure of said hydrogen being sufficient to substantially repress undesirable side reactions, but insufficient to substantially repress the isomerization reaction.

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