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2,994,727

PROCESS FOR THE PREPARATION OF SPECIFIC GEOMETRIC OLEFIN ISOMERS

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This invention relates to a process for the preparation of specific geometric olefin isomers, and more particularly relates to a process for shifting the double bond in an alpha-olefin containing more than three carbon atoms to a more centrally located position in said olefin and simultaneously therewith producing one geometric olefin isomer in quantities larger than predicted by equilibrium values. Still more specifically, this invention relates to a process for the conversion of 1-butene to a mixture of cis- and trans-2-butene in which the ratio of cis to trans isomers is greater than the equilibrium value. Still more specifically, this invention relates to a process for the separation of isobutylene from a four carbon atom olefin hydrocarbon fraction.

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 isoparaffins 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. Furthermore, these four carbon atom olefin hydrocarbon fractions or streams usually contain substantial quantities of isobutylene in addition to 1-butene and 2-butene. In these higher temperature double bond shifting processes suggested in the prior art polymerization of the isobutylene in these four carbon atom olefin hydrocarbon streams or fractions usually takes place concurrently with the double bond shifting reaction. This occurs because isoolefins polymerize more readily than do n-olefins. In addition, this isobutylene polymerization is not simple self polymerization but usually involves some of the other olefinic hydrocarbons present in so-called cross polymerization. To avoid this difficulty, the prior art suggests selective removal of isobutylene from these streams by cold acid treatment followed by double bond shifting. It has now been discovered that this two step process is no longer necessary and can be replaced by a single step process by the utilization of the process of the present invention. 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 if so desired, to obtain conversion of alpha-olefins to a mixture of cis and

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trans olefins in which the double bond is more centrally located and in which the ratio of cis to trans isomers is greater than the equilibrium value, and without concurrent isoolefin polymerization or cross polymerization taking place. In this manner the degree of branching of the product from catalytic alkylation of isoparaffins with these olefins is increased since alpha-olefins are eliminated from the olefin feed stock to the catalytic alkylation process. This increased branching of the product from catalytic alkylation, as is well known in the prior art, results in increased octane number of the alkylate product.

Furthermore, the process of the present invention has additional utility resulting from the ability to shift the double bond in alpha-olefins to a more centrally located position without concurrent isoolefin polymerization. This can perhaps be best understood from the most simple illustration thereof. The respective boiling points of the four carbon atom olefin hydrocarbons are presented in the following table:

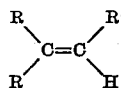
TABLE I

Boiling points of four carbon atom olefins

	° C.
Isobutylene	-6.9
1-butene	-6.3
Trans-2-butene	0.88
Cis-2-butene	3.7

From this table it is readily observed that isobutylene cannot be satisfactorily fractionated from a mixture of four carbon atom olefins since its boiling point of -6.9° C. is only 0.6° C. different from the boiling point of 1-butene. Conversion of the 1-butene to 2-butene without isobutylene polymerization leads to a mixture of isobutylene and 2-butene which can be separated by fractionation due to the difference in boiling point of almost 8° C. Furthermore, if the ratio of cis-2-butene can be increased to greater than that of the equilibrium value, this further enhances the utility of the separation process since cis-2-butene has a boiling point 10.6° C. above the boiling point of isobutylene. Isobutylene is in wide demand in the chemical industry, particularly for the introduction of tertiary butyl radicals into aromatic compounds by the alkylation process. Since it is obvious from the above table that isobutylene cannot be separated by fractionation from other four carbon atom olefins, it is now prepared for such uses by selective polymerization from such mixtures, fractionation of the polymer and depolymerization. The process of the present invention provides a means by which isobutylene can be directly separated from four carbon atom olefin hydrocarbon streams or fractions by a simple one step conversion process followed by fractionation. Furthermore, this fractionation which results in the production of an overhead isobutylene product, also results in the production of a bottoms 2-butene product which is a particularly desirable four carbon atom olefin for use for the alkylation of isobutane.

One embodiment of this invention relates to a process for preparing a cis and trans olefin mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises passing an olefin of the following structure.

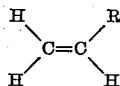


in which R is selected from alkyl and hydrogen and at least one R is hydrogen, and R' is alkyl, over a deactivated catalyst comprising an alkali metal disposed on a support at a temperature within the range of from about

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0° to about 100° C., and recovering a mixture of cis and trans olefins from the product.

Another embodiment of this invention relates to a process for preparing a cis and trans olefin mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises passing an alpha-olefin of the following structure



in which the R is an alkyl group over a deactivated catalyst comprising an alkali metal disposed on a precalcined high surface area support at a temperature within the range of from about 0° to about 100° C., and recovering a mixture of cis and trans olefins from the product.

A more specific embodiment of this invention relates to a process for preparing a cis- and trans-2-butene mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises passing 1-butene over a deactivated catalyst comprising sodium disposed on a precalcined high surface area alumina support at a temperature within the range of from about 0° to about 100° C., and recovering a mixture of cis- and trans-2-butene from the product.

A specific embodiment of this invention relates to a process for preparing a cis- and trans-2-butene mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises passing 1-butene over a deactivated catalyst comprising sodium disposed on a precalcined high surface area alumina support at a temperature within the range of from about 0° to about 100° C., said deactivation having been accomplished by prior use of the catalyst in hydrocarbon conversion reactions, and recovering a mixture of cis- and trans-2-butene from the product.

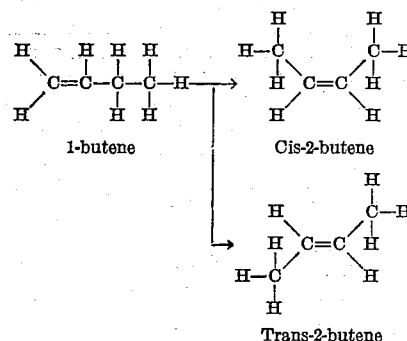
Another specific embodiment of the present invention relates to a process for the separation of isobutylene from a four carbon atom olefin fraction which comprises passing said fraction at a temperature within the range of from about 0° to about 100° C. over a hydrocarbon conversion reaction deactivated catalyst comprising sodium disposed on a precalcined high surface area alumina support, passing effluents from said reaction to a fractionation zone, and recovering isobutylene from the overhead and 2-butene from the bottoms thereof.

In the last few years the prior art has disclosed the utilization of alkali metals as catalysts for various reactions including some hydrocarbon conversion reactions, and more specifically olefin isomerization reactions. This prior art, however, discloses minimum operable temperatures for these hydrocarbon conversion reactions including olefin isomerization reactions in the neighborhood of about 150° C. In some instances, the use of extremely high pressures such as over 100 atmospheres have been disclosed as necessary. Attempts to overcome the necessity for such high pressure 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 order 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 catalyst is effective for the shifting of 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 a mixture of four carbon atom olefins, at 277° C. a conversion of 1-butene to 2-butene of 84% is

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the maximum which can be achieved because of equilibrium. A lowering of the reaction temperature to 27° C. can increase this theoretical conversion to greater than 95% of 2-butene. As set forth hereinabove, such an increase in 2-butene content in a four carbon atom 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 agents which can be utilized as fixed beds in reaction zones and which lend themselves to adoption in processes of the so-called continuous fixed bed type which are extremely desirable for adoption in commercial scale processes. These supported alkali metal catalytic agents, however, all suffer from one inherent disadvantage. When properly disposed on a suitable support, these catalytic agents are not only active for desired reactions such as the shifting of a double bond in an olefin hydrocarbon but they also cause polymerization of isoolefins. It has been discovered that proper deactivation of these catalytic agents results in their having selective activity. In other words, they can be utilized for the preparation of cis and trans olefin mixtures in which the ratio of cis to trans isomers is greater than the equilibrium value, they can be utilized for the conversion of alpha-olefins to such cis and trans olefin isomer mixtures, and these conversions can be carried out without simultaneous isoolefin polymerization. The means for proper deactivation of these catalysts will be described in detail hereinafter.

When processing alpha-olefins over deactivated catalysts comprising alkali metals disposed on a support in accordance with the process of this invention, an unusual product distribution is obtained. Not only does the double bond in the alpha-olefin shift to a more centrally located position in the hydrocarbon but the geometry of the products shows that this shift has been accomplished to give a yield of cis isomer in larger amounts than would be predicted by the equilibrium values for the distribution of such products. A readily observed example of this specific type of reaction is found in the conversion of 1-butene to a mixture of cis- and trans-2-butene in the presence of these catalysts and at a reaction temperature of from about 0° to about 100° C. This conversion is illustrated further by the following equation:



The equilibrium data for this reaction are found in an article by Kilpatrick, J. E., et al., Journal of Research National Bureau of Standards, 36, 559 (1946). These data show that at 0° C. the ratio of cis to trans isomers at equilibrium is 0.125 and that the conversion of 1-butene to 2-butene at this temperature is 94.7%. At 100° C. the ratio of cis to trans isomers goes up to 0.458 and the conversion of 1- to 2-butene at this temperature is 91.7%. At any selected temperature between 0° and 100° C., the theoretical equilibrium quantities of cis- and trans-2-butene can be found from the above reference. From these values the ratio of cis to trans isomers can be calculated and will fall between 0.125 and 0.458 as lower and upper limits, respectively. Then by utilization of the process of the present invention, it has

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unexpectedly been found that when converting 1-butene to 2-butene the ratio of isomers is higher than would be expected based upon these equilibrium values. For example, at 27° C. the equilibrium cis to trans ratio is about 0.33. By this process ratios greater than one and as high as 4:1 or higher have been found in the products. Such stereospecific activity of any catalyst is rare and has not been noted in any catalytic system for double bond shifting prior to the present discovery thereof. Not only is the process of the present invention applicable to the above described system but the abnormal cis to trans ratio of olefin isomers is also obtained when processing other alpha-olefins including 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, etc. Some alpha-olefins inherently cannot form cis and trans isomers because of their original structure. Thus, 2-methyl-1-pentene cannot form cis and trans products upon double bond shifting. Therefore, this limitation means that each of the carbon atoms which form the double bond in the alpha-olefin must originally have attached thereto at least one hydrogen atom. The alpha carbon atom of the alpha-olefin may have attached thereto either one or two hydrogen atoms. The beta carbon atom of the alpha-olefin must have attached thereto one and only one hydrogen atom. In accordance with this limitation, alpha-olefins which also may be utilized include 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4-methyl-1-octene, 5-methyl-1-octene, 6-methyl-1-octene, 7-methyl-1-octene, etc. Further examples of operable olefins are readily apparent to one skilled in the art.

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 the 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 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 and without danger of isoolefin polymerization, for example, isobutylene polymerization. The process of the present invention can likewise be utilized for shifting the double bond in 1-pentene or in 2-methyl-1-butene or 3-methyl-1-butene to produce pentenes in which the double bond is in a more centrally located position. When utilized with these isoamylenes, cis and trans products are obviously not produced since such are not possible from these starting materials. Likewise, hexenes such as 1-hexene can be converted to a mixture of cis- and trans-2-hexene in which the ratio of cis to trans isomers is greater than equilibrium value. A similar double bond shift in 2-hexene to 3-hexene also results in a mixture of cis to trans isomers in which the ratio is greater than equilibrium value. The double bond shifting reaction of the present invention of 1-olefins or alpha-olefins to olefins in which the double bond is in a more centrally located position is readily adaptable to any feed stocks as disclosed in the prior art, and without the danger of isoolefin polymerization which, as set forth hereinabove, occurs in prior art processes. While the present invention is discussed in detail in relation to the shifting of the double bond in 1-butene to produce cis- and trans-2-butene in a cis to trans isomer ratio greater than the equilibrium value, this discussion is introduced merely for the purpose of convenience and with not in-

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tention of unduly 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 the olefinic hydrocarbon to a more centrally located position in the olefinic hydrocarbon and to produce a mixture of cis and trans olefins in which the ratio of cis to trans isomers is greater than equilibrium value is effected in the presence of a deactivated catalyst comprising an alkali metal disposed on a support. The methods for, means of, and description of the deactivation of these catalysts will be set forth hereinafter. The alkali metal catalysts which, after deactivation, are 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 those 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 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 catalysts for use in the process of this invention. Alpha-alumina is usually characterized by a surface area ranging from about 10 to about 25 square meters per gram. In contrast, 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 on 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 areas are also not satisfactory supports. Such aluminas include dried aluminum 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 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 on the use of any particular support is one of freedom from combined or adsorbed water in combination with the desired surface area of the selected support.

The alkali metal may be disposed on a support in

any manner. One manner which has been found suitable 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 the desired type of 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 order of from about 100° to about 150° C. This can be accomplished, for example, by melting sodium and by dropping the sodium on the support or by the passage of a stream of an 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 even 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 temperature which can be used in the disposal of potassium on the support. Supported lithium catalysts appear to be less active than sodium or potassium catalysts 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 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 passageways of the support can be filled and blocked by the addition of excess quantities of alkali metal. This is obviously undesirable and supported alkali metal catalysts containing excess alkali metal are likewise inactive in the process.

After preparation of the initial alkali metal disposed on a support, the catalytic activity of the composite is lowered to eliminate isoolefin polymerization activity. This deactivation may be accomplished in various manners and by various means. One method for deactivation is by the passage of dry air or dry oxygen over the composite. Apparently some polymerization activity of the composite is decreased or destroyed by oxidation in this manner with the resultant production of a catalytic agent active for double bond isomerization and for the production of cis to trans isomers in a ratio greater than equilibrium value. The exact manner in which the air or oxygen deactivates the composite is not known. Another means or method for deactivation of the polymerization activity of the composites is to utilize them for a hydrocarbon conversion reaction until their activity for such reaction declines, and then to use them in the process of the present invention. For example, utilization of the catalyst composite of an alkali metal disposed on a support for the polymerization of isoolefins until isoolefin conversion decreases, and then utilization of the thus deactivated composite in the process of the present invention results in satisfactory catalyst activity in this process. The catalytic agents comprising alkali metals disposed on supports may also be deactivated by utilization in other hydrocarbon conversion reactions including paraffin isomerization, side chain alkylation, isoparaffin alkylation, cracking, etc. In some instances, mere passage of a hydrocarbon such as isobutane over the catalytic agent results in a sufficient decrease in catalyst activity so that the catalyst may be used as a deactivated one in the process of this invention. The alkali metal catalysts disposed on supports may also be deactivated by

alloying with non-catalytic metals. These non-catalytic metals may be divided into three classes, namely, those which form solutions with alkali metals, those in which alkali metals are partially soluble, and those in which alkali metals are slightly soluble or relatively insoluble. Examples of the non-catalytic metals in which the alkali metals are soluble include antimony, tin, arsenic, bismuth, cadmium, gold, lead, mercury, and silver. Zinc is an example of a metal in which the alkali metals are partially soluble, and examples of metals in which the alkali metals are slightly soluble include cerium, gallium, germanium, indium, platinum, palladium, and nickel. The alloys are usually prepared by combining an equimolecular quantity of the alkali metal and non-catalytic metal to be alloyed therewith, although greater or smaller amounts of the non-catalytic metal may be utilized. Of the above mentioned non-catalytic metals which may be alloyed with alkali metals, those in which the alkali metals are soluble are definitely preferred. Due to the solubilizing property of these particular non-catalytic metals, liquid melts with alkali metals can be readily prepared and utilized for or as a means of disposal of the alkali metal on the support. For example, equimolecular proportions of sodium and arsenic form a solution which can readily be added to a selected support such as a precalcined high surface area alumina support. Likewise, an alloy of sodium and mercury may be utilized as the means for disposing the alkali metal on the preselected support. Due to the varying molecular weights of the respective non-catalytic alloying metals the actual quantity of alloying metal in the final deactivated catalyst composites may vary over a relatively wide range of from about one to about 40% by weight based on the support.

The catalytic composite utilized in the process of the present invention may be deactivated in a further manner, that is, by utilization under processing conditions at which conversion to equilibrium mixtures is not obtained. As set forth hereinabove, one of the features of the process of the present invention is that the catalytic composites may be utilized at relatively low temperature, that is, from about 0° to about 100° C. With the freshly prepared composites comprising alkali metals disposed on a support conversion of alpha-olefins to equilibrium mixtures of cis and trans olefins in which the double bond is more centrally located are readily obtained. These conversions to equilibrium mixtures are attained at relatively low hourly liquid space velocities based on the olefin in the range of from about 0.1 to about 2. As the hourly liquid space velocity is increased to 4 or 8 or 16 or more, the total conversion tends to drop off somewhat, but it is observed that the products produced no longer contain equilibrium mixtures of cis and trans isomers but the mixtures contain the cis isomer in quantities greater than would have been predicted by equilibrium, and the trans isomer in quantities less than would have been predicted by equilibrium. From this type of a product distribution it is obvious that the cis to trans ratio will be greater than that which can be calculated from the equilibrium quantities of the respective cis and trans isomers at the temperature utilized for the conversion reaction. Therefore, deactivated catalysts, in the sense in which the term deactivated catalyst is used in this specification and in the appended claims, also means a catalyst with which deactivation has been accomplished by utilization of the catalyst at high hourly liquid space velocity conditions. This particular feature will be illustrated further in connection with the examples utilizing the conversion reaction of 1-butene to a mixture of cis- and trans-2-butene.

As set forth hereinabove, catalysts of the alkali metal type disposed on a support and deactivated 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 deactivated catalysts are particularly adapted for use in so-called fixed bed processes. The double bond shifting

reaction of the present invention to produce a mixture of olefins in which the cis to trans ratio is greater than equilibrium value 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 1000 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 in vapor phase. Thus, the pressure utilized may be selected purely from the most advantageous pressure based on 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 on the quantity of olefinic hydrocarbon charged may be varied within the relatively wide range of from about 0.1 to about 20 or more. The lower space velocities are utilized with what may be considered to be predeactivated catalysts and the higher space velocities are utilized with catalysts which have not been deactivated prior to use but with which deactivation is accomplished by use at these higher space velocities.

The attainment of the desired shifting of the double bond in an olefinic hydrocarbon to a more centrally located position with the production of cis and trans isomers in a ratio greater than the equilibrium value 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 organo metallic 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 a process similar to that of the process of the present invention at so-called moderate pressures and temperatures. As set forth above, it has now been found that such promoters are not needed and that the process of the present invention may be carried out at relatively low pressures and temperatures by utilization of the deactivated catalysts comprising an alkali metal

0.8%. This mixture was charged to the autoclave along with 10 grams of sodium metal. After the two hour contacting time, the hydrocarbons were removed from the autoclave, condensed, and analyzed again. The analysis of the hydrocarbon product in mol percent is as follows: propane, 0.3%; propylene, 0.2%; normal butane, 0.1%; 1-butene, 96.9%; cis-2-butene, 1.3%; and trans-2-butene, 1.2%.

These results show that finely divided metallic sodium is not an effective catalyst at a temperature of 110° C. for the conversion of 1-butene to 2-butene. While sodium alone is a catalyst for this conversion at higher temperatures, at higher pressures, and in the presence of added promoters, it is obvious that it is not an effective catalyst in the temperature range where equilibrium considerations result in the highest yield of 2-butene.

EXAMPLE II

The catalyst utilized in this example was prepared by adding sodium to a stirred mass of freshly calcined gamma-alumina in a nitrogen atmosphere. The gamma alumina prior to use was freed from adsorbed and combined water by calcination at 650° C. After calcination it had a surface area of about 200 square meters per gram. Sufficient molten sodium was dropped onto the stirred alumina mass so that the resultant composite of sodium on alumina contained about 16% by weight of sodium based on the alumina. During the impregnation of the alumina with the sodium, the temperature of the alumina mass stayed between about 150° to about 170° C.

In several experiments, 100 milliliters of the above sodium dispersed on gamma-alumina was placed as a fixed bed in a reaction tube surrounded by heating means. The same C₄ olefinic hydrocarbon described in Example I was then passed over this fixed bed of catalyst at room temperature, at 300 p.s.i.g., and at varying hourly liquid space velocities. Prior to each test period sufficient prerun periods, for example up to three hours duration, were carried out to insure that the reaction had reached constant conversion. The hourly liquid space velocities utilized, maximum temperature attained, and product analyses for five tests at varying space velocities are presented in the following table:

TABLE II
Shift in cis-trans ratio with hourly liquid space velocity
at 300 p.i.s.g.

[Product Analysis, Mol Percent]

Test No.	LHSV	T., ° C., Max.	1-Butene	2-Butene		cis/trans Ratio	Equilibrium cis/trans Ratio
				cis	trans		
1-----	1	41	2.9	26.5	69.9	0.379	0.333
2-----	2	33	2.7	26.2	70.4	0.372	0.333
3-----	4	42	3.7	29.6	66.0	0.449	0.333
4-----	8	56	5.1	33.4	60.9	0.550	0.333
5-----	16	41	20.8	45.6	33.0	1.38	0.333

disposed on a preselected support. This feature of the invention will be illustrated further in the examples.

EXAMPLE I

This example is introduced for the purposes of comparison. In this example, unsupported sodium was used in an attempt to catalyze the conversion of 1-butene to 2-butene. The experiment was carried out at a pressure of 350 p.s.i.g., a temperature of 112° C., and for a residence time of 120 minutes. The experiment was conducted in a one liter capacity turbomixer autoclave which provides a highly efficient stirring means for contacting, and which during the contacting disperses the sodium throughout the reaction vessel in a finely divided form in the reactants.

The hydrocarbon charged to the turbomixer autoclave comprises 300 cc. of a C₄ fraction having the following analysis in mol percent: propane, 0.3%; isobutane, 0.2%; normal butane, 0.1%; 1-butene, 98.6%; and 2-butene,

Table II illustrates the fact that sodium disposed on gamma-alumina is a highly effective catalyst for the conversion of 1-butene to 2-butene at low temperatures, and at hourly liquid space velocities up to 8, conversions close to the theoretical are obtained. At an hourly liquid space velocity of 16, and at room temperature, conversion was not complete. However, the higher hourly liquid space velocities were effective for producing 2-butene isomers such that the ratios were greater than the equilibrium value. The ratios are apparently within experimental error for the hourly liquid space velocities of 1 and 2. Marked increase in cis to trans ratio is obtained at the hourly liquid space velocities of 4, 8, and 16. At 16 hourly liquid space velocity the cis to trans ratio of 1.38 is four times greater than the equilibrium ratio indicating the stereospecificity of the reaction under these conditions.

EXAMPLE III

In this example, another 100 milliliters of the catalyst

prepared as described in Example II was utilized. However, in this example the catalyst was treated with air after placement as a fixed bed in the reaction tube. Air was passed over the fixed bed of catalyst until the evolution of heat due to this treatment ceased.

The same C_4 olefinic hydrocarbon feed stock described in Example I and comprising mainly 1-butene was passed over the fixed bed of air treated sodium-alumina composite. Conditions utilized included 300 p.s.i.g., a maximum catalyst temperature of 32° C., and an hourly liquid space velocity of 2.0. Analysis of the condensable gas product showed that it contained 6.3% of 1-butene, 48.2% of cis-2-butene, and 45.1% of trans-2-butene. The ratio of cis to trans isomers obtained is 1.07, or about three times higher than would be expected from the equilibrium ratio of 0.33 for this temperature.

EXAMPLE IV

The catalyst for this example was prepared by calcining 46 grams of gamma-alumina at a temperature of 650° C. to remove combined and adsorbed water. This gamma-alumina has a surface area of about 200 square meters per gram. This alumina was placed in a flask and heated to 200° C. in an atmosphere of argon. Then, 8.5 grams of sodium was added. The final catalyst composite contains 15.6% sodium.

The above catalyst, 100 milliliters, was placed as a fixed bed in a reaction zone and tested for the conversion of 1-butene to 2-butene at room temperature, a pressure of 300 p.s.i.g., and at an hourly liquid space velocity of 16.0. The C_4 olefinic hydrocarbon feed stock was the same as that described hereinabove in Example I. The condensable gas analysis showed that the product contained 22.4 mol percent 1-butene, 55.9 mol percent cis-2-butene, 19.1 mol percent trans-2-butene, and 2.6 mol percent other components. A cis to trans isomer ratio of 2.92 was obtained in comparison to the theoretical value of 0.33 for this temperature.

EXAMPLE V

Another catalyst was prepared by calcining 46 grams of gamma-alumina at 650° C. to remove combined and adsorbed water and to develop a surface area of about 200 square meters per gram. Then, 11.7 grams of potassium were added in three gram portions at 60–70° C. The final composite was a blue-black color and contained 20.5% by weight of potassium.

In this example, 100 milliliters of the catalyst composite was again disposed as a fixed bed in a reaction zone. Another sample of the same C_4 olefinic hydrocarbon described in Example I was passed over this catalyst at room temperature, 300 p.s.i.g., and at an hourly liquid space velocity of 16.8. At this space velocity, the product contained 9.0 mol percent 1-butene, 30.0 mol percent cis-2-butene, 53.7 mol percent trans-2-butene, and 7.3 mol percent other components. This cis to trans isomer ratio of 0.56 is greater than the equilibrium ratio of 0.33 for this temperature.

EXAMPLE VI

Another catalyst was prepared utilizing gamma-alumina calcined for four hours at 500° C. This alumina has a surface area of about 225 square meters per gram. After calcination, while hot, the alumina is placed in a flask and a stream of nitrogen passed therethrough to provide an inert atmosphere. When the temperature decreased to less than 100° C. sodium was added so that the final composite contained 12.5% by weight of sodium. This catalyst was then utilized for the polymerization of isobutylene until it become deactivated for this reaction. The percent polymer produced had dropped from an original 79% based on the isobutylene feed to 28% when the catalyst was considered to be deactivated.

A sample of this catalyst, 100 milliliters, was placed as a fixed bed in a reaction tube and utilized for the conversion of 1-butene to 2-butene at room temperature, 300

p.s.i.g., and at a space velocity of about 4. In one test analysis of the condensable gas showed that it contained 29.7 mol percent 1-butene, 57.9 mol percent cis-2-butene, 12.3 mol percent trans-2-butene, and 0.1 mol percent other components. In a second test analysis of the condensable gas showed that the product contained 55.7 mol percent 1-butene, 38.3 mol percent cis-2-butene, 5.7 mol percent trans-2-butene, and 0.3 mol percent other components. The ratio of cis to trans isomers for these test periods was 4.7 and 6.7, respectively, in comparison to the theoretical ratio of isomers of 0.33.

EXAMPLE VII

Another catalyst was prepared utilizing 45.7 grams of gamma-alumina which was dried at 500° C. and poured while hot into a flask. Nitrogen was passed through the flask to flush air out of the system. Molten sodium in the quantity of 6.5 grams was added in three gram portions. The temperature during this addition was kept below 100° C. This sodium impregnated alumina was disposed as a fixed bed in a reaction tube and isobutane passed through the reaction tube for three hours at an hourly liquid space velocity of 8.0.

At the end of this time, the hydrocarbons passed over the sodium-alumina composite were switched from isobutane to the same C_4 olefinic hydrocarbon feed stock described in Example I. At this point the conditions utilized were 300 p.s.i.g., room temperature, and an hourly liquid space velocity of 16. The condensable gases in the reaction zone effluent were analyzed and contained 54.0 mol percent 1-butene, 36.0 mol percent cis-2-butene, 7.9 mol percent trans-2-butene, and 2.1 mol percent other components. The ratio of cis to trans isomers obtained in this reaction zone effluent was 4.57 in contrast to the value of 0.33 at equilibrium. This example again illustrates the utilization of deactivated catalysts in the process of this invention.

EXAMPLE VIII

Another catalyst was prepared utilizing 46 grams of gamma-alumina which was dried at 500° C. and poured while hot into a flask. Argon was passed through the flask to flush air out of the system. A mixture comprising 0.34 gram of mercury and 6.6 grams of sodium was added to the alumina at about 100° C. The final composite contained 12.5% sodium alloyed with mercury.

One hundred milliliters of the above composite was placed as a fixed bed in a reaction tube and utilized for the conversion of 1-butene to 2-butene. Conditions utilized included a pressure of 300 p.s.i.g., room temperature, and an hourly liquid space velocity of 16. Analysis of the condensable gas product showed that it contained 56.2 mol percent 1-butene, 33.8 mol percent cis-2-butene, 7.3 mol percent trans-2-butene, and 2.7 mol percent other components. The ratio of cis- to trans-2-butene isomers obtained was 4.63 in contrast to the equilibrium value of 0.33.

EXAMPLE IX

Another alloy catalyst was prepared containing arsenic and sodium. Here again 46 grams of gamma-alumina previously dried at 500° C. was utilized. This alumina was placed in a flask which was then flushed with nitrogen. When the alumina had cooled to a temperature of 115° C., 3.5 grams of arsenic dissolved in 6.6 grams of sodium was added. The final composite contained 12.3% sodium alloyed with arsenic.

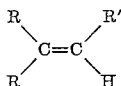
This catalyst in the quantity of 100 milliliters was again placed as a fixed bed in a reaction tube and utilized for the conversion of 1-butene to 2-butene. The same C_4 olefinic hydrocarbon feed stock described in Example I was again utilized. The conditions utilized for this experiment included room temperature, a pressure of 300 p.s.i.g., and an hourly liquid space velocity of 16. After a prerin period to insure that constant conditions had been attained, a test period was carried out. The analy-

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sis of the condensable gas therefrom showed that it contained 61.7 mol percent 1-butene, 27.8 mol percent cis-2-butene, 6.3 mol percent trans-2-butene, and 4.2 mol percent other components. The ratio of cis to trans isomers obtained during this test was 4.35 in comparison to the equilibrium value of 0.33. Here again, the production of a mixture of cis and trans isomers in a ratio greater than the equilibrium value is demonstrated by the utilization of the process of this invention.

We claim as our invention:

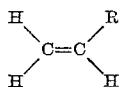
1. A process for preparing a cis and trans olefin mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises isomerizing an olefinic hydrocarbon feed whose olefin content consists essentially of at least one olefin of more than three carbon atoms per molecule and having the following structure:



in which R is selected from alkyl and hydrogen and at least one R is hydrogen, and R' is alkyl, in the presence of a deactivated catalyst comprising an alkali metal disposed on a substantially anhydrous support at a temperature within the range of from about 0° to about 100° C., said support having a surface area of from about 25 to about 500 square meters per gram and said catalyst having had its catalytic activity lowered, prior to use in said process, sufficiently to eliminate isoolefin polymerization activity, and recovering a mixture of cis and transolefins from the product.

2. The process of claim 1 further characterized in that said feed is a hydrocarbon fraction consisting essentially of C₄ olefinic and paraffinic hydrocarbons.

3. A process for preparing a cis and trans olefin mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises isomerizing an olefinic hydrocarbon feed whose olefin content consists essentially of at least one alpha-olefin of the following structure:

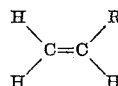


in which R is an alkyl group of at least two carbon atoms, in the presence of a deactivated catalyst comprising an alkali metal disposed on a substantially anhydrous support at a temperature within the range of from about 0° to about 100° C., said support having a surface area of from about 25 to about 500 square meters per gram and said catalyst having had its catalytic activity lowered, prior to use in said process, sufficiently to eliminate isoolefin polymerization activity, and recovering a mixture of cis and trans olefins from the product.

4. A process for preparing a cis and trans olefin mix-

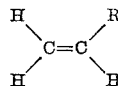
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ture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises isomerizing an olefinic hydrocarbon feed whose olefin content consists essentially of at least one alpha-olefin of the following structure:



10 in which R is an alkyl group of at least two carbon atoms, in the presence of a deactivated catalyst comprising an alkali metal disposed on a precalcined alumina support at a temperature within the range of from about 0° to about 100° C., said support having a surface area of from about 25 to about 500 square meters per gram and said catalyst having had its catalytic activity lowered, prior to use in said process, sufficiently to eliminate isoolefin polymerization activity, and recovering a mixture of cis and trans olefins from the product.

5. A process for preparing a cis and trans olefin mixture in which the ratio of cis to trans isomers is greater than the equilibrium value which comprises isomerizing an olefinic hydrocarbon feed whose olefin content consists essentially of at least one alpha-olefin of the following structure:



30 in which R is an alkyl group of at least two carbon atoms, in the presence of a deactivated catalyst comprising sodium disposed on a precalcined alumina support at a temperature within the range of from about 0° to about 100° C., said support having a surface area of from about 25 to about 500 square meters per gram and said catalyst having had its catalytic activity lowered, prior to use in said process, sufficiently to eliminate isoolefin polymerization activity, and recovering a mixture of cis and trans olefins from the product.

6. The process of claim 3 further characterized in that said alpha-olefin is 1-butene.

7. The process of claim 5 further characterized in that said alpha-olefin is 1-butene.

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