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ISOMERIZATION OF PARAFFIN HYDROCARBONS

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The present invention relates to a process wherein straight chain paraffin hydrocarbons are converted into the more desirable branched chain hydrocarbons in the presence of aluminum halides, particularly aluminum bromide. The invention is especially concerned with a liquid phase paraffin hydrocarbon isomerization process wherein undesirable cracking of the hydrocarbons is suppressed or avoided.

In general, in the petroleum industry isoparaffins and branched paraffin hydrocarbons are of greater commercial value than the corresponding straight chain hydrocarbons. The branched chain hydrocarbons in petroleum gasoline fractions have greater octane ratings than the corresponding straight chain hydrocarbons. This is of considerable importance in view of the increased demands for high anti-knock rating motor fuels to satisfy the requirements of modern high compression engines. One of the commercially important processes for supplying high octane motor fuels involves isomerization of the light naphtha components of such fuels.

The isomerization of normal paraffin hydrocarbons of from 4 to 7 carbon atoms into the corresponding branched chain homologs is well known. For effecting the isomerization, it is customary to employ certain metal halides, particularly aluminum chloride or aluminum bromide, in conjunction with certain promoters, such as hydrogen chloride, hydrogen bromide or boron fluoride. Insofar as the isomerization of light naphthas is concerned, the lower the temperature of isomerization, within limits, the more favorable is the equilibrium for converting straight chain paraffin hydrocarbons into isomers of high octane rating. Aluminum bromide has been found to be more active than aluminum chloride at lower isomerization temperatures, e.g. in the range of about 40° to about 120° F.

Although, as stated, the lower isomerization temperatures that are possible when using aluminum bromide favor the production of high yields of isomers of high octane rating, the system is extremely sensitive to the occurrence of cracking, which can result in poor selectivity to the desired product and which can also cause a rapid decrease in the rate of isomerization. In the past, various cracking suppressors, such as aromatic hydrocarbons and naphthene hydrocarbons, have been employed. This is not an entirely satisfactory solution to the problem, however, because the aromatics and naphthenes can be used only in small amounts; the use of larger amounts tends to suppress the isomerization reaction unduly. If cracking does occur during isomerization, an attempt to prevent this by increasing the amounts of aromatics or naphthenes used simply serves to reduce the isomerization activity to an undesirably low level. Thus, there has been a need for a system for reducing cracking tendencies during isomerization without adversely affecting the isomerization reaction itself.

It is one object of the present invention to preserve the activity of aluminum bromide as an isomerization catalyst while at the same time suppressing undesired

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cracking of the reactants or the isomerization products.

In accordance with the present invention, the isomerization of normal paraffinic hydrocarbons of from 4 to 7 carbon atoms is conducted in the presence of aluminum bromide or in the presence of a mixture of aluminum chloride and aluminum bromide along with a second catalyst comprising platinum sulfide, platinum oxysulfide, or their mixtures. When the mixed aluminum bromide-aluminum chloride is used, the proportions may range up to 1 to 2 parts of the chloride for each part of the bromide, by weight. The reaction is conducted at a temperature in the range of from about 40° to 120° F.

It is preferred that both the aluminum bromide and the platinum sulfides be associated with suitable supports.

The support for the platinum may be the same as or may be different from the aluminum halide support. Among the supports or carriers that may be used in this invention are included activated carbon, activated alumina, pumice, silica gel, fuller's earth, various activated clays and calcined bauxite. A partially dehydrated calcined bauxite known commercially as Porocel may also be used. Partial dehydration to prepare the Porocel for use may include heating for 2 to 3 hours at 1200° to 1400° F. or for from 15 to 18 hours at 900° to 1000° F. Typical bifunctional catalysts that may be used in the present invention include a mixture of platinum sulfide supported on silica gel along with aluminum bromide or mixed aluminum bromide-aluminum chloride on a suitable support or aluminum bromide supported on ferric oxide plus platinum sulfide or oxysulfide supported on silica gel or on treated bauxite.

The aluminum bromide may be placed on the support by impregnating the support with the bromide at an elevated temperature in the gas phase or, alternatively, a support can be placed in the reaction zone and the aluminum bromide can be carried into the reaction zone along with the hydrocarbon feed. Another method of preparation is to mix the aluminum halide with the support and to heat the mixture to effect impregnation. If desired, loosely held aluminum halide may be removed from the catalyst mass by heating the mass and passing through it a gas such as carbon dioxide, methane, hydrogen or nitrogen.

Alternatively the support may be impregnated by dissolving the aluminum halide in a suitable solvent such as ethylene dichloride or dioxane, for example, and the porous carrier impregnated with this solution, followed by heating to remove the solvent and loosely held aluminum halide. Still another alternative is to employ a powdered support or promoter, mix the aluminum halide with it, and compress the mixture into pellets.

The proportion of support to aluminum halide catalyst should be at least 2 to 1 by weight but from a practical standpoint should not exceed about 50 to 1. Stated conversely, the ratio of aluminum halide to support should be in the range of 2 to 50 parts of the halide for each 100 parts of support. The preferred range is from about 5 to 40 parts of aluminum halide per 100 parts of support.

The supported platinum sulfide catalyst may conveniently be prepared by impregnating a suitable support such as alumina gel, silica gel, activated carbon, Porocel, or the like with an aqueous solution of chloroplatinic acid in an amount that will deposit about 0.01 to 5 wt. percent, preferably about 0.1 to 1.0 wt. percent, of platinum metal on the support, and thereafter sulfiding in a manner known per se. Alternately, the supports are impregnated directly with 0.01 to 1% of platinum sulfide or oxysulfide. The process of preparing the catalyst is not a part of the present invention.

Although batch operations may be used, the process is preferably conducted as a continuous operation using flow rates of from about 0.1 to about 2 v./v./hr. (volume

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of feed per volume of total catalyst including support per hour). The apparatus employed may be of a conventional nature and may comprise a tower containing a fixed bed of the catalyst through which the reacting hydrocarbons are circulated, using an external recycle line to send the reactants back through the bed any number of times.

Aromatics and other materials that tend to be detrimental to the isomerization reaction may be removed from the feed by conventional means, such as acid treating, solvent extraction, mild hydrogenation or the like. Solvent extraction is preferred. When conventional promoters such as HF, HBr or HCl are used, these may be added along with the feed. These are usually employed in amounts of about 1 to 10% based on the feed.

The following examples and data are offered to set forth the advantages of the present invention.

Example 1

Aluminum alcoholate solution was hydrolyzed in 10 volumes H_2O and left to stand at room temperature for a week. The slurry was filtered and oven dried. This material is alumina beta trihydrate. A portion of this was calcined at 1000° F. This material will be referred to as support "A" in the following example.

Example 2

A portion of the alumina beta trihydrate prepared as described in Example 1 was calcined at 1000° F. This was impregnated with $PtCl_4$ solution of sufficient concentration to incorporate 0.6% Pt on the alumina, oven dried and calcined at 1000° F. This material is referred to as support "B" in the following examples.

Example 3

A portion of the alumina beta trihydrate prepared as described in Example 1 was calcined at 1000° F. and then placed in a dish. In a separate vessel 51 cc. of a dilute $PtCl_4$ (Pt 1.08 gr.) solution admixed with 57 cc. of a solution comprising 1 cc. of 26% ammonium sulfide solution. As the precipitate of PtS_2 slowly started to form, the mixture was quickly added to the alumina. Oven dried and calcined 6 hours at 1000° F. This material comprises 1% Pt (as PtS_2) on alumina and is designated support "C" in the following examples.

Example 4

Commercial Porocel, which is an impure alumina comprising iron oxide, was calcined at 1000° F. This material, which is the standard support in isomerization, is designated support "D" in the following example.

Example 5

Supports "A," "B," "C" and "D" described above were composited with aluminum bromide and a hydrocarbon feed mixture and tested for their isomerization properties. The tests were made as follows: 2 grams of the support were placed in a bottle, 1 gram $AlBr_3$ added, and then 7.4 cc. of a hydrocarbon mixture comprising 67% n-heptane and 33% methylcyclohexane. The methylcyclohexane is present as a cracking inhibitor. The bottles were each capped tightly, placed in a mechanical shaker at room temperature and shaken for two hours. At this point hydrocarbon samples were withdrawn and analyzed by gas chromatography. The results follow:

Support.....	A	B	C	D
Percent Conversion of n-heptane to isomers.....	58.5	2.6	68.3	65.1

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These data show that support "C" which is the support of the present invention is to be preferred to Porocel, the commercial standard. The data also show that the superior performance of this support does not evolve from the alumina base ("A") or the presence of Pt on alumina per se ("B") but is due to platinum sulfide on alumina as the active support.

Example 6

Supports "C" and "D" were examined in an isomerization operation conducted over longer periods of time. Two grams of support were placed in a bottle, 1 gram $AlBr_3$ added, and then 7.4 cc. of a hydrocarbon mixture comprising 67% n-heptane and 33% methylcyclohexane. The bottles were each tightly capped and placed in a mechanical shaker for 3 hours. The results follow.

Support.....	"C"		"D"	
Time, hours.....	2	3	2	3
Percent Conversion of n-heptane to isomers.....	68.3	81.8	65.1	78.0

These data further attest to the fact that support "C," which is the support in the present invention, is superior to Porocel, the commercial, high activity support. In addition, it was found that with support "C" in the 3 hours operation, 4.3% triptane was found in the isomerized product. This compares with 2-3% triptane in the similar run with support "D."

Example 7

Further tests to evaluate platinum sulfide on a support for Friedel-Crafts isomerizations of n-paraffins to their branched chain isomers are here presented. These tests were made in a similar manner as described in Example 6 except that they were carried out for 1 hour. The results are as follows:

7.4 ml. feed (67% n-heptane + 33% methylcyclohexane)
1 gram support (20%)
1 gram $AlBr_3$ (20%)

In this run, platinum sulfide on alumina was compared to Porocel and gave 41.3% conversion (no cracking) to 28.6% for Porocel. This is at a 20 wt. percent support level which is rather low for isomerization reactions. Even at this low concentration, the platinum sulfide appears to be very reactive. When cutting the $AlBr_3$ concentration to 10%, 26.8% conversion with platinum sulfide was obtained as compared to 22.5% Porocel. Thus, the use of platinum sulfide enables a 50% reduction in $AlBr_3$ to obtain the same conversion using Porocel.

It is clear from the data above that the platinum sulfide support is very much more reactive and selective for isomerization than Porocel, alumina and other supports.

What is claimed is:

1. A process for converting normal paraffin hydrocarbons of from 4 to 7 carbon atoms to the corresponding branched chain isomers which consists of contacting said hydrocarbons at a temperature in the range of from about 40° to about 120° F. with a supported bifunctional catalyst comprising an aluminum halide selected from the group consisting of aluminum bromide and aluminum bromide-aluminum chloride mixtures and a support carrying about 0.01 to 5 wt. percent of platinum, said platinum being in the form of a sulfide compound.

2. The process as defined by claim 1 wherein said aluminum halide is supported on calcined bauxite and admixed with said support carrying the platinum sulfide compound.

3. Process as defined by claim 1 wherein said support carrying the platinum sulfide compound is alumina.

4. Process as defined by claim 1 wherein said support carries about 0.1 to 1 wt. percent platinum.

5. A process for converting normal paraffin hydrocarbons of from 4 to 7 carbon atoms to the corresponding branched chain isomers which consists in contacting said hydrocarbons at a temperature in the range of from about 40° to about 120° F. with a catalyst comprising a support carrying aluminum bromide and 0.01 to 5 wt. percent of platinum, said platinum being in the form of a sulfide compound.

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