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PROCESS FOR SHIFTING THE DOUBLE BOND IN AN OLEFINIC HYDROCARBON

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This application is a continuation-in-part of our copending application Serial No. 44,249, filed July 21, 1960, now Patent No. 3,114,785.

This invention relates to a process for shifting the double bond of an olefinic hydrocarbon to a more centrally located position in the hydrocarbon chain. More specifically, this invention relates to the shifting of said double bond in the presence of a boron trifluoride-modified substantially anhydrous silica-alumina.

It is generally well recognized that the high compression, ignition type automobile engines in present day use require fuel of a high anti-knock value to give the optimum performance for which they are designed. The industry has accorded recognition to the fact that high antiknock values are attributable to the molecular structure of the hydrocarbons which comprise the gasoline fractions; that highly branched chain hydrocarbons have better antiknock characteristics than their corresponding isomers of straight chain or relatively unbranched structure.

Motor fuels containing highly branched chain hydrocarbon components may be produced by the condensation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an acidic condensation catalyst, the process being generally referred to as alkylation. The more desirable alkylates of this process result from the condensation of isoparaffins with olefinic hydrocarbons wherein the double bond of said olefinic hydrocarbon is in a centrally located position of the hydrocarbon chain rather than in a terminal position. Thus, for example, the alkylation of isobutane with 2-butene yields trimethylpentanes with an exceptionally high octane number, whereas 1-butene, reacted similarly, gives dimethylhexanes which possess a much lower octane rating. One may generalize and state that 1-alkenes react with isobutane to yield dimethylalkanes of poor octane rating.

The olefinic feed stocks generally available for alkylation purposes, and subject to treatment in accordance with the present process, are generally a mixture of olefinic hydrocarbons of approximately the same molecular weight including the 1-isomer, 2-isomer, and other position isomers, capable of undergoing isomerization to an olefin in which the double bond occupies a more centrally located position in the hydrocarbon chain. In order to provide an olefinic feed stock for alkylation purposes containing an optimum amount of the more centrally located double bond isomers, it is desirable to convert the 1-isomer, or other position isomer, component of the mixed feed stock, into the corresponding 2-isomer, or into olefins wherein the double bond is more centrally located in the carbon atom chain. When higher molecular weight olefinic feed stocks are utilized, such as hexene, the 1- and 2-position isomer components are desirably converted into isomers containing the double bond located in the 2- and 3-positions.

It is an object of this invention to present a process for shifting the double bond of an olefinic hydrocarbon to a more centrally located position in the hydrocarbon chain. It is a more specific object to effect such shifting of the double bond in the presence of an isomerization catalyst comprising boron trifluoride-modified substantially anhydrous silica-alumina.

In one of its broad aspects, the present invention embodies a process for shifting a double bond of an olefinic hydrocarbon to a more centrally located position in the hydrocarbon molecule, which process comprises isomerizing said olefinic hydrocarbon at isomerization reaction conditions and in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina.

Other objects and embodiments of the process of this invention will become apparent in the following detailed specification.

The olefinic hydrocarbons treated according to the process of this invention are hydrocarbons of more than three carbon atoms per molecule and may be derived from various sources. This process is particularly suited to the conversion of 1-butent to 2-butene. The 1-butene may be charged in a pure state or in admixture with other hydrocarbons. Thus, a mixture containing 1-butene as well as isobutylene, 2-butenes, n-butane, and isobutane, recovered for example, as the light vapor overhead product of a catalytically crack gas oil fraction, may be treated in accordance with the present process. By proper regulation of the isobutane content of such a mixture it will be recognized as a typical alkylation charge stock. Thus, the process of the present invention may be utilized for the conversion of a 1-butene content in an alkylation charge stock to the more desirable 2-butene prior to utilization of the charge in the alkylation process. The process of this invention can be further utilized to shift the double bond of higher molecular weight olefinic hydrocarbons to a more centrally located position. For example, 1-pentent, 3-methyl-1-butene, 1-hexene, 2-hexene, and 4-methyl-1-pentene, can be readily isomerized to 2-pentene, 3-methyl-2-butene, 2-hexene, 3-hexene, and 4-methyl-2-pentene respectively. However, it is not intended to limit the process of this invention to those enumerated olefins set out above as it is contemplated that shifting of the double bond to a more centrally located position may be effected in straight or branch chain olefinic hydrocarbons containing up to about 20 carbon atoms per molecule according to the process of the present invention.

The preferred catalyst composition comprises boron trifluoride-modified substantially anhydrous, but not completely dry, silca-alumina. Substantially anhydrous, but not completely dry, silica-alumina means calcined silica-alumina, which, on an anhydrous basis, contains from about 0.1 wt. percent to about 10 wt. percent water in chemical or physical association therewith. The amount of silica in such silica-alumina composites may range from about 5 to about 95% by weight. The silica-alumina composites may be prepared by any of many well-known techniques including precipitation, impregnation, co-precipitation, etc. In any case, it will be dried and then calcined at high temperature prior to boron trifluoride modification thereof. The exact reason for the specific utility of the silica-alumina in the process of this invention is not fully understood but it is believed to be connected with the number of residual hydroxyl groups occurring on the surface of the particular crystalline silica-alumina.

The above-described silica-alumina can be modified with boron trifluoride by various methods. The so-called modification of silica-alumina with boron trifluoride is an exothermic process resulting in, for example, an initial temperature rise to about 100° C. or more when boron trifluoride is passed over the silica-alumina at about room temperature. In general, the silica-alumina is contacted with boron trifluoride at a predetermined temperature until boron trifluoride is no longer adsorbed, or otherwise taken up, by the silica-alumina. It has been observed that in the treatment of substantially anhydrous silica-alumina with boron trifluoride, the capacity of the silica-alumina for boron trifluoride is determined by the particular temperature at which said treatment takes place and, at a given temperature, the boron trifluoride content of the silica-alumina reaches a fixed maximum which is not further increased by contact with additional quantities of boron trifluoride at the given temperature. The capacity of silica-alumina for boron trifluoride increases with temperature. The exact manner in which the boron trifluoride acts to modify the silica-alumina is not understood. It may be that the modification results from complexing of the boron trifluoride with the silica-alumina or, on the other hand, it way be that the boron trifluoride reacts with the residual hydroxyl groups on the silica-alumina surface. In any case, the process of the present invention is preferably effected in contact with a catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina wherein said silica-alumina has been modified by contact with at least a slight excess of boron trifluoride at a temperature of from about 0° C. to about 250° C.

One suitable method of preparing the boron trifluoride-modified substantially anhydrous silica-alumina comprises placing the substantially anhydrous silica-alumina in a fixed bed located in a suitable reactor and passing a stream of boron trifluoride therethrough at a preselected temperature until such time as boron trifluoride is no longer adsorbed, or otherwise taken up, by the silica-alumina. When the silica-alumina composite is thus treated with boron trifluoride it is noted that no boron trifluoride passes through the silica-alumina until substantially all of the silica-alumina has been modified with boron trifluoride in the manner herein contemplated. The boron trifluoride stream may be diluted with an inert gas including nitrogen, hydrogen, helium, or the like, as desired.

The isomerization reaction of the present invention is effected at a temperature of from about 20° C. to about 250° C. and at a pressure ranging from about atmospheric to about 1000 p.s.i. or more. In general, the reactants can be processed in either the liquid or gaseous phase. In certain cases it may be desirable to maintain the reactants in a liquid phase downflow over the catalyst as a deterrent to polymer formation thereon.

One preferred embodiment of the process of this invention relates to the process for shifting the double bond of 1-butene to produce 2-butene which comprises isomerizing said 1-butene at an isomerization temperature of from about 20° C. to about 250° C. and in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina.

Another preferred embodiment is in a process for shifting the double bond of 1-pentene to produce 2-pentene which comprises isomerizing said 1-pentene at an isomerization temperature of from about 20° C. to about 250° C. and in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina.

Still another preferred embodiment of this invention is in a process for shifting the double bond of a 1-hexene to a more centrally located position, which process comprises isomerizing said 1-hexene at an isomerization temperature of from about 20° C. to about 250° C. and in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina.

The present process may be effected in any conventional or otherwise convenient manner and may comprise either a continuous or a batch type of operation. According to one method of operation, the olefinic hydrocarbon is continuously charged to a reactor containing therein a fixed catalyst bed comprising boron trifluoride-modified silica-alumina, the reaction zone being maintained under reaction conditions previously described. The reactor effluent, comprising the isomerization reaction product, is continuously withdrawn from the opposite end of the reactor at a rate which will insure an adequate residence time therein. The hourly space velocity of the olefinic hydrocarbon starting material may be varied over a relatively wide range. For example, a gaseous hourly space velocity of from about 50 to about 8000 or more is operable in the case of an olefinic hydrocarbon in the gaseous phase, while olefinic hydrocarbons in the liquid phase can be charged at a liquid hourly space velocity of from about 0.1 to about 20 or more. However, equilibrium conversion conditions are attained within a more limited range of from about 50 to about 4000 space velocity in the case of gaseous olefinic hydrocarbons and from about 0.1 to about 10 space velocity in the case of liquid olefinic charge stocks.

Other suitable methods, including the moving bed type of operation in which the hydrocarbon charge is passed either concurrently or countercurrently to a moving catalyst bed, or a fluidized system in which the hydrocarbon is charged upflow through a dense catalyst phase in a reactor to maintain the catalyst in a state of turbulence under hindered settling conditions, may be utilized. Still another type of operation is the slurry or suspensoid type of operation in which the catalyst is carried as a slurry or as a suspension into a reaction zone.

In a batch type of operation the olefinic hydrocarbon and the boron trifluoride-modified silica-alumina are charged to an autoclave maintained at the desired temperature and pressure, and the reaction continued until the desired degree of isomerization is attained, usually a period of one hour or less. A batch type of operation is particularly suitable when processing a liquid hydrocarbon charge stock comprising olefinic hydrocarbons of a relatively high molecular weight, for example, such olefins as the octenes, nonenes, decenes, etc. In a batch process of the above type, the catalyst and the olefinic hydrocarbon are preferably mixed during the course of the reaction, for example, by utilizing a reactor containing stirring paddles, or a rotating autoclave.

Utilization of the present process to shift the double bond of an elofinic hydrocarbon to a more centrally located position results in a number of advantages. With respect to the catalytic activity of the boron trifluoride-modified silica-alumina, optimum conversion of said olefinic hydrocarbon to the desired isomer or isomers thereof is readily obtained under mild operating conditions. For example, the 2-butene content of a charge stock, resulting from the conversion of 1-butene in contact with said boron trifluoride-modified silica-alumina at a temperature of about 150° C., approaches thermodynamic equilibrium composition. In addition the migration of the double bond is not usually accompanied by a skeletal rearrangement within the molecule.

The boron trifluoride-modified silica-alumina, as utilized in the present process, is characterized by an exceptionally long catalyst life and obviates the necessity of promoters as generally practiced in the prior art. It is contemplated that under extended periods of operation the catalyst will decline some what in activity. However, the nature of the catalyst is such that it may be readily regenerated simply by passing a stream of boron trifluoride through the catalyst bed, preferably in admixture with the hydrocarbon charge, thus obviating the necessity of shutting down the operation to charge a fresh catalyst. A further advantage to be realized from the utilization of the present process is in the comparative ease with which the catalyst can be prepared and subsequently handled. The transfer of the catalyst requires only ordinary precautions against undue exposure to the atmosphere. On the other hand, the catalyst can be prepared in situ. For example, the silica-alumina can be placed in a bed within the reactor subsequently to be used in the isomerization process. The boron trifluoride is then passed through the silica-alumina bed at a predetermined temperature whereby the desired catalyst compostion is attained. The catalyst thus prepared stands ready for use in the double bond isomerization reaction process.

The following examples are presented in illustration of the specific embodiments of this invention and are not intended as an undue limitation of the generally broad scope of this invention.

Example I

This example illustrates the relative inactivity of boron trifluoride per se with respect to the isomerization of 1-butene as herein contemplated. A normally gaseous hydrocarbon charge stock comprising 60.7 wt. percent 1-butene and admixed with about 365 p.p.m. boron trifluoride based on the total charge, continuously charged to a 60 cc. reacting zone packed with $\frac{3}{16}''$ stainless steel helicies at a temperature of about 120° C., and at a rate of about 80 grams per hour, resulted in a reaction product substantially as charged and comprising 61.4 wt. percent 1-butene.

Example II

A substantially anhydrous silica-alumina containing approximately equimolar quantities of silica and alumina, was calcined for 31 hours at 650° C. This silica-alumina had a surface area of 315 sq. meters per g., a pore volume of 0.437 cubic centimeter per gram, and a pore diameter of 55 Angstrom units. It apparently still contained about 5.25% water which was the weight loss experienced on heating the silica-alumina at 900° C. After boron trifluoride modification, the aforesaid silica-alumina contained 3.0 wt. percent boron and 7.2 wt. percent fluorine. It had an apparent bulk density of 0.594 gram per milliliter and its color was white.

About an 85% conversion of 1-butene to the 2-butene isomer thereof is effected on passing a light vapor overhead from a catalytically cracked gas oil, containing about 25% 1-butene, through a fixed bed of the above-described boron trifluoride-modified substantially anhydrous silica-alumina at a rate of about 35 grams per hour per 60 cc. of catalyst used, an isomerization temperature of about 150° C., and at a pressure of about 525 p.s.i.g.

Example III

A charge stock comprising 1-pentene, continuously charged to a fixed bed of about 30 grams of the above-described boron trifluoride-modified silica-alumina at an isomerization temperature of about 150° C., at a rate of about 50 grams per hour, and at a pressure of about 300 p.s.i.g. is converted to an effluent stream comprising the desired 2-pentene isomer of said 1-pentene.

Example IV

A charge stock comprising 1-hexene, continuously charged to a fixed bed of about 30 grams of the above-described boron trifluoride-modified silica-alumina at an isomerization temperature of about 150° C., a rate of about 50 grams per hour, and at a pressure of about 200 p.s.i.g., is converted to an effluent stream comprising a 2-hexene isomer and the 3-hexene isomer of said 1-hexene.

We claim as our invention:

1. A process for shifting a double bond of an olefinic hydrocarbon of more than three carbon atoms per molecule to a more centrally located position in the hydrocarbon molecule, which consists essentially of isomerizing said olefinic hydrocarbon in contact with a preformed combined boron trifluoride-silicia-alumina catalyst prepared by treating substantially anhydrous silica-alumina with boron trifluoride at a temperature of from about 0° C. to about 250° C. until boron trifluoride no longer combines with the silica-alumina.

2. A process for shifting a double bond of an olefinic hydrocarbon of more than three carbon atoms per molecule to a more centrally located position in the hydrocarbon molecule, which consists essentially of isomerizing said olefinic hydrocarbon at an isomerizing temperature of from about 20° C. to about 250° C. and in contact with a preformed combined boron trifluoride-silica-alumina catalyst prepared by treating substantially anhydrous silica-alumina with boron trifluoride at a temperature of from about 0° C. to about 250° C. until boron trifluoride no longer combines with the silica-alumina.

3. The process of claim 2 further characterized in that said olefinic hydrocarbon is 1-butene.

4. The process of claim 2 further characterized in that said olefinic hydrocarbon is 1-pentene.

5. The process of claim 2 further characterized in that said olefinic hydrocarbon is 1-hexene.

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