

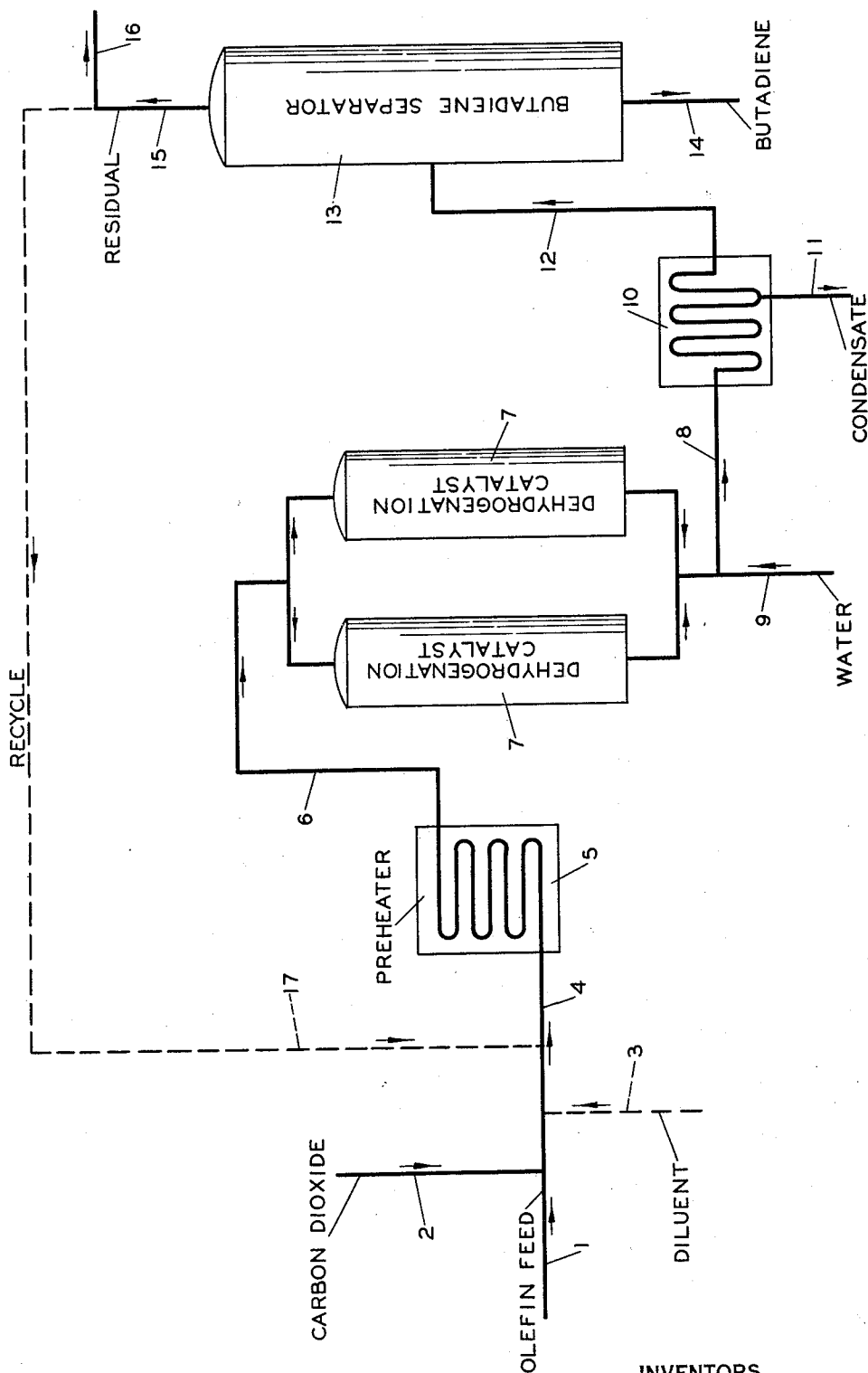
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PROCESS FOR DEHYDROGENATION OF HYDROCARBONS

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PROCESS FOR DEHYDROGENATION OF HYDROCARBONS

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4 Claims. (Cl. 260—680)

This invention relates to a process for the catalytic dehydrogenation of hydrocarbons. More specifically, it relates to an improved process for catalytic dehydrogenation of olefins to produce diolefins, and has particular reference to the production of low boiling aliphatic diolefins from the corresponding olefins.

In the preparation of the valuable aliphatic diolefins by catalytic dehydrogenation of olefins, one of the primary considerations has been to bring about this dehydrogenation at satisfactory conversion levels without causing any considerable proportion of the hydrocarbon feed or products to undergo alteration of the carbon skeleton. This alteration accompanying cracking and/or polymerization reactions results in production of either lower boiling gaseous products or on the other hand of tars or high boiling polymeric material. To reduce the rupture of the carbon skeleton when dehydrogenating olefins and to suppress concurrent production of undesirable by-products of greater or lesser number of carbon atoms, it is desirable to carry out the treatment of olefins at reduced concentrations and the correspondingly reduced partial pressures of the reactants and products.

One way in which catalytic dehydrogenation at reduced pressure of reactants may conveniently be carried out is by the use of a suitable diluent gas, thereby obtaining a lowered partial pressure of olefins while at the same time maintaining the total pressure at atmospheric or low superatmospheric levels. Processes for olefin dehydrogenation employing this principle are disclosed in our copending applications, Serial No. 352,786, filed August 15, 1940, and Serial No. 353,961, filed August 23, 1940.

It has also been noted that one very advantageous way of carrying out dehydrogenation reactions is in the presence of minor quantities of oxygen, whereby the hydrogen liberated in the primary dehydrogenation reaction is at least partly oxidized to water vapor. The resulting decrease in hydrogen concentration affects the primary equilibrium favorably to promote dehydrogenation and yield additional unsaturated hydrocarbons. This type of dehydrogenation reaction, in which hydrogen and/or other by-products of the primary dehydrogenation are burned by the introduction of a gas comprising free oxygen, has been broadly termed oxidative dehydrogenation.

Processes of oxidative dehydrogenation have not been generally applied in practice, however, because of the inherent operating difficulties and

very unfavorable recovery of hydrocarbon products accompanying the utilization of free oxygen. The introduction of the free oxygen-containing gas may result in serious overheating at the points of introduction of said gas, because of the highly exothermic nature of the combustion occurring. Indeed, unless precautions are taken to disperse the oxygen-containing gas rapidly and completely throughout the hydrocarbon, flame formation will occur. Oxidation thus poorly controlled is not confined to the hydrogen or other by-products including carbon, but proceeds at the expense of the valuable olefins and diolefins. Various processes and complicated arrangements of apparatus have been proposed in an effort to overcome these inherent difficulties in the use of free oxygen, with only doubtful adaptability to olefin dehydrogenation.

It is an object, therefore, of this invention to provide an improved process for the catalytic dehydrogenation of low-boiling aliphatic olefins wherein the diluent gas supplied to produce low partial pressures of reactants has the additional function of oxidizing hydrogen and carbon formed during conversion to an extent which effectively promotes the conversion.

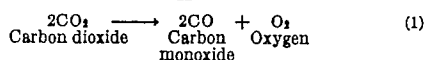
It is a further object of this invention to provide an improved process for the catalytic dehydrogenation of low boiling aliphatic olefins to produce the corresponding diolefins, wherein oxidation of the hydrogen and other by-products produced is practiced without the addition of free oxygen.

A still further object of this invention is the provision of a diluent gas capable of supporting oxidation under conversion conditions, whereby said oxidative dehydrogenation is carried out with selective oxidation of hydrogen and other undesirable by-products and with substantially no combustion of valuable hydrocarbon reactants or products. Still further objects will be apparent from the following disclosure.

We have now found that when a hydrocarbon stock to be dehydrogenated is diluted with a gas comprising a major proportion of carbon dioxide a dual purpose is accomplished. The partial pressure of the olefin charge is reduced to satisfactory sub-atmospheric levels, and, in addition, the carbon dioxide serves as an oxidizing medium under the conditions employed and in the presence of hydrogen and other reducing agents. In this latter service, the dehydrogenation is promoted by oxidation without the difficulties associated with the use of free oxygen.

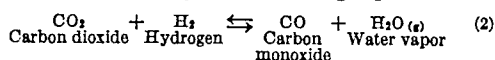
Since the carbon dioxide is probably only neg-

ligibly dissociated at the temperatures employed for dehydrogenation, the action of free oxygen is not involved, and the problems of controlling the addition and mixing of the oxidizing gas are not entailed. The reaction

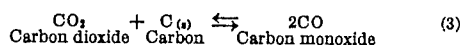


does not occur to an appreciable extent until temperatures of about 2000 to 2200° F. are reached. Thus, carbon dioxide may be added to the hydrocarbon stream by conventional means, and the addition may take place either before or after the preheater used to raise the vapor mixture to dehydrogenation temperatures. Furthermore, carbon dioxide may be added at suitable temperatures directly to the catalyst space if desired.

The reactions of carbon dioxide which are utilized in our process to promote dehydrogenation may be illustrated by the following equations:



and



These reactions proceed measurably to the right at temperatures in the dehydrogenation range of 1000° to about 1400° F. and account for the removal of hydrogen and the gasification of carbon deposits on the catalyst. The oxidative function of carbon dioxide, therefore, is substantially limited to hydrogen and carbon, and while the reactions may be regarded as the liberation and/or transfer of oxygen, the presence of specific reducing agents is required to initiate oxidation.

In one specific embodiment, our invention comprises the steps of (1) diluting low-boiling aliphatic olefin stocks comprising C₄ or heavier hydrocarbons with a considerable proportion of diluent, comprising in turn considerable quantities of carbon dioxide; (2) treating the resultant hydrocarbon-carbon dioxide mixture over a catalyst to dehydrogenate the olefins oxidatively, i. e., with formation of diolefins and water; and (3) separating the diolefin so produced from the unconverted hydrocarbons and other products.

The process may be illustrated by reference to the drawing, which is a flow diagram of one arrangement of conventional equipment for application of our invention to dehydrogenation of low-boiling aliphatic olefins. In the drawing, fresh, olefin-containing feed enters by line 1, and carbon dioxide is added by line 2. Further diluent, such as light refractory hydrocarbons, or the like, may be added through line 3, if desired. The hydrocarbon-carbon dioxide mixture passes through line 4 to heater 5, where it is heated to reaction temperature. The hot vapors then pass through line 6 to catalyst cases 7, containing a suitable dehydrogenation catalyst, and the treated vapors exit through line 8. The hot vapors passing through line 8 may be chilled by water injection through line 9, if desired, and pass to condenser 10, wherein water vapor is condensed and condensate removed through line 11. The hydrocarbon vapors then pass through line 12 to diolefin separator 13, in which diolefin is extracted and removed through line 14. This may be effected by any one of several conventional methods, such as chemical separation, solvent extraction, or the like. The residual vapors leave the system through line 16. Provision is made to return all, or a part of the hydrocarbon vapors of

the proper boiling range to the system for further conversion if desired. In such a case, hydrogen and other light vapors may be removed from the recycle portion by means of fractionators and/or other conventional arrangements of apparatus, not shown. Carbon dioxide may be removed from the stream at any point after leaving the catalyst cases, as may be required by the butadiene separation step or the fractionating processes employed. Any of the well known processes for such removal may be employed, including regenerative-type chemical removal methods.

In the operation of our process, the charge to the preheating furnace is usually prepared in such proportions that the partial pressure of olefins therein is less than 0.5 atmosphere and ordinarily we prefer to operate within the range of 0.1 to 0.3 atmosphere partial pressure of olefin. The volume of diluent added is, therefore, from about 50 per cent to as high as 90 or more per cent of the total mixed feed, being regulated to such a quantity that the partial pressure of olefin is maintained at the desired value.

The carbon dioxide diluent used in our process may be added to the hydrocarbon stream ahead of the preheater as illustrated above, or, if independent heating means are provided, the diluent or a portion thereof may be added after the preheater. For example, carbon dioxide preheated to suitable temperatures may be added to the hydrocarbon feed stream just prior to passage into the catalyst chamber, or regulated amounts of carbon dioxide may be injected directly into the catalyst chamber at a series of points spaced along the path of the vapors travelling through the catalyst bed.

Carbon dioxide may serve as the sole added diluent; and indeed, we often prefer to operate in this manner. When other diluents are present, a considerable proportion, usually a major proportion, of carbon dioxide is desirable in our process. To obtain satisfactory conversions of olefins to diolefins, temperatures in the range 1000 to 1300° F. are ordinarily employed, with a somewhat narrower range of 1100 to 1300° F. being preferred for applications of the present invention. Within this range, the reactions of carbon dioxide with hydrogen and with carbon occur to a somewhat limited extent. It is therefore desirable, in order to produce the maximum possible reaction, according to Equations (2) and (3) to have a high concentration of carbon dioxide present. Other diluents which may be employed in conjunction with carbon dioxide include light refractory hydrocarbons, particularly methane, the paraffin hydrocarbon of corresponding carbon atom skeleton, propylene, and steam. Although the use of a considerable proportion of steam in the diluent has been found to possess many advantages, its effects in oxidative dehydrogenation, in which hydrogen is converted to water vapor, may be to repress the desired oxidation. For this reason, as well as because of the relatively minor quantity of any supplementary diluent needed, its use is severely limited. We prefer, where mixed diluents are employed, that the carbon dioxide constitute at least 50 volume per cent of the total diluent to allow the proper degree of oxidation and for best results.

We prefer to operate our process at low total pressures of atmospheric to 100 pounds gage. Low total pressure is desirable to increase the yield of diolefin. Also, since the partial pressure of olefin is ordinarily kept below 0.5 atmosphere, it is essential to operate at low total pres-

sure in order to have maximum volume concentration of this component.

To obtain satisfactory conversion of low boiling aliphatic olefins, flow rates of from 1 to 10 liquid volumes of olefin charge per hour per volume of catalyst are ordinarily employed. In terms of the total vapor mixture charged to the catalyst, space velocities of 500 to 5000 volumes per hour are satisfactory under proper conditions. The particular combination of flow rate and temperature for a specific operation will depend upon the catalyst employed, the composition of the charge, and on the degree of conversion desired.

As catalysts in our process, we prefer to employ dehydrogenation catalysts of the water-resistant type, by which we mean those catalysts which are not rendered inactive by the presence of more than a trace of water vapor. By the use of such catalysts, we are able to obtain the full benefit of the reduction in hydrogen content of the partially dehydrogenated vapors which is produced by reaction of said hydrogen with carbon dioxide to form water vapor. We may, however, if we choose to employ other dehydrogenation catalysts which are more or less sensitive to water vapor, thereby gaining to a somewhat lesser extent the same advantages of increased dehydrogenation and reduced hydrogen content as when employing the preferred catalysts.

Of particular value for this dehydrogenation are catalysts prepared by the treatment of bauxite with hydroxides or oxides of barium and/or strontium in such a manner that the adsorbent material ore is impregnated with minor proportions, usually from 1 to 10 per cent by weight of the metal hydroxide. Such a catalyst and methods for manufacturing it have been disclosed in our copending application, Serial No. 353,961, filed August 23, 1940. These catalysts are active even in the presence of large quantities of steam. Therefore, as the hydrogen is consumed by reaction with CO₂, dehydrogenation still proceeds unabated throughout the catalyst bed toward the equilibrium concentrations of dehydrogenated products.

In addition to the above-mentioned highly satisfactory catalysts, many other catalysts may be employed. Among those which possess the quality of water resistance to a marked degree are the difficultly reducible oxides of natural or synthetic origin such as bauxite and brucite which may or may not have been treated to produce water resistance. The oxides of aluminum and magnesium have been found to give especially satisfactory catalysts, as have also those of titanium and zirconium. Both synthetic preparations of the substantially pure oxides, hydrated oxides, or hydroxides, and also natural mineral ores comprising these oxides can yield satisfactory catalysts. High porosity, or specific surface and other qualifications of good catalysts are desirable in these materials, both in the untreated state, and after any treatment to produce water-resistant qualities. Many other catalytic materials for dehydrogenation have been found and may be employed satisfactorily in our process.

We have found that various alkaline materials when added to the untreated catalysts in such a manner as to thoroughly impregnate the catalyst serve to impart the quality of water resistance to a marked degree. While catalysts can be prepared by impregnating with alkali oxides, we have found the specific alkaline earth

oxides and/or hydroxides of barium and strontium to be most effective.

Dehydrogenation of olefins is an endothermic reaction, and it is usually necessary to supply heat throughout the catalyst bed from an external source to maintain the temperature at a level at which satisfactory conversion occurs. One way in which this may be accomplished is by multipoint injection of further quantities of diluent preheated to a temperature somewhat above the desired reaction temperature. In our process, such multipoint injection of additional carbon dioxide is applied with excellent results. It is an advantage of our process that the carbon dioxide injected multipointwise serves not only to maintain conversion temperatures but also provides the benefits of an increased concentration of carbon dioxide which by mass action furthers conversion of hydrogen to water vapor and directly furthers dehydrogenation. Also, no local overheating or flame formation is possible when injecting carbon dioxide as would be the case in injecting gases containing free oxygen into the catalyst space.

After passing over the selected dehydrogenation catalysts, the vapor effluents are cooled to condense water and any high boiling polymers. The method of cooling may be designed to provide an extremely rapid reduction of temperature, such as by the introduction of a quenching medium, for which purpose water is generally satisfactory.

The method of recovering diolefins from the effluent hydrocarbon mixture may be any of several well-known methods. Among those which can be successfully applied are extraction with cuprous chloride reagents, solvent extraction and other chemical methods. Fractionation may also be practiced, if desired. Substantially pure butadiene can be produced by any of these processes and nearly complete recovery of diolefins from the residual vapors may be obtained if economically feasible.

Normally dehydrogenation processes carbonaceous residues are deposited on the catalyst, resulting in decreased activity. It is an advantage of our process that the rate at which these deposits accumulate is greatly reduced. Carbon dioxide serves to oxidize carbon deposits within the range of our preferred operating temperatures. In the presence of the large quantity of carbon dioxide which we employ the reaction shown above by Equation (3) proceeds to the right to such an extent as to very substantially reduce carbon deposits and to correspondingly lengthen conversion periods. We find, however, that a little of the carbon is deposited in a form which is slow to react. For this reason, carbonaceous deposits do gradually accumulate, and it is necessary to reactivate the catalyst at intervals with a strongly oxidizing gas containing free oxygen. By the use of carbon dioxide diluent, however, these periods of reactivation are made much less frequent, and the economic advantage of a greater proportion of the catalyst service in dehydrogenation is obtained.

Since dehydrogenation is an equilibrium reaction a portion of the butene will always remain unconverted. Obviously, further diolefin could be obtained from the unconverted olefin in the effluent vapors by recycling all or any desired proportion thereof. Normally, the hydrogen and other light gases present in the treated vapors will be removed or the concentrations thereof will be suitably adjusted before recycling to avoid

repressing the dehydrogenation. Numerous arrangements of conventional equipment may be used to accomplish this purpose. The carbon dioxide may be recycled or, as may be desirable with most conventional fractionation equipment, removed prior to separation of light gases or even prior to butadiene separation.

The following examples will further illustrate specific applications of our process.

Example I

A C₄ hydrocarbon fraction from a refining cracking operation which contained about 90 per cent of normal butenes and 10 per cent butane was diluted by the addition of carbon dioxide to reduce the butene content to about 25 per cent. The mixture as subsequently charged to the pre-heater had approximately the following composition:

	Volume per cent
n-Butenes	25
Butane	3
Carbon dioxide	72

The charge was heated to 1190° F. and passed over a water-resistant catalyst, consisting of bauxite impregnated with 3 per cent by weight of barium hydroxide, at a vapor space velocity of 1200 volumes per hour and a catalyst case inlet pressure of 5 pounds gage.

Before processing to remove butadiene, a sample of the effluent hydrocarbons was removed for analysis. The C₄ hydrocarbon fraction represented a volume yield of 80 per cent based on the total C₄ hydrocarbon content of the charge. Based on the charge, the following quantities of C₄ hydrocarbons were recovered:

	Volume per cent
Butadiene	20
n-Butenes	50
Butane	10

This represented approximately 45 per cent per pass conversion of the butenes charged and about 50 per cent efficiency in the production of butadiene. The per pass yield of butadiene was thus about 22 per cent of the butenes charged.

In a test made under identical conditions except with nitrogen replacing the carbon dioxide diluent, the corresponding per pass conversion was only 40 per cent of the butenes charged, and the efficiency, based on butadiene yield was only about 40 per cent. The per pass yield of butadiene was 16 per cent of the butenes charged. This showed the increased conversion due to the oxidative function of the carbon dioxide, and the increase was reflected almost quantitatively in the increased yield of butadiene with carbon dioxide diluent.

Example II

The C₄ fraction of Example I was diluted with carbon dioxide to reduce the butene content to 25 volume per cent.

The charge was heated to 1190° F. and passed over a dehydrogenation catalyst comprising calcined 12-20 mesh bauxite, at a vapor flow rate of 1200 volumes per hour and an inlet pressure of 3 pounds gage.

The C₄ hydrocarbon effluents were found, by analysis of a sample removed from the stream, to represent a volume yield of 79 per cent based on the total C₄ hydrocarbon charged. On the

same basis the quantities of hydrocarbons recovered were:

	Volume per cent
Butadiene	17.5
n-Butenes	51.5
Butane	10

This represented a per pass conversion of approximately 43 per cent of the butenes charged with 45 per cent efficiency in the conversion to butadiene.

Example III

A C₅ hydrocarbon charge stock containing 95 per cent n-pentenes and 5 per cent pentane was diluted with 3 volumes of carbon dioxide, reducing the pentene content to 24 per cent.

The resultant mixed vapors were passed over bauxite-barium hydroxide catalyst after preheating to 1150° F. at a vapor flow rate of 1300 volumes per hour and inlet pressure of 3 pounds gage.

By analysis of the effluents, a total volume yield of 78.5 per cent was indicated, based on the total volume of C₅ hydrocarbon charged. The following quantities of C₅ hydrocarbons were recovered:

	Volume per cent
Pentadienes	21.5
Pentenes	52
Pentane	5

This represented approximately 45 per cent per pass conversion of the pentenes charged, and about 50 per cent efficiency in the conversion to pentadienes. The conversion obtained was markedly greater than that obtained using methane as diluent instead of carbon dioxide, and the yield of C₅ diolefins was substantially higher.

The improved results which are obtained through the use of carbon dioxide are seen to be due to both increased dehydrogenation and lengthened conversion periods. The first effect since it is substantially specific to the olefin-diolefin conversion results in greater diolefin yields and consequent operating economies, for example, through decreased plant capacity and feed costs. The second effect likewise contributes to process efficiency through decreased time requirements for catalyst reactivation. The function of the carbon dioxide is denoted by the more or less constant formation of carbon monoxide and water vapor in the effluent vapors. Carbon dioxide may ordinarily be provided through combustion of fuel gas, or may be cheaply obtained from flue or stack gases which are usually available in great quantities. For the purposes described, substantially complete removal of oxygen is required, although minor amounts of impurities such as carbon monoxide, water vapor and the like may be tolerated in some instances.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of our process, other modifications will be obvious and within the scope of our disclosure. No limitations are, therefore, intended except as defined in the appended claims.

We claim:

1. A process for the catalytic dehydrogenation of normal butenes to produce butadiene which comprises admixing a hydrocarbon mixture containing said butenes with sufficient gaseous diluent comprising at least 50 volume per cent carbon dioxide to produce butene partial pressures below 0.5 atmosphere at the pressure of the de-

hydrogenation step hereinafter recited, and passing the resulting mixture over a water resistant catalyst consisting of bauxite impregnated with a minor proportion of barium hydroxide at temperatures in the range of 1100 to 1300° F. and pressures in the range of zero to 100 pounds gage, whereby the butenes are partially converted to butadiene and the carbon dioxide serves as a selective oxidizing agent for hydrogen resulting from the dehydrogenation, separating the butadiene from the effluent vapors, and returning unconverted butenes to the catalyst.

2. In the process of claim 1, the step of adding a minor proportion of carbon dioxide preheated to conversion temperatures by direct injection at several points into the catalyst bed.

3. A process for the catalytic dehydrogenation of low-boiling aliphatic olefins having four to five carbon atoms per molecule to form the corresponding diolefins which comprises forming a mixture of said olefins with a diluent comprising methane and carbon dioxide, the carbon dioxide being present in said diluent in excess of 50 volume per cent; said mixture containing sufficient diluent, at least 50 per cent by volume, to produce an olefin partial pressure below 0.5 atmosphere under the condition of the dehydrogenation step, hereinafter recited; and passing said mixture at a pressure within the range of about one atmos-

phere to about 100 pounds per square inch gage and at temperatures within the range of 1100 to 1300° F. into contact with a dehydrogenation catalyst comprising bauxite impregnated with a minor proportion, 1 to 10 weight per cent, of barium hydroxide.

4. A process for the catalytic dehydrogenation of olefins of four to five carbon atoms per molecule to produce the corresponding diolefins which comprises admixing carbon dioxide with a hydrocarbon mixture containing said olefins to form a mixture containing carbon dioxide in excess of the non-olefin hydrocarbons present in said hydrocarbon mixture and said olefins in concentrations below 50 volume per cent of said mixture, and passing said mixture at a pressure within the range of about atmospheric pressure to about 100 pounds per square inch gage and temperatures within the range of 1100 to 1300° F. into contact with a water resistant difficultly reducible metal oxide dehydrogenation catalyst consisting of bauxite impregnated with minor proportions of barium hydroxide effecting conversion of at least a portion of the olefin to the corresponding diolefin.

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