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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 co-pending 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 alumina-boria.

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 anti-knock values are attributable to the molecular structure of the hydrocarbons which comprise the gasoline fractions; that highly branched chain hydrocarbons have better anti-knock 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 a 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 alumina-boria.

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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 alumina-boria.

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-butene 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 cracked 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 the 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 a higher molecular weight olefinic hydrocarbon to a more centrally located position. For example, 1-pentene, 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 branched chain olefinic hydrocarbons containing up to about 20 carbon atoms per molecule according to the process of the present invention.

The isomerization catalyst of this invention comprises a boron trifluoride-modified, substantially anhydrous, but not completely dry alumina-boria. The description "substantially anhydrous, but not completely dry, alumina boria," relates to calcined alumina-boria which, on a dry basis, contains from about 0.1 wt. percent to about 10 wt. percent water in either physical or chemical combination with the alumina-boria. The amount of boria in such alumina-boria composites may range from about 5 wt. percent to about 95 wt. percent. The alumina-boria composites may be prepared by any of the many well-known techniques including precipitation, impregnation, coprecipitation, 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 alumina-boria in the process of this invention is not apparent but is believed to be related to the number of the residual hydroxyl groups occurring on the surface of the alumina-boria.

The above-described alumina-boria can be modified with boron trifluoride by various methods. The so-called modification of alumina-boria 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 alumina-boria at about room temperature. In general, the alumina-boria is contacted with the boron trifluoride at a predetermined temperature until boron trifluoride is no longer adsorbed, or otherwise taken up, by the alumina-boria. It has been observed that in the treatment of substantially anhydrous alumina-boria with boron trifluoride, the capacity of the alumina-boria 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 alumina-boria reaches a fixed maximum which is not further increased by contact with additional quantities of boron trifluoride at the given temperature. The capacity of alumina-boria for boron trifluoride increases with temperature. The exact manner in which the boron trifluoride acts to modify the alumina-boria is not understood. It may be that the modification results from complexing of the boron trifluoride with the alumina-boria, or on the other hand, it may be that the boron trifluoride reacts with the residual hydroxyl groups on the alumina-boria 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 alumina-boria wherein said alumina-boria has been thus 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 alumina-boria comprises placing the substantially anhydrous alumina-boria 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 alumina-boria. When the alumina-boria is thus treated with boron trifluoride it is noted that no boron trifluoride passes through the alumina-boria until substantially all of the alumina-boria has been modified by 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 the present invention relates to a process for shifting the double bond of 1-butene to produce 2-butene and comprises isomerizing said 1-butene at an isomerization temperature of from about 20° C. to about 250° C. in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous alumina-boria.

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

Still another preferred embodiment of this invention is in a process for shifting the double bond of 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 alumina-boria.

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 alumina-boria, the reaction zone being maintained under the 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 hydrocarbons 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 employed. Still another type of operation is the slurry or suspensoid type of operation in which the catalyst is carried as a slurry or suspension into a reaction zone.

In a batch type of operation the olefinic hydrocarbon and the boron trifluoride-modified alumina-boria 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 1 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 olefinic hydrocarbon to a more centrally located position results in a number of advantages. With respect to the catalytic activity of the boron trifluoride-modified alumina-boria, 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 isomerization of 1-butene in contact with said boron trifluoride-modified alumina-boria at a temperature of about 150° C., approaches thermodynamic equilibrium composition. In addition, the migration of the double bond is not usually accompanied by skeletal rearrangement within the molecule.

The boron trifluoride-modified alumina-boria 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 somewhat 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 alumina-boria 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 alumina-boria bed at a predetermined temperature whereby the desired catalyst composition 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

Alumina-boria was prepared by dissolving 400 grams of boric acid in 1600 grams of hot water. This mixture was then poured over 2370 grams of wet alumina 1/16" diameter spheres. After standing for about 1 hour, the mixture was filtered to remove water and the spheres then dried at 120° C. over a three-day period. After drying, the spheres were calcined for three hours at 500° C. They had an apparent bulk density of 0.499 gram per cubic centimeter. The alumina-boria had a surface area of 162 square meters per gram, a pore volume of 0.35 cubic centimeter per gram, and a pore diameter of 86 Angstrom units.

The above-described alumina-boria was treated with boron trifluoride by passing the same over the alumina-boria at 150° C. until boron trifluoride was observed in the effluent gas stream therefrom. After boron trifluoride modification, the alumina-boria contained 4.0 wt. percent boron and 4.5 wt. percent fluorine. At this time, and after the boron trifluoride modification, the surface area of the modified alumina-boria had been reduced to 131 square meters per gram, its pore volume to 0.30 cubic centimeter per gram and its pore volume was increased to 91 Angstrom units. It had an apparent bulk density of 0.547 gram per cubic centimeter, and its color was light gray.

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 alumina-boria at a rate of about 35 grams per hour per 60 cc. of catalyst utilized, an isomerization temperature of about 150° C., and at a pressure of about 525 p.s.i.g.

Example II

This example serves to illustrate 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 cubic centimeter reaction zone packed with 3/16" stainless steel helices, 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 III

A charge stock comprising 1-pentene, continuously charged through a fixed bed of about 30 grams of the

above-described boron trifluoride-modified alumina-boria 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 about 80% of the desired 2-pentene isomer of said 1-pentene.

Example IV

A charge stock comprising 1-hexene, continuously charged through a fixed bed of about 30 grams of the above-described boron trifluoride-modified alumina-boria at an isomerization temperature of 150° C., at 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 the 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 hydrocarbor molecule, which consists essentially of isomerizing said olefinic hydrocarbon in contact with a preformed combined boron trifluoride-alumina-boria catalyst prepared by treating substantially anhydrous alumina-boria with boron trifluoride at a temperature of from about 0° C. to about 250° C. until boron trifluoride no longer combines with the alumina-boria.

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-alumina-boria catalyst prepared by treating substantially anhydrous alumina-boria with boron trifluoride at a temperature of from about 0° C. to about 250° C. until boron trifluoride no longer combines with the alumina-boria.

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.

References Cited by the Examiner

UNITED STATES PATENTS

2,301,342	11/42	Sumerford et al.	260—683.2
2,939,890	6/60	Hervert et al.	260—671
3,054,836	9/62	Hervert et al.	260—671
3,114,785	12/63	Hervert et al.	260—683.2

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