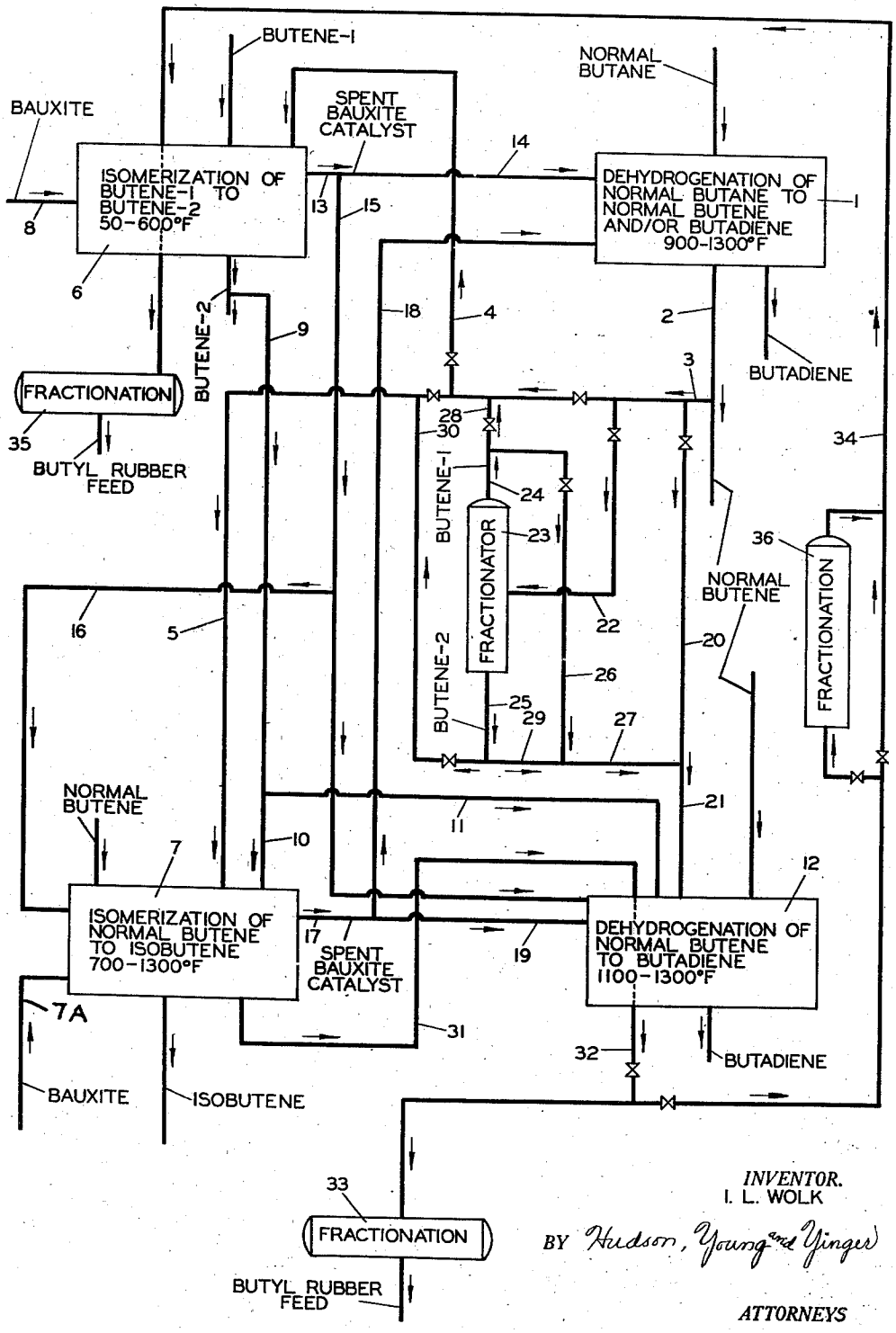
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PROCESS OF TREATING HYDROCARBONS

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INVENTOR.
I. L. WOLK

BY Hudson, Young and Yingling

ATTORNEYS

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PROCESS OF TREATING HYDROCARBONS

I. Louis Wolk, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to a hydrocarbon conversion process and more particularly to a process of catalytically dehydrogenating hydrocarbons specifically paraffins or olefins to the corresponding olefins or diolefins.

The principal object of the present invention is to provide an improved process of catalytically dehydrogenating paraffins or olefins. Another object is to provide a catalytic dehydrogenation process wherein the catalyst is a difficulty reducible metal oxide catalyst and especially bauxite which has been previously treated to spend its olefin isomerizing capacity. Another object is to provide an improved process of making iso-olefins from the corresponding normal paraffins, and especially isobutene from normal butane. Another object is to provide an improved process of making butene-2 from normal butane. Still another object is to provide an improved process of making butadiene from normal butane. Yet another object is to provide an improved process for preparing both butadiene and isobutene from normal butane. Still another object is to provide an improved process for preparing butadiene and isobutene in proportions suitable for making butyl rubber directly. Another object is to conserve heat in a catalytic dehydrogenation process. Still another object is to provide a process for simultaneously or sequentially conducting catalytic isomerization of olefins and catalytic dehydrogenation of paraffins or olefins. Numerous other objects will hereinafter appear.

The accompanying drawing portrays diagrammatically one arrangement of equipment and process steps, all or a suitable portion of which may be utilized for carrying out the present invention. It is to be understood that while the drawing indicates the transfer of catalyst, in practice usually the catalyst itself is not transferred but the same effect is secured by switching the hydrocarbon flow among the several converters in manner known to the art. It will also be obvious that a plurality of converters of the several types are ordinarily employed, some of which may be on-stream while the rest are being regenerated.

In carrying out dehydrogenation of hydrocarbons, especially of normal paraffins and/or normal olefins, over a difficulty reducible metal oxide dehydrogenating catalyst such as bauxite, the catalyst possesses under the dehydrogenation conditions marked olefin isomerizing activity and effects substantial isomerization of the feed olefins, the intermediate olefin (in the case of dehydrogenation of paraffins to diolefins in a single stage), or the product olefin to isomeric forms which are frequently undesirable and objectionable. For example, in the dehydrogenation of normal butane to normal butene, some isobutene normally appears in the effluent and this may be undesirable because it contaminates the normal butene sought and requires separation which is expensive. Again, in dehydrogenating normal butane and/or normal butene to butadiene some isobutene is formed and is objectionable because it is incapable of dehydrogenation to butadiene. Likewise in dehydrogenating pure butene-1 or butene-2 to butadiene, the formation of the other normal butene by isomerization during the dehydrogenation may be objectionable because it interferes with the maintenance of optimum conditions for conversion of either pure butene-1 or butene-2 to butadiene.

I have found that the dehydrogenation of paraffins, preferably normal paraffins, or olefins or of mixtures of paraffins and olefins to the corresponding olefins or diolefins or mixtures thereof may be more advantageously carried out using as a catalyst bauxite which has been previously employed for the isomerization of olefins, and preferably of normal olefins to iso-olefins.

My invention is based on the fact that bauxite possesses both isomerizing and dehydrogenating catalytic properties under suitable conditions. In accordance with my invention the isomerizing capacity of the bauxite is first neutralized prior to its use as the dehydrogenation catalyst, by employing the bauxite preliminarily as a catalyst for the isomerization of olefins and especially for the isomerization of normal olefins to iso-olefins. In this way the present invention effects utilization of both the isomerizing and the dehydrogenating properties of the bauxite in an efficient manner and enables the dehydrogenation to be conducted without accompanying undesirable isomerization.

The catalytic olefin isomerization may be the simple shifting of the double bond in the olefin, as from either the 1- or 2-position to the other, but usually is the conversion of a normal (straight-chain) olefin to a branched-chain olefin, since the latter presents a much more troublesome problem in the dehydrogenation art.

In many cases the dehydrogenation reaction is employed to convert normal paraffins to normal olefins and the olefins for use in the isomerizing step are obtained from this dehydrogenation step, the same catalyst being used first in the

isomerization step and then, after being spent or substantially spent therein, being employed in the dehydrogenation step. Preferably the catalyst is transferred from one step to the other, usually by switching the hydrocarbon flow, thus utilizing the residual heat in the catalyst and effecting substantial thermal economies. Further thermal economies may be effected by passing the effluent from the dehydrogenation step in heat exchange with cold inlet gases and then into the isomerization step at suitable isomerization temperatures.

While bauxite is highly preferred as the common dehydrogenation and isomerization catalyst for use in accordance with the present invention, I may, though much less preferably, employ other difficulty reducible metal oxide catalysts which are capable of effecting isomerization of olefins and dehydrogenation of paraffins or olefins. Examples are oxides of zirconium, titanium, thorium, vanadium, calcium, strontium, barium, magnesium, beryllium, scandium, yttrium, uranium, tungsten, molybdenum, chromium and aluminum. In other words the oxides of the metals of the left hand columns of Groups II, III, IV, V and VI of the Periodic System, in addition to aluminum oxide, may be used. Bauxite is much preferable to aluminum oxide even in the form of so-called "activated alumina." In the case of chromium oxide, it is preferred to employ this oxide supported on a suitable carrier such as bauxite, activated alumina, diatomaceous earth, silica gel, etc. The same may be said of molybdenum oxide (MoO_2) and tungsten (WO_3). In addition to the catalysts enumerated, I may use any other difficultly reducible metal oxide catalyst which possesses both dehydrogenating activity and olefin isomerizing power to a substantial extent.

The broad principle of the invention, outlined above, may be applied specifically in a great many ways with advantage. Among these specific applications are those detailed in the following.

Example I

In this embodiment, I may isomerize a 1-olefin to a 2-olefin, e. g. butene-1 to butene-2, using bauxite or other difficultly reducible metal oxide catalyst at temperatures ranging from atmospheric (say 50° F.) to 600° F., preferably about 350° F. It is preferred to dehydrate the bauxite preliminarily. The method described in copending application of H. E. Drennan, Serial No. 450,797, filed July 13, 1942, may be used for this step.

As the next step, olefins, such as butenes, preferably normal butenes especially butene-2, and conveniently the butene-2 derived from the effluent of the first step, are dehydrogenated to the corresponding diolefin, especially butadiene, over the catalyst after it has been used in the first step. Thus, double use of the catalyst is obtained, and the normal isomerizing tendency of the catalyst in the dehydrogenation step is overcome. Moreover, the catalyst carries its residual heat from the first step into the second step, thereby conserving heat since the catalyst is not allowed to cool substantially below the isomerization temperature before the hydrocarbon flow is switched to effect the dehydrogenation to butadiene.

The dehydrogenation temperature may be 1100 to 1300° F. The conditions for dehydrogenation to butadiene over difficultly reducible metal oxide catalysts are now well known to the art and need not be set forth in detail.

If desired, butene-1 may be dehydrogenated to butadiene in the second step. In this case, as in the case of pure butene-2, optimum conditions for dehydrogenation of this normal butene are employed and the tendency for isomerization to butene-2 in this step is eliminated. Again, instead of a normal butene feed to this dehydrogenation step, I may use a feed of normal butane or of a mixture of normal butane and a normal butene. Under other circumstances I may dehydrogenate normal butane to normal butene only in the dehydrogenation step.

Example II

Step 1.—A 1-olefin is catalytically isomerized to a 2-olefin, for example butene-1 to butene-2, as in the first step of Example I, using fresh bauxite as before.

Step 2.—The effluent from Step 1, or the butene-2 content thereof where the effluent contains significant or objectionable amounts of butene-1, is passed to a dehydrogenation zone where it is dehydrogenated to butadiene over a catalyst which has been used for isomerizing normal butene to isobutene in Step 3.

Step 3.—Normal butene, such as butene-1 or butene-2 or a mixture thereof, but preferably butene-1, is catalytically isomerized to isobutene over a catalyst which has been used for isomerizing butene-1 to butene-2 in Step 1 and so spent for isomerization of butene-1 to butene-2. This may be done at temperatures ranging from 700 to 1300° F. The principles of effecting this step over bauxite are disclosed in copending application of Hillyer et al., Serial No. 427,830, filed Jan. 22, 1942. When the isomerization is carried out at temperatures in the dehydrogenation range, shorter contact times than are used in dehydrogenation are desirable as described in the copending application of Hillyer et al. referred to. These contact times may be readily determined by experiment and may be about 1000 to 1500 or more gas volumes of reactant per volume of catalyst per hour. Isobutene is recovered from the effluent in the usual way.

The advantages are much the same as for the procedure of Example I. The catalyst is used thrice, the residual heat of the catalyst from Step 1 is conserved for Step 3, and the residual heat from Step 3 is likewise conserved for Step 2. Moreover, the tendency of the catalyst to shift the olefin double bond is avoided in Steps 2 and 3 and its tendency to form isobutene in Step 2 similarly is eliminated.

Example III

Step 1.—Normal olefins are isomerized to isoolefins, e. g. normal butene to isobutene, over bauxite which may conveniently be fresh. The isobutene is recovered from the effluent as before in any suitable way.

Step 2.—Normal olefins are dehydrogenated to diolefins, as normal butene (butene-1 and/or butene-2, though preferably pure butene-2) to butadiene, over the bauxite catalyst which has been used in Step 1. The hot catalyst from Step 1 is preferably used directly without cooling, as by immediately switching the hydrocarbon flow, in order to conserve the heat of the catalyst and avoid delay. The conditions of contact time in this step differ sufficiently from those in Step 1 to effect dehydrogenation to butadiene. As before, the isomerizing tendency of the catalyst has been removed.

Example IV

Step 1.—Normal paraffins are catalytically dehydrogenated to the corresponding normal olefins or to mixtures of the corresponding normal olefins and diolefins, as for example, normal butane to normal butene or to normal butene and butadiene, over a bauxite catalyst which has been used to isomerize normal butene to isobutene in Step 2.

Step 2.—Normal butene, and preferably normal butene derived from the effluent of Step 1 is catalytically isomerized to isobutene over fresh bauxite catalyst.

Example V

Step 1.—Normal paraffins are catalytically dehydrogenated to the corresponding 1- and 2-olefins, for example normal butane to a mixture of butenes-1 and -2, over bauxite catalyst which has been used for the isomerization of butene-1 to butene-2 in Step 2.

Step 2.—Butene-1 derived from the effluent of Step 1 is catalytically isomerized to butene-2 over fresh bauxite catalyst.

Example VI

Step 1.—Normal butane is dehydrogenated to a mixture of butenes-1 and -2 over a bauxite which has been used to isomerize butene-1 to isobutene in Step 2. The effluent is fractionally distilled to separate a butene-1 fraction and a butene-2 fraction.

Step 2.—The butene-1 derived from Step 1 is converted to isobutene over a bauxite catalyst, a portion of which is thereafter used in Step 1 and another portion of which is thereafter used in performing Step 3.

Step 3.—The butene-2 fraction formed in Step 1 is dehydrogenated to butadiene over a portion of the catalyst which has been used in Step 2.

Example VII

Step 1.—Normal butane is catalytically dehydrogenated to a mixture of butenes-1 and -2 over catalyst which has been used in Step 3. The butenes are separated.

Step 2.—The butene-1 formed in Step 1 is isomerized to butene-2 at 350° F. over fresh bauxite.

Step 3.—The butene-2 derived from either of Steps 1 or 2 is isomerized to isobutene over bauxite which has been used in Step 2.

Step 4.—The butene-2 not passed to Step 3 is catalytically dehydrogenated to butadiene over catalyst which has been used in Step 3.

Example VIII

Step 1.—Normal butene is isomerized to isobutene over bauxite at 700–1300° F. as before.

Step 2.—A stream comprising the isobutylene and the normal butene content of the effluent of Step 1, and which stream may consist of the entire effluent, is fed to a catalytic dehydrogenation zone where the unconverted normal butene is dehydrogenated to butadiene in such amounts as to give an effluent wherein the isobutylene and butadiene are present in such relative proportions as to be suitable as a butyl rubber feed, namely, 70–99.5% isobutylene and 0.5–30% butadiene. The effluent may be fractionated to segregate these two components, by themselves or along with any other unobjectionable components, as the butyl rubber charge.

This dehydrogenation step is conducted over bauxite catalyst which has been used in Step 1.

Example IX

Example VIII is duplicated except that the effluent from Step 2 which contains substantial amounts of butene-1 which is impossible to separate from butadiene and isobutylene by fractional distillation. Accordingly the effluent, or at least the isobutylene, butadiene and butene-1 content thereof, is passed over fresh bauxite catalyst at 350° F. to convert the butene-1 to butene-2 which is then segregated from the isomerization effluent to give a butyl rubber feed.

The catalyst spent in this final isomerization step may advantageously be used in Step 1 of Example VIII therein.

Referring now to the accompanying drawing, normal butane may be fed to dehydrogenation zone 1 where it is dehydrogenated to normal butene at temperatures for example of 900 to 1100° F. or to butadiene at temperatures ranging from 1100 to 1300° F. or to mixtures of both at temperatures of from 900 to 1300° F.

The normal butene effluent leaves via line 2 whence it may be removed from the system or passed via line 3 and thence either via line 4 to isomerization unit 6 where isomerization by means of shifting of double bond takes place, or via line 5 to isomerization unit 7 where isomerization to isobutene occurs.

Fresh bauxite catalyst may be introduced to unit 6 via line 8 and to unit 7 via line 7A. The butene-2 derived from the effluent of unit 6 may be removed from the system or passed via line 9 and thence either via line 10 to serve as feed to unit 7 or via line 11 to serve as feed to a second stage dehydrogenation unit 12 wherein normal butene is dehydrogenated to butadiene under known conditions.

The catalyst in Step 6 may thereafter be utilized in either of Steps 1, 7 or 12, as indicated diagrammatically by line 13 and thence lines 14, 15 or 16, respectively.

The catalyst in Step 7 may thereafter be used in Step 1 as indicated by lines 17 and 18 or in Step 12 as indicated by lines 17 and 19.

It will be understood that conventional equipment not shown is employed for recovering the desired components from the effluents of the several conversion steps. Also provision for recycling is not shown because obvious to those skilled in the art.

The normal butene recovered from Step 1 may be in part or in toto directed via lines 20 and 21 to serve as feed to unit 12. Alternatively, where it comprises both butenes-1 and -2, it may in part or in toto be passed via line 22 to fractionator 23 where it is separated into butene-1 as the overhead via line 24 and butene-2 via line 25. The butene-1 may then be passed via lines 26 and 27 to serve as feed to unit 12, or by lines 28 and 4 to unit 6 or by lines 28 and 5 to unit 7.

The butene-2 leaving via line 25 may be passed via lines 29 and 27 to unit 12. This is a preferred feed for making butadiene. Or it may be passed via lines 30 and 5 to unit 7.

If desired, the isobutene-normal butene containing effluent from unit 7 may be passed via line 31 through dehydrogenation unit 12. The effluent may pass via line 32 either to fractionation Step 33 where a butyl rubber feed is separated or via line 34 to isomerization Step 6 whence the effluent passes to fractionation Step 35 where the butene-2 is separated to give a butyl rubber feed. If desired the effluent in line 32 may have been treated in fractionator 36 to

segregate only the butadiene, isobutylene and butene-1 content thereof for charging to unit 6.

From the foregoing a great many advantages of my invention will at once be apparent to those skilled in the art. Among them are the fact that dehydrogenation is accomplished without accompanying isomerization so that optimum conditions are more readily maintained and optimum yields are obtained. The process is capable of a high degree of flexibility to yield any desired proportion of products from a given raw material. Heat is utilized in an efficient manner. If desired separate feeds may be treated in the individual units, the only connection therebetween being the successive use of catalyst as described. Or the effluent from one stage may be passed to one of the other stages in the flexible manner described, thereby giving an unusually compact process which is readily adaptable to a wide variety of needs.

I claim:

1. In a process for the catalytic dehydrogenation of paraffins and olefins by contacting under dehydrogenating conditions of temperature and pressure with a difficultly reducible metal oxide catalyst which when fresh is capable of effecting ooth isomerization of olefins and dehydrogenation of paraffins and olefins, the step which comprises preliminarily catalytically isomerizing an olefin by means of said catalyst until the olefin isomerizing activity of said catalyst is spent in a separate step prior to use thereof in said dehydrogenation step.

2. The process which comprises catalytically isomerizing an olefin by means of a difficultly reducible metal oxide catalyst which when fresh is capable of effecting both isomerization of olefins and dehydrogenation of paraffins and olefins until said catalyst is spent for said isomerization, and thereafter in a separate step catalytically dehydrogenating a hydrocarbon selected from the group consisting of paraffins and olefins by means of said catalyst after it has become spent for said isomerization step.

3. The process which comprises catalytically isomerizing a normal olefin to an isoolefin by means of a difficultly reducible metal oxide catalyst which when fresh is capable of effecting both isomerization of normal olefins to isoolefins and dehydrogenation of paraffins and olefins until said catalyst is spent for said isomerization, and thereafter in a separate step catalytically dehydrogenating a hydrocarbon selected from the group consisting of paraffins and olefins by means of said catalyst spent for said isomerization.

4. The process which comprises catalytically isomerizing an olefin by means of bauxite as a catalyst until said bauxite is spent for olefin isomerization, and thereafter in a separate step catalytically dehydrogenating a hydrocarbon selected from the group consisting of paraffins and olefins by means of said bauxite after it has become spent for said isomerization step.

5. In a process for the preparation of iso-olefins by catalytic dehydrogenation of normal paraffins of at least four carbon atoms to the corresponding normal mono-olefins and catalytic isomerization of said normal mono-olefins to the corresponding iso-olefins, the steps which comprise contacting the normal mono-olefin with a difficultly reducible metal oxide catalyst which when fresh is capable of effecting both isomerization of normal olefins to iso-olefins and dehydrogenation of paraffins and olefins under isomerizing conditions of temperature and pressure to produce said iso-olefin until said catalyst is spent for olefin isomerization, and utilizing the spent catalyst from the isomerizing step as catalyst for the dehydrogenation of the normal paraffin to the corresponding mono-olefin.

6. In a process for the preparation of isobutene by catalytic dehydrogenation of normal butane to normal butene and catalytic isomerization of said normal butene to isobutene, the steps which comprise contacting said normal butene with bauxite as a catalyst under isomerizing conditions of temperature and pressure to produce said isobutene until said bauxite is spent for said isomerization, and utilizing the spent catalyst from the isomerizing step as catalyst for the dehydrogenation of said normal butane to said normal butene.

7. The process which comprises catalytically isomerizing normal butene to isobutene with bauxite as a catalyst until said bauxite is spent for said isomerization, and thereafter and in a separate step catalytically dehydrogenating normal butane with said spent bauxite after it has catalyzed said isomerizing step.

8. A process for the preparation of butene-2 which comprises dehydrogenating normal butane over a bauxite catalyst to produce a mixture of butenes-1 and -2, isomerizing the butene-1 contained in said mixture to butene-2 by contact with a bauxite catalyst under isomerizing conditions of temperature and pressure until said catalyst is spent for said isomerization, and utilizing the spent catalyst from the isomerization step as the catalyst for the dehydrogenation of normal butane.

9. A process for the preparation of butadiene and isobutene from normal butane which comprises dehydrogenating normal butane over a bauxite catalyst to produce a butenes-1 and -2 containing mixture, separating said butene-2 from said butene-1, contacting the butene-1 with a bauxite catalyst under isomerizing conditions of temperature and pressure to produce isobutene until said catalyst is spent for said isomerization, employing a portion of the spent catalyst therefrom as the catalyst in said dehydrogenation step, and contacting the butene-2 with a portion of the spent catalyst from said isomerization step to convert said butene-2 to butadiene.

10. The process which comprises catalytically dehydrogenating normal butane to normal butene over a bauxite catalyst, splitting the butene content of the effluent into at least two portions, catalytically isomerizing one of said butene portions to isobutene over a bauxite catalyst until said catalyst is spent for said isomerization, catalytically dehydrogenating the other of said butene portions to butadiene over a bauxite catalyst, and utilizing the spent bauxite catalyst from said isomerizing step in at least one of said dehydrogenating steps as the catalyst therefor.

11. The process which comprises catalytically dehydrogenating normal butane to normal butene over a bauxite catalyst, catalytically isomerizing butene-1 derived from the dehydrogenation effluent to butene-2 over a bauxite catalyst until said catalyst is spent for said isomerization, catalytically isomerizing butene-2 derived from one of the dehydrogenation and isomerization effluents to isobutene over a bauxite catalyst until said catalyst is spent for said isomerization to isobutene, catalytically dehydrogenating butene-2 derived from one of said dehydrogenation and said first-named isomerization effluents to butadiene over a bauxite catalyst, using the catalyst

spent in said first-named isomerization step as the catalyst in said second-named isomerization step, and using the catalyst spent in said second-named isomerization step as the catalyst in one of said dehydrogenation steps.

12. The process which comprises catalytically dehydrogenating normal butane to normal butene over a bauxite catalyst, catalytically isomerizing butene-1 derived from the dehydrogenation effluent to butene-2 over a bauxite catalyst until said catalyst is spent for said isomerization, catalytically isomerizing butene-2 derived from one of the dehydrogenation and isomerization effluents to isobutene over a bauxite catalyst until said catalyst is spent for said isomerization to isobutene, catalytically dehydrogenating butene-2 derived from one of said dehydrogenation and said first-named isomerization effluents to butadiene over a bauxite catalyst, using the catalyst spent in said first-named isomerization step as the catalyst in said second-named isomerization step, and using the catalyst spent in said second-named isomerization step as the catalyst in said first-named dehydrogenation step.

13. The process which comprises catalytically isomerizing butene-1 to butene-2 at temperatures ranging from atmospheric to 600° F. over a bauxite catalyst until said catalyst is spent for said isomerization, and thereafter in a separate step catalytically dehydrogenating the butene-2 to butadiene over the bauxite catalyst spent in said isomerization step and which has not been allowed to cool substantially below the isomerization temperature.

14. The process which comprises catalytically dehydrogenating normal butane to normal butene over a bauxite catalyst, catalytically isomerizing butene-1 derived from the dehydrogenation effluent to butene-2 over a bauxite catalyst until said catalyst is spent for said isomerization, catalytically isomerizing butene-2 derived from one of the dehydrogenation and isomerization effluents to isobutene over a bauxite catalyst until said catalyst is spent for said isomerization to isobutene, catalytically dehydrogenating butene-2 derived from one of said dehydrogenation and said first-named isomerization effluents to butadiene over a bauxite catalyst, using the catalyst spent in said first-named isomerization step as the catalyst in said second-named isomerization step, and using the catalyst spent in said second-named isomerization step as the catalyst in said second-named dehydrogenation step.

15. The process which comprises catalytically isomerizing normal butenes to isobutene at temperatures ranging from 700 to 1300° F. over a bauxite catalyst until said catalyst is spent for said isomerization, and thereafter in a separate step dehydrogenating normal butene to butadiene over the bauxite catalyst spent in said isomerization step and which has not been allowed to cool substantially below the isomerization temperatures.

16. The process which comprises catalytically isomerizing normal butene over a bauxite catalyst at temperatures from 700 to 1300° F. to convert normal butene to isobutene until said catalyst is spent for said isomerization, and catalytically dehydrogenating a stream derived from the effluent and comprising the isobutylene and normal butene content thereof over the bauxite catalyst spent in said isomerization step to convert said normal butene to butadiene and form an effluent containing isobutylene and butadiene in the relative proportions of at least 70% of isobutylene and not over 30% of butadiene.

17. The process which comprises catalytically isomerizing normal butene over a bauxite catalyst at temperatures ranging from 700 to 1300° F. to convert normal butene to isobutene until said catalyst is spent for said isomerization, catalytically dehydrogenating a stream derived from the effluent and comprising the isobutylene and normal butene content thereof over the bauxite catalyst spent in said isomerization step to convert said normal butene to butadiene and form an effluent containing isobutylene and butadiene in the relative proportions of at least 70% of isobutylene and not over 30% of butadiene and also containing butene-1, catalytically isomerizing a stream comprising said isobutylene, said butadiene and said butene-1 over a bauxite catalyst at temperatures ranging from atmospheric to 600° F. to convert said butene-1 to butene-2 until said catalyst is spent for said isomerization to butene-2, fractionally distilling the effluent from said last-named step to separate said isobutylene and butadiene in said proportions free from butene-2, and utilizing the catalyst spent in said second-named isomerization step as the catalyst in said first-named isomerization step.

I. LOUIS WOLK.