United States Patent Office 2,952,719 Patented Sept. 13, 1960

2,952,719

PROCESS FOR SHIFTING A DOUBLE BOND IN AN OLEFINIC HYDROCARBON

Herbert R. Appell, North Riverside, Ill., assignor, by mesne assignments, to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

No Drawing. Filed Apr. 14, 1958, Ser. No. 728,096

6 Claims. (Cl. 260—683.2)

This invention relates to a process for shifting the double bond in an olefinic hydrocarbon to a more centrally located position therein, and more particularly relates to a process for shifting the double bond in a 1-olefin containing more than three carbon atoms to a more centrally located position in said olefin, and still more particularly relates to a process for the conversion of 1-butene to 2-butene.

The recent introduction of automobile engines of high compression ratios has led to the need for the utilization of processes in the petroleum refining industry for the production of extremely high antiknock hydrocarbons as fuels. One process for the production of such high antiknock hydrocarbons is the catalytic alkylation of isoparaffin hydrocarbons with olefins. In this alkylation process various catalytic agents have been suggested including concentrated sulfuric acid and liquid hydrogen fluoride. With these catalytic agents, for example, the alkylation of isobutane with four carbon atom olefin fractions or streams has been practiced commercially on a wide scale. There has been a general feeling in the practice of these alkylation processes, however, that utilization of 2-butene as the primary olefinic hydrocarbon results in the production of higher octane number alkylate product than does the utilization of 1-butene. As the demand for higher and higher octane number motor fuels has increased, the necessity for the development and utilization of a process for the conversion of 1-butene to 2-butene has widened. Various processes for such double bond shifting have been suggested in the prior art. However, in the main, these processes have been relatively high temperature ones in which the shifting of the double bond has been limited by equilibrium considerations. It is an object of the present invention to provide a process which can be utilized at relatively low temperatures, in liquid or vapor phase as may be desired, and in a continuous manner for long periods of time if so desired, to obtain equilibrium conversions of 1-olefins to olefins in which the double bond is more centrally located. In this manner the degree of branching of the product from the catalytic alkylation of isoparaffins with these olefins is increased. This increased branching as is well known in the prior art results in increased octane number of the alkylate product.

One embodiment of this invention relates to a process for shifting the double bond in an olefinic hydrocarbon to a more centrally located position therein which comprises subjecting said olefinic hydrocarbon to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of hydrogen and a catalyst comprising an alkali metal disposed on a support, and recovering the resultant product.

Another embodiment of the present invention relates to a process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of hydrogen and a catalyst comprising an alkali metal disposed on a precalcined high surface area support, and recovering the resultant product.

A further embodiment of the present invention relates to a process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of hydrogen and a catalyst comprising sodium disposed on a precalcined high surface area alumina support, and recovering the resultant product.

A specific embodiment of this invention relates to a process for shifting the double bond in 1-butene to 2-butene which comprises subjecting said 1-butene to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of hydrogen and a catalyst comprising sodium disposed on a precalcined high surface area alumina support, and recovering the resultant product.

In the last few years the prior art has disclosed the use of alkali metals as catalysts for various reactions including some hydrocarbon conversion reactions, more specifically, olefin isomerization reactions. This prior art, however, discloses minimum operable temperatures for these reactions in the neighborhood of about 150° C. In some instances the use of extremely high pressures such as over 100 atmospheres has been disclosed as necessary. Attempts to overcome the necessity for such high pressures has led to the discovery of the use of certain so-called promoters for these alkali metals. However, while the use of such promoters has resulted in the discovery that lower pressures are operable, the use of operating temperatures in the neighborhood of about 150° C. or higher has still been considered necessary. It has recently been discovered that these operating temperatures can be substantially lowered by the simple expedient of disposing the alkali metal catalyst on a support, and that the resultant composite is effective for shifting the double bonds in olefins at relatively moderate pressures in the absence of any added catalyst promoter. This discovery is important not only because of the economies in necessary equipment which may be achieved during the utilization of the process, but also because of equilibrium considerations. For example, utilizing 1-butene as the olefin, at 277° C. a conversion to 84% of 2-butene is maximum. A lowering of the reaction temperature to 27° can increase this theoretical conversion per pass to greater thn 95% of 2-butene. As set forth hereinabove, such an increase in 2-butene content in an olefin stream utilized for reaction with an isoparaffin to produce high octane number alkylate is extremely important from the octane number standpoint of the alkylate. Furthermore, alkali metals disposed on supports result in catalytic composites which can be utilized as fixed beds in reaction zones and which thus lend themselves to adoption in processes of the so-called fixed bed type which are extremely desirable for adoption on

a commercial scale. These catalytic composites comprising alkali metals disposed on supports, however, have been found to suffer from one inherent disadvantage in spite of the fact that they are extremely active and can be utilized at the low temperatures set forth hereinabove. These catalytic composites tend to deactivate relatively rapidly during use as a fixed bed for the isomerization of double bonds in olefinic hydrocarbons. It has now been discovered that this deactivation can be substantially reduced, or for all practical purposes eliminated, by the concurrent passage of hydrogen along with the olefinic hydrocarbon being subjected to double bond isomerization over the catalyst comprising an alkali metal disposed on a support. This is surprising since the hydrogen apparently has no chemical effect during the reaction and since the concurrent use thereof might be expected to saturate at least some of the double bonds present in the olefinic hydrocarbon feed stock. However, such is not the case, and long catalyst life has now been achieved in a most practical manner by the simple expedient of hydrogen utilization. Since substantially no hydrogen is consumed in the reaction, the hydrogen may be readily separated from the reaction products by well known means and recycled to the reaction zone for reuse therein. This outstanding feature of the process of the present invention will be described further in detail hereinafter.

The olefinic hydrocarbons which are utilized in the process of this invention all contain more than three carbon atoms and may be derived from various sources. As pointed out hereinabove, the process of the present invention is particularly suited for or adapted to conversion of 1-butene to 2-butene. The 1-butene may be charged to the process of this invention in pure form or in admixture with other hydrocarbons including any or all of 2-butene, isobutylene, normal butane, isobutane, etc. By the proper balance of the isobutane content of such a mixture, it will be recognized that the mixture may be a typical alkylation feed stock. Thus, the process of the present invention may be utilized for the conversion of the 1-butene content in an alkylation feed stock to 2-butene prior to utilization of the feed stock in the alkylation reaction. The process of the present invention can likewise be utilized for shifting of the double bond in n-amylenes or isoamylenes to produce amylenes in which the double bond is in a more centrally located position. Likewise, hexenes such as 1-hexene or 2-hexene can be converted to 2- or 3-hexene by utilization of the process of this invention. This double bond shifting reaction of 1-olefins or alpha-olefins to olefins in which the double bond is in a more centrally located position is readily adaptable to many feed stocks as disclosd in the prior art. For example, the process may be utilized with feed stocks comprising 1-olefins such as 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, etc., 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-1-hexene, 3-methyl-1-hexene, 4-methyl-1-hexene, 5-methyl-1-hexene, 2-methyl-2-hexene, 3-methyl-3-hexene, 4-methyl-3-hexene, 5-methyl-3-hexene, 2-methyl-1-heptene, 3-methyl-1-heptene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 2-methyl-2-heptene, 3-methyl-2-heptene, 4-methyl-2-heptene, 5-methyl-2-heptene, 6-methyl-2-heptene, 2-methyl-1-octene, 3-methyl-1-octene, 4-methyl-1-octene, 5-methyl-1-octene, 6-methyl-1-octene, 7-methyl-1-octene, etc While the present invention is discussed in detail in relation to the shifting of the double bond in 1-butene to produce 2-butene, this discussion is introduced merely for the purpose of convenience and with no intention of limiting the olefinic hydrocarbons which can be converted in accordance with this process.

As set forth hereinabove, the process for shifting the double bond in an olefinic hydrocarbon to a more centrally located position in an olefinic hydrocarbon is effected in the presence of hydrogen and in the presence of an alkali metal catalyst. The alkali metal catalysts utilizable in the process are selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium, or mixtures thereof. Of these alkali metals, the more plentiful and less expensive sodium and potassium are preferred, either alone or in admixture with one another. These alkali metals are disposed on a support in a quantity ranging from about 2% to about 30% by weight based on the support. Not every support can be utilized as a satisfactory one for disposal of an alkali metal thereon. As is well known, the alkali metals react violently with water and thus care must be taken to utilize a support which is relatively or substantially free from water. In most cases this freedom from water of the support is achieved by precalcination of the support. This precalcination is usually carried out at relatively high temperature, for example, in the range of from about 400° to about 700° C. and for a time sufficient to effect substantial removal of adsorbed or combined water from the support. These times will vary depending upon the support, and depending upon whether the water is in a combined or in merely a physically adsorbed form. In addition to the necessity for freedom from water, the support is additionally characterized in the necessity for having a high surface area. By the term high surface area is meant a surface area measured by adsorption techniques within the range of from about 25 to about 500 or more square meters per gram. For example, it has been found that certain low surface area supports such as alpha-alumina which is obviously free from combined water and which has been freed from adsorbed water is not a satisfactory support for the alkali metals in the preparation of the catalysts for use in the process of this invention. Alpha-alumina is characterized by a surface area ranging from about 10 to about 25 square meters per gram. In contrast to alpha-alumina, gamma-alumina which has a surface area ranging from about 100 to about 300 square meters per gram, and which has been freed from adsorbed water, and which contains no combined water, is a satisfactory support. Celite, a naturally occurring mineral, after precalcination, is not a satisfactory support. Celite has a surface area of from about 2 to about 10 square meters per gram. Likewise, alkali metal dispersions on sand or other low surface area silicas are not satisfactory catalysts in this process. In addition, aluminas which contain combined water but which have relatively high surface area are also not satisfactory supports. Such aluminas include dried alumina monohydrates which have not been sufficiently calcined to remove combined water and to form gamma-alumina. These alumina hydrates may have surface areas ranging from about 50 to about 200 square meters per gram but because they contain combined water are not satisfactory supports. Particularly preferred supports for use in preparation of catalysts utilized in the process of this invention include high surface area crystalline alumina modifications such as gamma-alumina and theta-alumina, high surface area silica, charcoals, magnesia, silica-alumina, silica-alumina-magnesia, etc. However, as is obvious from the above discussion, the limitation of the use of any particular support is one of freedom from combined or adsorbed water in combination with the surface area of the selected support.

The alkali metal may be disposed on a support in any suitable manner. One manner which has been found particularly advantageous is vaporization of the alkali metal and passage of the vapors over the support. In this manner of preparation care must be taken to utilize relatively low temperatures since heat is given off on contact of the alkali metal with the support and since high temperatures tend to destroy the amount of surface in the

support, and may also cause certain chemical reactions of the support with the alkali metals which are detrimental to catalytic activity. Sodium melts at about 97° C. and in impregnating a selected support with sodium it is preferred to carry out the impregnation or disposal of the sodium thereon at temperatures in the range of from about 100° to about 150° C. This can be accomplished, for example, by melting sodium and dropping the molten sodium on the support or by passage of a stream of inert gas such as nitrogen or argon through the molten sodium and over a bed of the selected support disposed in a separate zone maintained at the desired temperature with cooling or heating means connected therewith. Potassium melts at about 62° C. and thus the impregnation of a selected support with potassium can be carried out at lower temperatures. Potassium disposed on one of the above mentioned supports appears to be a more active catalyst for the reactions disclosed herein than does sodium and this difference in activity may be due to the lower temperatures which can be used in the disposal of potassium on the support. Supported lithium catalysts appear to be less active and this may be a reflection of the higher melting point of lithium, 186° C., and the higher temperatures which must occur on contact of the lithium with the support. Furthermore, disposal of the selected alkali metal on the support must be carried out in a manner so that the high surface area of the support in combination with the alkali metal is not destroyed by incorporation of excess quantities of the alkali metal therein. In other words, the pores and passage ways of the support can be filled and blocked by the addition of excess quantities of the alkali metal. This is obviously undesirable and supported alkali metals containing excess alkali metal are likewise inactive in the process.

As set forth hereinabove, catalysts of the alkali metal type disposed on a support and prepared in the manner described may be utilized in the process in a manner which enables the process to be carried out at so-called mild operating conditions. As set forth hereinabove, the thus prepared catalysts are particularly adapted for use in so-called fixed bed processes. The double bond shifting reaction of the present invention can thus be carried out in the presence of these catalysts at temperatures in the range of from about 0° to about 100° C. and at pressures ranging from atmospheric to about 100 pounds per square inch or more. Pressure does not appear to be a critical variable in the process since the conversion reaction may be carried out in either liquid phase or vapor phase. Thus, the pressure utilized may be selected purely from the most advantageous pressure based upon economic considerations and upon the stability of the particular olefinic hydrocarbon charged to the process under the necessary processing conditions. In carrying out the process of this invention in a continuous manner, hourly liquid space velocities based upon the quantity of olefinic hydrocarbon charged may be varied within the relatively wide range of from about 0.1 to about 20 or more, equilibrium conversions being attained within the range of from about 0.1 to about 10. If equilibrium conversion of the olefinic hydrocarbon to the double bond isomer thereof is not necessary, higher space velocities may be utilized to attain the preselected approach to equilibrium conversion.

The attainment of the desired shifting of the double bond in an olefinic hydrocarbon to a more centrally located position is accomplished by the process of the present invention in the absence of so-called alkali metal catalyst promoters as taught by the prior art. These promoters include organic compounds capable of reacting with a portion of the alkali metal and forming organometallic compounds in situ during the residence time of the reactants in the reaction zone in the presence of the alkali metal. Heretofore it has been considered necessary to utilize such promoters to carry out the process of this invention at so-called moderate pressures and temperatures. As set forth hereinabove, it has now been found that such promoters are not needed and that the reaction may be carried out at relatively low pressures and temperatures by utilization of the alkali metal disposed on a preselected support.

In utilizing these catalytic composites comprising alkali metals disposed on supports at low temperature conditions, at moderate pressures, and at space velocities preselected for desired conversion, one deficiency in their ability to promote the process has been noted. These supported alkali metal catalytic composites are all extremely active initially. However, in use they tend to lose some of this activity for reasons which are not understood. For example, a catalyst composite comprising sodium disposed on alumina which gives equilibrium conversion of 1-butene to 2-butene at room temperature, at 300 p.s.i.g., and at 16 hourly liquid space velocity, decreases in activity to about one-half of its original activity in a relatively short period of time. This decrease in activity is, of course, undesirable when an attempt is made to utilize these catalytic composites commercially since suitable commercial catalytic composites must not only exhibit desired activity but must also have the property of relatively long life in use. This is particularly true of so-called fixed bed type catalysts where it becomes necessary to open reactors, remove spent catalyst, and replace the same. As is readily apparent to one skilled in the art, these steps require time which could otherwise be utilized for additional processing. As set forth hereinabove, it has now been found that the initial activity of these catalytic composites can be substantially retained during long periods of use when the processing of the olefinic hydrocarbon over these catalytic composites is conducted in a hydrogen atmosphere. The quantity of hydrogen utilized along with the olefinic hydrocarbons does not appear to be critical and thus may vary over a relatively wide range of from about 0.01 to about 10 mols of hydrogen per mol of olefinic hydrocarbon. As is the case with pressure discussed hereinabove, the selection of the exact amount of hydrogen utilized can be based on economic considerations. This hydrogen may be introduced along with the olefinic hydrocarbon or may be introduced at multipoints in the reactor and its desirable effect maintained under either processing scheme. Furthermore, it has been found that passage of hydrogen over previously deactivated catalytic composites comprising alkali metal disposed on a support tends to reactivate the catalyst and that this reactivated catalyst may be successfully utilized for processing as herein discussed. For example, these supported alkali metal catalysts are useful catalysts for polymerization reactions, such as the polymerization of ethylene or isobutylene. After such use their activity for the double bond shifting reaction in the process of the present invention is decreased. This activity can be restored to a high level and these catalysts utilized for long periods of time by the simple expedient of treating the thus deactivated composite with hydrogen and then utilizing hydrogen along with the olefinic hydrocarbon being charged to the process in accordance with the present invention. After passage of the olefinic hydrocarbon and hydrogen over a bed of this catalyst composite, the hydrogen may be separated from the olefinic hydrocarbon by means well known in the art including high pressure separation, flashing under pressure, by fractionation, etc. The hydrogen which is thus recovered is then compressed to a preselected pressure and may again be recycled and reused in this process. Hydrogen consumption by reaction with the olefinic hydrocarbon in this process is for all practical purposes negligible. Most hydrogen loss is due to solubility in the hydrocarbons after processing and thus it has been found that makeup hydrogen is usually needed only in an amount to balance that which is soluble in the hydrocarbons under the con-

ditions of temperature and pressure utilized for the separation of the hydrogen from the hydrocarbons. The hydrogen utilized may be in pure form or it may be diluted with various inert materials including nitrogen, methane, ethane, etc., which have little or no effect on the reaction or upon the catalytic composite comprising an alkali metal disposed on a support. In commercial refinery operations such hydrogen is readily available as a byproduct from catalytic reforming, for example. However, since such hydrogen usually contains minor quantities of oxygenated compounds or hydrogen sulfide, it is usually advisable to purify the same for the removal of such impurities which will react with or deactivate the presently disclosed catalytic composites.

The following examples are introduced for the purpose of illustration of specific embodiments of this invention but with no intention of unduly limiting the above disclosed generally broad scope of this invention.

EXAMPLE I

This example was carried out and is described herein for comparative purposes. The catalyst utilized in this experiment was 16.6% sodium disposed on alumina. The alumina utilized was in the form of 1/16 inch spheres which had been precalcined at 650° C. in a nitrogen atmosphere to insure freedom from adsorbed and combined water. These alumina spheres after calcination had a surface area of about 180 square meters per gram and an apparent bulk density of about 0.5 grams per milliliter. X-ray diffraction analyses showed that they were substantially anhydrous gamma-alumina.

The disposal of sodium on these gamma-alumina spheres is carried out by placing the spheres in a glass flask equipped with heating and stirring means. The flask is purged with nitrogen to insure freedom from air. The temperature of the spheres is then raised to about 150–170° C., and sufficient molten sodium added thereto during stirring to attain the desired sodium content on the spheres. As stated above, these spheres after preparation contained 16.6% by weight of sodium.

A sample of the above spheres, 100 milliliters, was placed as a fixed bed in a reaction tube in a bench scale plant. The bench scale plant contained as auxiliary equipment, pumps, heating and cooling means for the reaction tube, product collection vessels for both gaseous and liquid products, and product removal means. This particular experiment was carried out at 300 p.s.i.g., approximately 16.0 hourly liquid space velocity, and with no heating or cooling of the reaction tube. The temperature was allowed to seek its own level in the catalyst bed and the hot spot in the bed produced by the reaction was followed as well as the average catalyst temperature. The feed stock used in this experiment was technical 1-butene.

This experiment was divided into four periods, the first three of one hour duration each, and the last period of one-half hour duration. The analyses which are presented hereinafter for each period were obtained from the product for the last 7½ minutes of each period. In period 1 a hot spot was observed in the catalyst bed, the temperature reaching 86° C. This obviously indicates high initial catalyst activity. The average catalyst temperature attained was 50° C. The product analysis from period 1 is as follows: 1-butene, 9.2 mol percent; cis-2-butene, 35.6 mol percent; trans-2-butene, 52.4 mol percent; and 2.8 mol percent other materials to balance. This result shows that conversion to equilibrium is readily attained. By period 2 the peak catalyst temperature had already dropped to 80° C. and the average catalyst temperature was 42° C. The analysis of the product from period 2 is as follows: 1-butene, 33.4 mol percent; cis-2-butene, 54.6 mol percent; trans-2-butene, 10.9 mol percent; and 1.1 mol percent other materials to balance. This result from the end of period 2 shows that the catalyst is already declining in conversion activity. Not only is the 1-butene content of this product high, but the cis to trans ratio in the 2-butene portion of the product is higher than the equilibrium figure. During period 3 the peak catalyst temperature again dropped to 53° C. and the average catalyst temperature was 37° C. The product analysis at the end of period 3 is as follows: 1-butene, 46.7 mol percent; cis-2-butene, 44.2 mol percent; trans-2-butene, 7.5 mol percent; and 1.6 mol percent other materials to balance. This again shows the catalyst is rapidly declining in activity, the 1-butene content of the effluent having risen again and the cis to trans ratio of the product still going higher. Period 4 was continued for only one-half hour since the supply of 1-butene was rapidly diminishing. During the period, the peak temperature attained was 44° C. and the average catalyst temperature was 32° C. The analysis of the effluent for the last 7½ minutes of this one-half hour period is as follows: 1-butene, 55.2 mol percent; cis-2-butene, 38.9 mol percent; trans-2-butene, 5.4 mol percent; and 0.5 other materials to balance. Here again, the 1-butene content of the effluent is higher as is the cis to trans ratio of the 2-butene portion of the product.

This example and experiment illustrate that sodium disposed on alumina is an olefin isomerization catalyst but that the activity of this catalyst rapidly decreases in use in the absence of added hydrogen. This effect of added hydrogen will be set forth in the following examples.

EXAMPLE II

In this example another 100 milliliter sample of the 16.6 weight percent sodium disposed on alumina described in Example I was utilized. This experiment was carried out in the same equipment described in Example I. The feed stock again was technical 1-butene. Conditions utilized in this example again include ambient temperature, 300 p.s.i.g. and about 16.0 hourly liquid space velocity for periods 1 and 2, and 0 p.s.i.g. and 0.85 hourly liquid space velocity for periods 3 and 4. During this experiment there was added approximately 0.36 cubic feet per hour of hydrogen. Prior to use this catalyst was treated with hydrogen at 200° C., 300 p.s.i.g., for two hours.

Period 1 had a duration of 30 minutes and a catalyst hot spot of 86° C. was observed. This catalyst hot spot corresponds to that observed during period 1 in Example I. No analysis of the period 1 product was obtained. The product from period 2 which had a duration of 7.5 minutes was analyzed. In contrast to period 2 in Example I, during which the catalyst peak temperature dropped to 80° C., indicating loss in catalyst activity, the catalyst peak temperature for the period 2 remained at 86° C. The product analysis is as follows: 1-butene, 9.0 mol percent; cis-2-butene, 37.9 mol percent; trans-2-butene, 52.2 mol percent; and 0.9 mol percent other materials to balance.

From the maintenance of the peak temperature in the catalyst bed and from the fact that conversion is maintained at a high level at the end of period 2, it is obvious that the presence of hydrogen results in the process being stabilized. In experiments in which hydrogen is not added, a relatively rapid decline in peak temperature with time occurs as well as a deterioration of product quality.

At this point the process conditions were changed to 0 p.s.i.g. and an hourly liquid space velocity of 0.85. The drop in pressure results in the reaction system changing from liquid phase to vapor phase operation. Period 3 was carried out for one hour and 20 minutes duration during which time the catalyst hot spot decreased to 36° C. and remained there. Then, period 4 was carried out for 15 minutes during which time the effluent was collected for analysis. During period 4 the catalyst peak temperature remained at 36° C., the same as had been

observed in period 3. The analysis of the product from period 4 is as follows: 1-butene, 6.9 mol percent; cis-2-butene, 33.5 mol percent; trans-2-butene, 59.1 mol percent; and 0.5 mol percent other materials to balance.

From the analysis of the effluent from period 4 it is obvious that the catalyst has maintained its activity through the change from liquid phase to vapor phase and over the additional hour and 35 minutes processing period. Equilibrium conversion of 1-butene to 2-butene isomers was attained at the end of period 4 even though the peak catalyst temperature was 36° C. This is indicative of exceptionally high catalyst activity.

EXAMPLE III

This example illustrates the utilization of a catalyst comprising sodium disposed on alumina without hydrogen addition, with hydrogen reactivation between periods, and then the stabilization of catalyst activity by the utilization of additional hydrogen during processing. The experiment described in this example was carried out in the same apparatus described hereinabove in Example I.

In this example a catalyst was prepared utilizing 45.7 grams of the same gamma-alumina described in Example I which had been calcined at 650° C. Since this gamma-alumina had been kept in storage, prior to use in the catalyst preparation, it was calcined at 500° C. to remove adsorbed water. This calcined and dried alumina was poured while hot into a glass flask equipped with heating and stirring means. Nitrogen was passed through the flask to flush out air and when the temperature of the alumina being stirred cooled to about 100° C., 5 grams of molten sodium were added batchwise in three portions. Stirring was continued until all of the sodium was absorbed by the alumina. The catalyst was uniformly dark at completion and contained 9.8 weight percent sodium.

This catalyst, comprising 100 milliliters, was then placed as a fixed bed in the reaction tube. The temperature of the mass was raised to about 100° C. and hydrogen passed therethrough for two hours at 300 p.s.i.g. Processing conditions utilized in this experiment include 300 p.s.i.g., approximately 16 hourly liquid space velocity, and no heating or cooling on the reactor so that the temperatures attained during reaction would be indicative of the amount of heat given off and thus catalyst activity. The feed stock utilized was technical 1-butene.

Period 1 of this experiment was carried out for 30 minutes during which time an average catalyst temperature of 66° C. and a peak catalyst temperature of 94° C. were attained. Then, period 2 was started and the product collected for 7½ minutes. The effluent from period 2 analyzed as follows: 1-butene, 33.7 mol percent; cis-2-butene, 36.9 mol percent; trans-2-butene, 26.5 mol percent; and other materials to balance, 2.9 mol percent. During period 2 it was noted that the average catalyst temperature dropped 3° C. although the peak temperature remained the same at 94° C.

Since the activity of this catalyst did not result in the attainment of equilibrium conversion, an attempt was made to activate or reactivate the same by a treatment with hydrogen. Therefore, hydrogen was again passed over the catalyst for two hours at 100° C. in the absence of hydrocarbons. Period 3 was then carried out for 30 minutes time and an average catalyst temperature of 61° C. and a peak catalyst temperature of 82° C. were observed. Then, another test for analysis of 7½ minutes duration was started. The results of the analysis of the period 4 reaction zone effluent are as follows: 1-butene, 35.9 mol percent; cis-2-butene, 42.6 mol percent; trans-2-butene, 16.2 mol percent; and other materials to balance, 5.3 mol percent. During period 4 the average catalyst temperature again dropped, this time to 57° C., and the peak catalyst temperature observed was 81° C. From the gradual decline in peak catalyst temperatures, and from the fact that the cis- to trans-2-butene ratio was increasing, it was apparent that the activity of the catalyst was not stabilized.

Prior to period 5, hydrocarbons were removed from the plant and the catalyst was treated with hydrogen for two hours at 200° C. in an attempt to reactivate and stabilize the same. Period 5 was carried out for 30 minutes time during which an average catalyst temperature of 80° C. and a peak catalyst temperature of 84° C. was observed. Then, period 6 was carried out for 7½ minutes and the product collected and analyzed. This analyuct is as follows; 1-butene, 24.5 mol percent; cis-2-butene, 40.3 mol percent; trans-2-butene, 17.5 mol percent; and other materials to balance, 1.4 mol percent. During period 6 the average catalyst temperature declined to 58° C. from the 80° C. observed during period 5, but the peak temperature only declined to 81° C. from the 84° C. observed in period 5. It was again obvious that the catalyst did not have a stable activity.

Therefore, the catalyst was again treated with hydrogen for two hours at 200° C. and during periods 7 and 8, 0.36 cubic feet of hydrogen per hour was added along with the hydrocarbon feed. During period 7, which lasted for one-half hour, the average catalyst temperature was 41° C. and the peak catalyst temperature was 78° C. Period 8 was another 7½ minute test carried out to obtain product for analysis. Analysis of the period 8 product is as follows: 1-butene, 24.5 mol percent; cis-2-butene, 56.4 mol percent; and trans-2-butene, 19.1 mol percent. During period 8 the average catalyst temperature was 42° C. which indicates maintenance of activity through periods 7 and 8. Likewise, the peak catalyst temperature remained at 78° C., the same as had been for period 7. These last two results indicate that the activity of the catalyst is stabilized by the addition of hydrogen during processing. Furthermore, comparison of the results from period 8 with those obtained from periods 2, 4, and 6 show that the catalyst was not only stable during periods 7 and 8, but was also more active for the double bond shifting reaction of the present invention, in particular the conversion of 1-butene to 2-butene.

EXAMPLE IV

This example illustrates the utilization of a catalyst comprising sodium disposed on alumina for the double bond shifting of 1-butene to 2-butene in the presence of hydrogen. In this example the feed utilized was a commercial C_4 fraction analyzing as follows: propane, 3.3 mol percent; propylene, 0.9 mol percent; isobutane, 27.8 mol percent; normal butane, 34.3 mol percent; 1-butene, 7.5 mole percent; isobutylene, 8.7 mol percent; cis-2-butene, 6.6 mol percent; trans-2-butene, 9.4 mol percent; and 2-methylbutane, 1.5 mol percent. In this example another 100 milliliters of the same catalyst described in Example I was utilized. This catalyst comprises 16.6% sodium disposed on 1/16 inch gamma-alumina spheres which have been precalcined at 650° C. Prior to use, the feed was purified by passage through a scrubber containing sodium-potassium alloy. This experiment was carried out at 300 p.s.i.g., approximately 16 hourly liquid space velocity, and no heating or cooling of the reaction tube. Here again, the temperature was allowed to seek its own level in the catalyst bed. Since the 1-butene content of the feed is low, very little, if any, heat was given off and thus the temperature remained constant at about 25° C. all through the various processing periods. Each processing period was of a one hour duration and the product from the last 7½ minutes of each hour was collected and analyzed. During the experiment hydrogen addition was maintained constant at about 0.40 cubic feet of hydrogen per hour. The results of the analyses for the last 7½ minutes of each period are presented in the following table.

Table I

ISOMERIZATION OF 1-BUTENE TO 2-BUTENE IN A COMMERCIAL C_4 FRACTION IN THE PRESENCE OF HYDROGEN AND ALUMINA CONTAINING 16.6% SODIUM

Feed	Mol percent of feed	Period									
		1	2	3	4	5	6	7	8	9	10
Propane	3.3	3.3	3.1	3.4	3.2	2.8	2.7	2.9	3.2	2.9	2.9
Propylene	0.9	0.8	0.8	0.8	0.8	0.7	0.8	0.9	0.8	0.7	0.7
Isobutane	27.8	28.3	28.9	29.6	27.4	26.6	27.6	28.6	28.6	28.3	28.4
n-Butane	34.3	36.5	34.9	34.3	35.5	35.1	34.5	33.7	34.6	35.1	35.5
1-butene	7.5	3.0	2.3	2.2	1.8	1.7	2.2	2.0	1.2	1.4	2.8
Isobutylene	8.7	6.5	7.6	8.0	8.3	8.5	8.2	8.5	9.7	9.3	6.3
Trans-2-butene	9.4	10.7	11.3	11.0	10.9	11.7	11.5	11.3	11.0	11.3	11.2
Cis-2-butene	6.6	9.2	9.6	9.3	9.8	10.4	10.6	10.2	9.8	9.9	10.0
2-methylbutane	1.5	1.7	1.5	1.4	2.1	2.5	1.9	1.9	1.1	1.1	1.2

From the above table it will be noted that the 1-butene content of the feed was decreased to approximately 25% of its original content at periods 1 through 10. The results at period 10 show that the catalyst was still maintaining its activity. In a like manner, the cis-2-butene content of the products shows that an increase from about 6.5 mol percent up to about 10 mol percent was observed. Some of the 1-butene converted to trans-2-butene since the product analyses show about 11 mol percent trans-2-butene in comparison to about 9.5 mol percent in the feed. These results show the operability of the process of the present invention and that the presence of hydrogen stabilizes the catalyst so that the activity does not descrease with time. These results are accomplished without substantial change in any of the other components in the commercial C_4 fraction. The resultant C_4 fraction produced by the process of this invention is more suitable as a feed stock for the alkylation of isobutane with butenes since the higher 2-butene content of the product will result in an alkylate having a higher octane number.

I claim as my invention:

1. A process for shifting the double bond in an olefinic hydrocarbon to a more centrally located position therein which comprises subjecting said olefinic hydrocarbon to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

2. A process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

3. A process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous silica support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

4. A process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous alumina support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

5. A process for shifting the double bond in a 1-olefin to a more centrally located position therein which comprises subjecting said 1-olefin to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous charcoal support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

6. A process for shifting the double bond in 1-butene to 2-butene which comprises subjecting said 1-butene to double bond isomerization at a temperature of from about 0° to about 100° C. in the presence of from about 0.01 to about 10 mols of added hydrogen per mol of olefin and a catalyst comprising an alkali metal disposed on a substantially anhydrous area alumina support having a surface area of from about 25 to about 500 square meters per gram, and recovering the resultant product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,375,687	Peterson et al.	May 8, 1945
2,740,820	Wilson et al.	Apr. 3, 1956
2,836,633	Esmay et al.	May 27, 1958
2,863,923	Bortnick	Dec. 9, 1958

OTHER REFERENCES

J.A.C.S., vol. 77, pp. 347 and 348, Jan. 20, 1955.