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3,476,824

PREPARATION OF ETHYLENICALLY UNSATURATED HYDROCARBONS WITH LOW ACETYLENIC CONTENT

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9 Claims

ABSTRACT OF THE DISCLOSURE

Method for dehydrogenation of hydrocarbon compounds to form ethylenically unsaturated hydrocarbons of low acetylenic content characterized by contacting the hydrocarbon in a first zone with oxygen and specified iron containing catalysts at a temperature of at least 600° F., and then feeding the reaction product from this first zone at a temperature of at least 800° F. into a second zone containing an alkalized iron oxide catalyst to produce the ethylenically unsaturated hydrocarbon product of low acetylenic content.

This application relates to a process for the production of ethylenically unsaturated hydrocarbons.

Unsaturated hydrocarbon compounds such as styrene, butene, butadiene, isoprene and the like are produced by the catalytic dehydrogenation of more saturated compounds. Improved processes have recently been developed whereby higher conversions, yields and selectivities of products are obtained by the dehydrogenation in the presence of oxygen and suitably a halogen. These processes are referred to as oxidative dehydrogenations.

One difficulty in these processes is that the reactor effluent contains acetylenes such as vinyl acetylene and methyl acetylene. While acetylenes may be present in a relatively small percentage, they interfere with the subsequent use of the unsaturated product and their removal has been the subject of considerable research effort. U.S. Patent 2,969,407 describes a process for the selective removal of acetylenes wherein the acetylene containing mixture is passed over an alkalized iron oxide catalyst at elevated temperatures with the resultant destruction of the acetylenes. However, such a process requires the addition of substantial quantities of heat in the form of steam. A further disadvantage is that the ethylenically unsaturated hydrocarbon tends to be destroyed by such a process.

It is therefore an object of this invention to provide an economical process for the production of high yields of ethylenically unsaturated hydrocarbons which contain only low concentrations of acetylenic compounds.

According to this invention these and other objects may be accomplished by a process comprising contacting a hydrocarbon to be dehydrogenated with free oxygen at a temperature of at least 600° F. and in the presence of a catalyst comprising oxygen, iron and at least one element other than iron selected from the group consisting of metals of Periodic Table Groups 2a, 2b, manganese, cobalt, nickel or mixtures thereof, feeding the reaction product from the said first zone at a temperature of at least 800° F. to a second zone comprising an alkalized iron oxide catalyst to produce the said ethylenically unsaturated hydrocarbon product.

The hydrocarbon composition to be fed to the first zone will preferably have from 2 to 8 carbon atoms such as propane, propylene, methyl acetylene, n-butane, isobutane, n-butene-1, n-butene-2, butadiene-1,3, vinyl acetylene, n-pentane, isopentane, n-pentene-1, n-pentene-

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2, ethyl benzene, cyclohexane and mixtures thereof. Excellent results may be obtained with acyclic hydrocarbons of 3 to 5 carbon atoms, and particularly hydrocarbons of 4 to 5 carbon atoms having a straight chain or at least 4 carbon atoms.

A preferred feature of this invention comprises a process for the production of high purity diolefins from a hydrocarbon stream containing impure monoolefin and diolefin mixtures. This hydrocarbon stream may contain hydrocarbon acetylene compounds such as vinyl acetylene and methyl acetylene as impurities. According to this embodiment of the invention, the hydrocarbon mixture is fed to a fractional distillation zone wherein diolefin is taken overhead. At the same time, a higher boiling fraction containing monoolefin as the major component is taken off at a lower point in the distillation zone. For example, the distillation zone may consist of a fractional distillation column. Any type of conventional fractional distillation column may be employed such as tray or plate type columns. The monoolefin rich mixture to be further processed may be either taken off as the bottoms from the distillation column or as a side stream from the distillation column. The monoolefin rich mixture may then be fed to the first and second zones as described above wherein in the first zone the mixture is contacted with a catalyst comprising oxygen, iron and at least one of the defined elements. In the second zone the composition is contacted with the alkalized iron oxide catalyst as described above. The effluent from the second zone contains the diolefin product of high purity. This unsaturated product of high purity may then be combined either directly or indirectly with the overhead from the fractional distillation zone. An example of an indirect combination of the overhead would be a process wherein the product of the second zone is recycled upstream in a purification sequence such as to the feed to a cuprous ammonium acetate or other purification step. Furthermore, a portion of the product may be recycled to the said fractional distillation zone. The preferred hydrocarbon mixture to be fed to the fractional distillation zone will contain n-butene, methyl pentene, isoprene or mixtures thereof as the major components. Particularly preferred is a composition containing a mixture of n-butene, vinyl acetylene, and butadiene-1,3 as the major components.

The catalyst in the first zone will comprise iron, oxygen and as a second component at least one element selected from the group consisting of metals of Periodic Table Groups 2a, 2b, manganese, cobalt, nickel or mixtures thereof. The preferred elements in Groups 2a, are Mg, Ca, Sr and Ba, with Mg being particularly preferred. The preferred elements in Group 2b are Zn and Cd. The Periodic Table referred to may be found e.g. on the back cover of the 45th Edition (1964-5) of the Handbook of Chemistry and Physics (Chemical Rubber Company, Cleveland, Ohio). Thus a preferred group of elements is Mg, Ca, Sr, Ba, Mn, Co, Ni, Zn, Cd and mixtures thereof. The catalyst will have iron in the catalyst surface in an amount from 20 to 95, and preferably from 30 to 90 weight percent of the total weight of iron and the second metallic element(s). The catalyst will comprise oxygen, and excellent results have been obtained when the defined elements are present in a crystalline structure. The best results have been obtained when the catalysts comprise ferrites. Examples of these catalysts are disclosed e.g. in Belgium Patent 657,827 issued June 30, 1965, which disclosure is herein incorporated by reference. Free oxygen must be present in the first zone. The quantity of oxygen will normally be present in an amount of at least 0.2 mols per mol of hydrocarbon compound fed to the zone. A usual range is from 0.1 to

2.5 mols of oxygen per mol of hydrocarbon compound and a preferred range is from 0.2 to 2.0 mols per mol. The oxygen may be present as such, or as air, as air enriched with oxygen, or the oxygen may be diluted with diluents such as nitrogen, helium, argon and the like. The oxygen may be introduced in any manner to the dehydrogenation zone.

The halogens employed, if any, will preferably be iodine, bromine or chlorine, and the form of the halogens may be the halogens themselves or any halogen-containing materials which liberate free halogen under the conditions of the reaction as defined hereinafter. For example, chlorine, bromine and iodine; hydrogen chloride, hydrogen bromide and hydrogen iodide; the alkyl halides such as alkyl iodides and bromides wherein the alkyl groups preferably contain 1 to 6 carbon atoms; ammonium halides including ammonium chloride, ammonium bromide, ammonium iodide and ammonium fluoride; and mixtures of these may also be employed. The halogens, hydrogen halides, ammonium halides and alkyl halides wherein the alkyl groups contain 1 to 5 carbon atoms, have been found to be particularly useful in the practice of this invention. Any suitable combination of reactants may be used as chlorine and hydrogen bromide; chlorine and bromine; hydrogen chloride and bromine; chlorine and hydrogen iodide, bromine and iodine and the like added together or separately.

The total amount of halogen used may be varied quite widely, usually an amount greater than 0.001 mol of halogen per mol of hydrocarbon compound to be dehydrogenated. More usually, at least about 0.005 mol of total halogens per mol of hydrocarbon compound will be employed. Large amounts of halogens may be used, as high as one-half to one mol or more per mol of hydrocarbon compound to be dehydrogenated if desired, but generally only very small amounts of halogens are used, normally less than about 0.2 mol total of halogens, per mol of organic compound to be dehydrogenated. The first zone may be a fixed or fluid bed reactor. Reactors such as those conventionally used for the dehydrogenation of hydrocarbons may be employed. The total pressure in the first zone may suitably be about atmospheric pressure. However, higher pressures or vacuum may be used. Pressures such as from about atmospheric (or below) up to about 100 to 200 p.s.i.g. may be employed. The first zone reaction will normally be conducted at a temperature of reaction between about 600° F. to about 1500° F. or higher although generally the maximum temperature in the reactor will be within the range of about 700° F. and 1300° F. The flow rates of the reactants may be varied quite widely and will be dependent somewhat on whether fixed or fluid bed reactor is employed. Good results have been obtained with flow rates of the hydrocarbon feed ranging from about 1/4 to 25 liquid volumes of hydrocarbon fed per volume of the first zone per hour, with the volumes of hydrocarbon being calculated as the equivalent amount of liquid hydrocarbons at standard conditions of 15.6° C. and 760 millimeters of mercury absolute. For the purpose of calculating flow rates the first zone is defined as the portion of the first zone which contains catalyst and which is at a temperature of at least 600° F. In other words, the volume of the first zone is equivalent to the volume of the catalyst zone if it were empty. The residence or contact time of the reactants in the first zone depends on several factors involved in the

reaction. Contact times such as about 0.001 to about 5, 10 or 25 seconds have been found to give excellent results. Under certain conditions, higher contact times may be utilized. Contact time is the calculated dwell time of the reaction mixture in the reaction zone assuming the mols of product mixture are equivalent to the mols of feed.

The second zone contains an alkalized iron oxide catalyst. These catalysts suitably contain iron oxide as the major component together with an alkali metal. These catalysts are disclosed e.g. in Davies et al. U.S. Patent 2,461,147, issued Feb. 8, 1949, which disclosure is herein incorporated by reference. The catalyst may also contain chromium oxide. Suitable catalysts will contain alkali (preferably potassium) in an amount of at least 5 mol percent alkali, (preferably about 5 to 50 mol percent alkali) calculated as Me₂O (Me being the alkali metal) based on the iron oxide, calculated as Fe₂O₃. Stabilizers such as chromium may be present such as from about 2 to 20 mol percent (calculated as Me₂O₃, e.g. Cr₂O₃, based on the iron oxide).

The temperature in the second zone should be maintained at least 800° F. and preferably the maximum temperature in the zone will be between about 800° F. and 1150° F. It is preferred that the temperature be maintained between 1000° F. and 1150° F. Good results are obtained at temperatures between 1040° F. and 1070° F. and exceptionally good results are obtained at temperatures between 1070° F. and 1150° F. It will be noted that the use of the combination catalyst permits the utilization of higher temperatures and thus greater efficiency in the process.

The flow rates in the second zone will be within the same ranges as those of the first zone.

The following examples describe my invention in greater detail; however, it is to be understood that the examples are for illustrative purposes only and the invention is not limited thereto.

EXAMPLE 1

A one-inch reactor tube is loaded with catalysts as follows: the bottom six inches of the tube (second zone) is filled with 3/16" pellets of a catalyst having 67% Fe₂O₃, 3% Cr₂O₃ and 30% KOH (all parts by weight); the middle ten inches of the tube is filled with vycor chips to separate the actives, and the top 4 inches of the tube (first zone) is filled with magnesium ferrite. A hydrocarbon stream containing, by mol percent, 30.9% trans butene-2, 46% cis-butene-2, 6.1% vinylacetylene and 16.9% butadiene was fed into the top of the reaction tube. Reaction conditions were held at 0.5 liquid hourly space velocity (LHSV) over the total reactor area, 0.25 mols oxygen per mol hydrocarbon, and 15 mols steam per mol hydrocarbon. The inlet temperature to the first zone is 715° F. Reaction temperature in the second zone is approximately 1075° F. The effluent from the second zone contained 27.3 mol percent butadiene and 0.4 mol percent vinylacetylene.

EXAMPLES 2 TO 4

The general procedure of Example 1 is repeated using different hydrocarbon feeds and reaction conditions. The results are shown in the table. The oxygen is fed as air.

TABLE

	Feed (Mol percent)							Product (Mol percent)					
	Buta- diene	Butene-2	Butene-1	Vinyl Acet- ylene	Butane n-	Flow Rate LHSV	Steam (Mols)	Temperature, ° F.		O ₂ /Hebn	Buta- diene	Vinyl Acet- ylene	Butene
								Inlet	Max.				
Example 2----	23.2	70.2	0.7	5.6	0.3	0.5	15	710	1,070	0.25	39.4	0.3	55.7
Example 3----	0.9	98.0	0.8	1.3	-----	0.5	15	725	1,100	0.25	23.0	0.03	74.3
Example 4----	13.7	81.0	0.5	4.7	0.1	0.5	14	717	1,085	0.25	30.1	0.2	65.0

EXAMPLE 5

A mixture of n-butane and butene is dehydrogenated in the presence of oxygen, ammonium bromide and oxygen to form a reaction effluent. The effluent is condensed, compressed and purified to form a C₄ hydrocarbon mixture which is then fractionally distilled in a tray tower. The bottoms from the tower are fed to the process of Example 1 above and the effluent from the two zone reactor is combined with the overhead from the fractional distillation tower to provide butadiene-1,3 of high purity containing less than 0.5% vinylacetylene.

I claim:

1. A method for the dehydrogenation of hydrocarbon compounds selected from the group consisting of n-butane, n-butene, methyl pentane, methyl pentene and mixtures thereof to form ethylenically unsaturated hydrocarbons of low acetylenic content comprising contacting in a first zone the hydrocarbon to be dehydrogenated with free oxygen at a temperature of at least 600° F. and in the presence of a catalyst comprising iron, oxygen, and at least one element selected from the group consisting of metals of Periodic Table Groups 2a, 2b, manganese, cobalt, nickel and mixtures thereof, directly feeding the reaction product from the said first zone at a temperature of at least 800° F. to a second zone comprising an alkalized iron oxide catalyst containing at least 5 mol percent alkali calculated as Me₂O (Me being the alkali metal) based on the iron oxide to produce the said ethylenically unsaturated hydrocarbon product of low acetylenic content.

2. The method of claim 1 wherein the catalyst in the first zone comprises a ferrite.

3. The method of claim 1 wherein the catalyst in the said first zone comprises magnesium ferrite.

4. The method of claim 1 wherein the catalyst in the second zone comprises an alkalized iron oxide catalyst containing chromium.

5. The method of claim 1 wherein the hydrocarbons

to be dehydrogenated comprises n-butene and the said hydrocarbon product is butadiene-1,3 of low vinylacetylene content.

6. The method of claim 1 wherein the temperature in the said second zone is between 1040° F. and 1150° F.

7. The method of claim 1 wherein the temperature in the said second zone is between 1070° F. and 1150° F.

8. A method for preparing high purity diolefin selected from the group consisting of butadiene-1,3, isoprene and mixtures thereof from a hydrocarbon mixture containing the said diolefin and the corresponding monoolefin of the same number of carbon atoms which comprises fractionally distilling in a fractional distillation zone the said mixture to take off overhead the diolefin and at the same time taking off a monoolefin rich mixture from a lower portion of the distillation zone, contacting in a first zone the said monoolefin rich composition with free oxygen at a temperature of at least 600° F. and in the presence of a catalyst comprising in a crystalline structure oxygen, iron and at least one element selected from the group consisting of metals of the Periodic Table Groups 2a, 2b, manganese, cobalt, nickel, and mixtures thereof, directly feeding the reaction product from the said first zone at a temperature of at least 800° F. to a second zone containing an alkalized iron oxide catalyst containing at least 5 mol percent alkali calculated as Me₂O (Me being the alkali metal) based on the iron oxide to produce the said diolefin of high purity.

9. The method of claim 8 wherein the monoolefin is n-butene and the diolefin is butadiene-1,3.

References Cited

UNITED STATES PATENTS

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