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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 cen-
trally 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-zirconia.

It is generally well recognized that the high compres-
sion, 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 struc-
ture 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 hydro-
carbon components may be produced by the condensa-
tion of an isoparaffinic hydrocarbon with an olefinic hy-
drocarbon in the presence of an acidic condensation
catalyst, the process being generally referred to as alkyla-
tion. The more desirable alkylates of this process result
from the condensation of isoparaffins with olefinic hy-
drocarbons wherein the double bond of said olefinic hy-
drocarbon is in a centrally located position of the hydro-
carbon 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 di-
methylhexanes 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 alkyla-
tion 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 posi-
tion isomers, capable of undergoing isomerization to an
olefin in which the double bond occupies a more cen-
trally 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 ole-
finic 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 anhy-
drous silica-alumina-zirconia.

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

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, and n-butane and isobutane,
recovered for example, as the light vapor overhead prod-
uct 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 higher molecular weight ole-
finic hydrocarbons 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 in-
tended 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 lo-
cated position may be effected in straight or branched
chain olefinic hydrocarbons containing up to 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, silica-alumina-zirconia. The de-
scription "substantially anhydrous, but not completely
dry, silica-alumina-zirconia," means that the composites
have been calcined sufficiently so that they contain from
about 0.5 wt. percent to about 10 wt. percent water, on a
dry basis, and that the water is chemically and/or physi-
cally in combination with the composite. Silica-alumina-
zirconia composites are well known and may be prepared
by various techniques such as spray drying, precipitation,
co-precipitation, co-jelling, etc. They contain silica as a
major component (greater than 50%) and alumina and
zirconia in varying quantities, generally from about 1 to
about 25% by weight thereof. The exact reason for the
specific utility of silica-alumina-zirconia in the process of
this invention is not apparent but is believed to be related
to the number of residual hydroxyl groups occurring on
the surface of the silica-alumina-zirconia.

The above-described silica-alumina-zirconia can be
modified with boron trifluoride by various methods. The
so-called modification of silica-alumina-zirconia with bo-
ron 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-zirconia composite at about room temperature.
In general, the silica-alumina-zirconia is contacted with
the boron trifluoride at a predetermined temperature until
boron trifluoride is no longer adsorbed, or otherwise

taken up, by the silica-alumina-zirconia. It has been observed that in the treatment of substantially anhydrous silica-alumina-zirconia with boron trifluoride, the capacity of the silica-alumina-zirconia 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-zirconia 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-zirconia for boron trifluoride increases with temperature. The exact manner in which the boron trifluoride acts to modify the silica-alumina-zirconia is not understood. It may be that the modification results from complexing of the boron trifluoride with the silica-alumina-zirconia, or on the other hand, it may be that the boron trifluoride reacts with the residual hydroxyl groups on the silica-alumina-zirconia surface. In any case, the process of the present invention is preferably effected in contact with a catalyst comprising boron trifluoride-modified substantially anhydrous silica-alumina-zirconia wherein said silica-alumina-zirconia 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 silica-alumina-zirconia comprises placing the substantially anhydrous silica-alumina-zirconia 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-zirconia. When the silica-alumina-zirconia is thus treated with boron trifluoride it is noted that no boron trifluoride passes through the silica-alumina-zirconia until substantially all of the silica-alumina-zirconia 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 downstream over the catalyst as a deterrent to polymer formation thereon.

One preferred embodiment of the process of this 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 silica-alumina-zirconia.

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 from about 20° C. to about 250° C. in contact with an isomerization catalyst comprising a boron trifluoride-modified substantially anhydrous silica-alumina-zirconia.

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 silica-alumina-zirconia.

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 hydro-

carbon is continuously charged to a reactor containing therein a fixed catalyst bed comprising the boron trifluoride-modified silica-alumina-zirconia, 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 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 up flow 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 suspension type of operation in which the catalyst is carried as a slurry or a suspension into a reaction zone.

In a batch type of operation the olefinic hydrocarbon and the boron trifluoride-modified silica-alumina-zirconia 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 liquid hydrocarbon charge stocks 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 silica-alumina-zirconia, 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-zirconia 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-zirconia, 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. 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-zirconia 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-zirconia 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

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 cc. reaction zone packed with $\frac{3}{16}$ " 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 II

A substantially anhydrous silica-alumina-zirconia, composite, calcined for about 4 hours at 650° C., and comprising 3% alumina, 7% zirconia, and 90% silica, was treated with boron trifluoride. Prior to modification with the boron trifluoride as hereinafter set forth, the silica-alumina-zirconia had a surface area of 466 square meters per gram, a pore volume of 0.472 cubic centimeters per gram, and a pore diameter of 41 Angstrom units. It apparently still contained about 1.8% water which was the weight loss experienced on heating the silica-alumina-zirconia at 900° C.

The above-described silica-alumina-zirconia was treated with boron trifluoride by passing the same over the silica-alumina-zirconia at 150° C. until boron trifluoride was observed in the effluent gas stream therefrom. After boron trifluoride modification, the silica-alumina-zirconia contained 4.1 wt. percent boron and 8.1 wt. percent fluorine. The surface area of the modified silica-alumina-zirconia was reduced to 223 square meters per gram, its pore volume to 0.406 cubic centimeter per gram, and its pore diameter was increased to 73 Angstrom units. It had an apparent bulk density of 0.719 gram per milliliter and its color was gray-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-zirconia 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 III

A charge stock comprising 1-pentene, continuously charged through a fixed bed of about 30 grams of the above-described boron trifluoride-modified silica-alumina-zirconia 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 silica-alumina-zirconia 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 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 hydrocarbon molecule, which consists essentially of isomerizing said olefinic hydrocarbon in contact with a preformed combined boron trifluoride-silica-alumina-zirconia catalyst prepared by treating substantially anhydrous silica-alumina-zirconia 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-zirconia.

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-zirconia catalyst prepared by treating substantially anhydrous silica-alumina-zirconia 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-zirconia.

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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