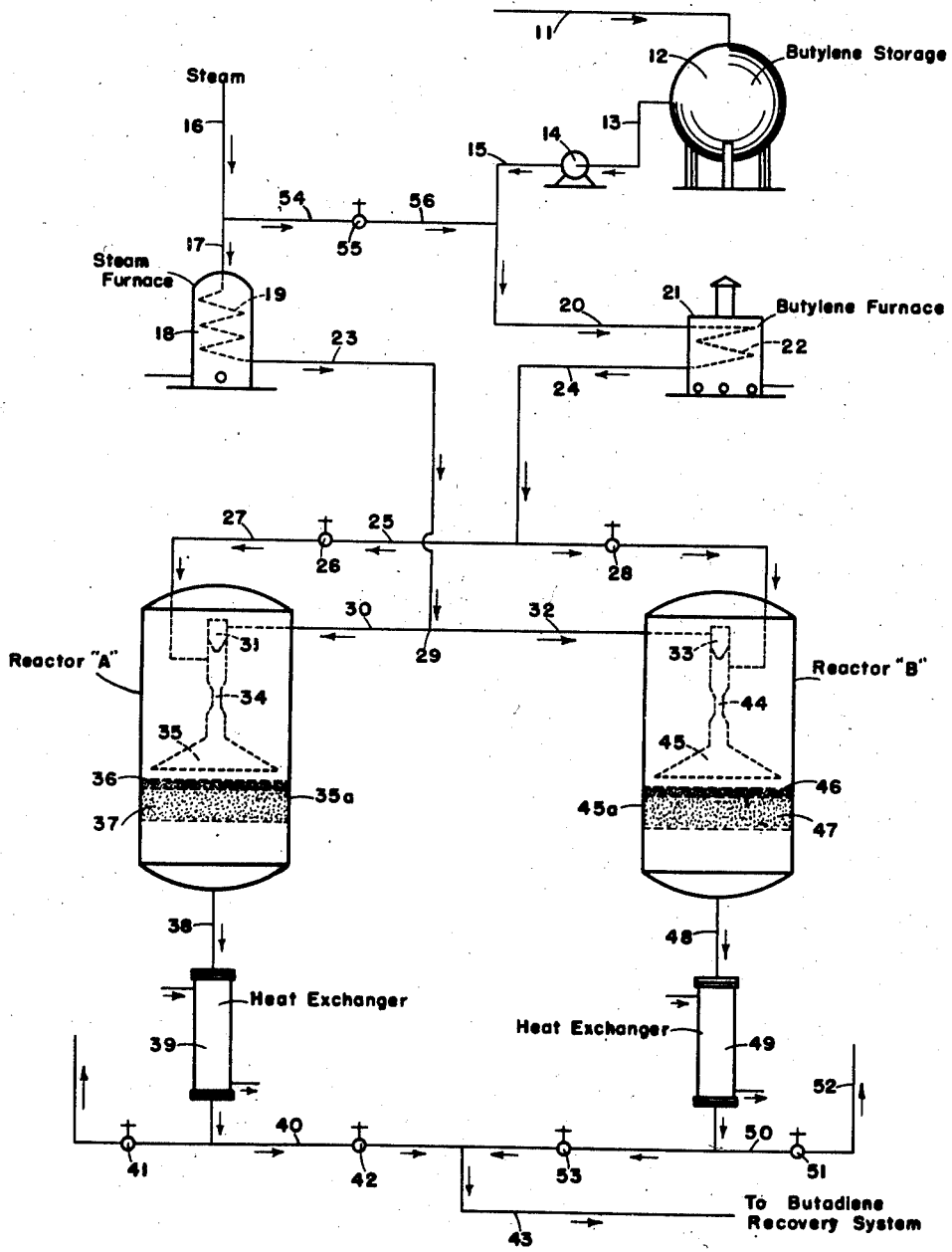
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CATALYTIC DEHYDROGENATION OF OLEFINIC HYDROCARBONS WHILE MAINTAINING THE POTASSIUM CONTENT OF THE CATALYST

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CATALYTIC DEHYDROGENATION OF OLEFINIC HYDROCARBONS WHILE MAINTAINING THE POTASSIUM CONTENT OF THE CATALYST

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1

This invention relates to a process for the catalytic dehydrogenation of mono-olefins to diolefins. More specifically, it relates to an improved process for the catalytic dehydrogenation of low boiling mono-olefins having more than three carbon atoms to produce the corresponding diolefins.

Hydrocarbon compounds, such as butadiene and isoprene, have become extremely important as starting materials for the production of rubber and rubber substitutes. Since the quantity of diolefins produced in ordinary cracking operations is relatively small, it has become necessary to devise processes specifically designed to accomplish the production of relatively large amounts of such diolefins. In one such process, normal butylenes are dehydrogenated to butadiene in the presence of a catalyst. The dehydrogenation reaction is extremely sensitive and it is necessary to take careful precautions to prevent the degradation of butadiene into undesirable side products during and immediately following its formation. To prevent such degradation, it is preferable to carry out the dehydrogenation reaction at low butylene partial pressures, such as from ¼ to $\frac{1}{10}$ atmospheric, in order to obtain good yields of butadiene.

Although low partial pressure operations can be obtained by operating in vacuo, it is preferable to dilute the charge with a gaseous diluent in order to eliminate explosion hazards, to simplify temperature control and to make the process more economical. Steam is an economical diluent and is preferable to gases, such as nitrogen, carbon dioxide and methane, for several reasons. In the first place, steam is readily separated by condensation from the dehydrogenation products. In addition, since steam reacts at elevated temperatures with the carbon deposited on the catalyst to form water gas, the activity of the catalyst may be maintained at a high level for longer periods of time than is otherwise possible. The residual carbon remaining on the catalyst after the dehydrogenation cycle has been completed is readily removed by periodically stopping the hydrocarbon feed and continuing the flow of steam through the fouled catalyst to effect complete removal of the carbon therefrom. It is seen that this type of operation is more economical than is the operation in which the catalyst must be purged free from hydrocarbons and subsequently contacted with an oxygen-containing gas to effect the oxidation of the carbon deposited on the catalyst.

Catalysts which are suitable for the dehydrogenation of olefins in the presence of steam usually contain a major portion of magnesium oxide as a base material and lesser amounts, from 3% to 49% of the total weight of the catalyst, of an active dehydrogenating compound, such as an oxide of iron, chromium, cobalt or nickel. They may also contain small amounts of a basic oxide as a promoter for the water gas reaction between steam and the carbon deposited on the catalyst. Oxides of potassium, sodium, lithium, barium or calcium in amounts of from 0.5 to 10% of the total weight of the catalyst may be used although potassium oxide has been found to be most effective. A stabilizer may also be added to the catalyst in small amounts to prevent the promoter from volatilizing at elevated temperatures or the catalyst from becoming inactive; such stabilizers as the oxides of copper, aluminum, thorium, zinc and silver may be used. Dehydrogenation catalysts may also be prepared with mixtures of two or more compounds from any of the above described groups of catalyst components, namely: the catalyst base materials, active dehydrogenating compounds, stabilizers and promoters.

2

In commercial dehydrogenation processes, two or more fluidly connected catalytic zones undergoing cyclic operation are frequently employed. The reactor containing an active catalyst is employed for the dehydrogenation cycle and at the same time a reactor containing catalyst fouled by deposits of carbon is undergoing the regeneration cycle. A mixture of steam and hydrocarbons is passed over the fresh catalyst bed at an elevated temperature while steam is passed over the fouled catalyst at an elevated temperature. This operation is continued for from about 1 to 2 hours after which time the catalyst undergoing the dehydrogenation cycle is sufficiently fouled with carbon to require regeneration and the regenerated catalyst is sufficiently free of carbon to be an active dehydrogenation catalyst. The cycle is then reversed so that the mixture of mono-olefins and steam is passed through the regenerated catalyst zone and the steam is passed through the fouled catalyst zone.

It has been found in such operations employing a catalyst comprising major quantities of magnesium oxide and minor quantities of iron, potassium and copper oxides that the catalyst gradually loses activity after repeated reaction and regeneration cycles. Since it is desirable to maintain a constant mono-olefins conversion level and selectively to diolefins to meet production schedules, it is necessary to increase the catalyst bed temperature periodically in order to compensate for the lowered catalyst activity and thus main-

tain these desired levels. It also has been found that the lowered catalyst activity results, for one thing, from the fact that the potassium oxide, even in the presence of a stabilizer such as copper oxide, gradually volatilizes from the catalyst at the high temperatures employed in the reaction after repeated reaction and regeneration cycles.

This volatilization of the potassium oxide occurs in the first portion of the catalyst bed contacted by the hydrocarbon charge stock, and the potassium oxide migrates downwardly through the catalyst zone. As a result, the top portion of the catalyst bed loses its activity for promoting the water gas reaction which removes carbon deposits from the catalyst. After continued operation, the potassium oxide content of the upper portion of the catalyst bed becomes so low that fresh catalyst must be used to replace the deactivated catalyst.

It is, therefore, an object of our invention to maintain the activity of a dehydrogenating catalyst at a desired level throughout the effective life of the catalyst.

It is a further object of our invention to provide catalysts for the dehydrogenation reaction which will not lose appreciable quantities of promoter for the water gas reaction during the effective life of the catalyst.

A specific object of our invention is to dehydrogenate butylenes catalytically in the presence of relatively large volumes of diluent steam to form butadiene by employing a catalyst bed comprising a first relatively thin layer of a dehydrogenation catalyst containing a relatively large amount of a basic oxide promoter and a second thick layer of a dehydrogenation catalyst containing a relatively small amount of a basic oxide promoter.

Other objects of our invention will appear from the following detailed description and claims.

The invention will be better understood by reference to the sole figure which is a diagrammatic flow plan of one embodiment of our process. A normal butylenes concentrate prepared by means well known to the art is charged through line 11 to a suitable butylenes storage tank 12. From tank 12 the butylenes concentrate is charged through line 13 and pump 14 to line 15 leading to a suitable heating medium for heating the butylenes.

Low temperature steam heated by means not shown, is introduced through lines 16 and 17 into steam heating zone 18 wherein the steam passes through coils 19 and is heated to temperatures somewhat above that required for dehydrogenating the butylenes, for example, from 1250° to 1400° F. The butylenes concentrate likewise passes from line 20 into heating zone 21 wherein it is heated in coils 22 up to temperatures somewhat below those required for dehydrogenation, for example, from 1050° to 1150° F. The effluents from coils 19 and 22 are routed by means of lines 23 and 24 to reactors A and B in a manner to be described in more detail hereinafter.

It will be assumed in this particular illustration that reactor A is on the reaction cycle and that reactor B is on the regeneration cycle. In this case, the heated butylenes concentrate from line 24 passes through line 25 and through valve 26 to line 27. Valve 28 is closed to prevent butylenes from entering reactor B. Steam leaves steam furnace 18 through line 23 to manifold 29. A major portion of the steam from manifold 29 passes through line 30 to steam ejector 31 in reactor A. The minor portion of steam from manifold 29 passes through line 32 to steam ejector 33 in reactor B.

The heated butylenes concentrate passes from line 27 into the low pressure side of steam ejector 31, and passes downwardly to Venturi throat 34. Steam entering by means of line 30 passes through steam ejector 31 to Venturi throat 34. The steam and butylenes are intimately mixed in the Venturi throat and pass downwardly through distribution shoe 35 to the catalyst zone 35a wherein the dehydrogenation reaction takes place. The upper portion 36 of the catalyst zone comprises a relatively thin layer of dehydrogenation catalyst containing a basic oxide promoter in amounts ranging from 5 to 20% of the total weight of the catalyst. The lower portion of the catalyst zone 37 comprises a relatively thick layer of dehydrogenation catalyst containing a basic oxide promoter in amount ranging from 0.5 to 10% of the total weight of catalyst. It is preferable in the case of these two layers to maintain a thickness ratio of the upper and lower catalyst beds of from 1/48:1 to 1/4:1.

The reactor effluent leaving catalyst zone 37 passes through line 38 and waste heat boiler 39 to conduit 40. Valve 41 is closed during this operation to prevent the reactants from being vented to the atmosphere. From conduit 40 the reactants pass through valve 42 and line 43 to the butadiene recovery system, not shown.

During the period that the above described process is taking place in reactor A, the minor portion of steam entering steam ejector 33 in reactor B passes downwardly through Venturi throat 44 and distribution shoe 45 to catalyst bed 45a comprising zones 46 and 47 of a relatively thin and a relatively thick layer of catalysts, respectively, as described in the case of reactor A. The heated steam reacts with carbon deposited on the catalyst in these two zones and thus serves to regenerate the catalyst to substantially its original activity. Steam containing the products of the water gas reaction taking place in catalyst zones 46 and 47 passes downwardly through line 48 to waste heat boiler 49 and thence through line 50, valve 51, and line 52 to the atmosphere. Valve 51 by controlling the effluent gases controls the amount of steam routed to reactor B. During this operation valve 53 is closed to prevent admixing the effluent from reactor A with the steam and other gaseous materials withdrawn from reactor B.

The butadiene recovery system is not shown; however, it may be any of those well known to the art. Systems which may be successfully applied for the purification of butadiene are extraction with cuprous chloride solution or with reagents containing a cuprous salt such as cuprous ammonium acetate, or by other chemical methods. Fractionation may also be practiced, if desired. Substantially pure butadiene may be produced by any of these processes and substantially complete recovery of butadiene from the residual vapors may be obtained.

It is to be understood that the fluidly connected reactors A and B are employed in cyclic operation so that after a suitable period of time, from 30 minutes to 2 hours, the operating cycle is reversed so that butylenes and steam enter reactor B which contains regenerated catalyst while steam enters reactor A containing the fouled

catalyst. In this operation, valves 41 and 51 are readjusted so that a major portion of the steam leaving steam furnace 18 enters reactor B while the minor portion enters reactor A.

If desired, a portion of the low temperature steam entering the system by means of line 16 may be routed through line 54, valve 55 and line 56 to be mixed with the butylenes concentrate in line 15. In this way, a mixture of butylenes and steam may be heated to fairly high temperatures in furnace 21 without appreciable degradation of the butylenes occurring in this steam furnace and in the lines leading to the reactors.

In carrying out the dehydrogenation reaction outlined above, pressures of from about 0.5 to 20 lbs./sq. in. gauge and temperatures of from 1100° to 1300° F. are preferably employed in the catalyst zone. The ratio of steam to hydrocarbons in the catalyst zone may vary from 10:1 to 30:1. The period required for the dehydrogenation reaction to take place may vary; however, it is usually preferable that reaction times of from 0.1 to 1 second be employed.

The ratio of the thicknesses of the catalyst beds containing, respectively, relatively large and relatively small amounts of basic oxide promoter will vary depending on the ease with which these promoters are volatilized at the high reaction temperatures employed. In the case of catalysts comprising major portions of magnesium oxide and minor portions of iron, copper and potassium oxides, it is usually preferable to employ a first layer, containing the relatively large amount of potassium oxide, of only about 1/48 to ¼ of the thickness of the lower catalyst bed containing the relatively small amount of basic oxide promoter. As mentioned previously, the basic oxide promoter content of the first catalyst zone may vary from about 5 to 20 per cent whereas that of the lower thick catalyst zone may vary from 0.5 to 10 per cent of the total weight of the catalyst.

It is thus seen that after reaction and regeneration cycles are repeated continuously, any promoter migrating from the upper catalyst zone into the lower parts of the catalyst bed will not cause the top portion of the catalyst bed to lose its effectiveness for promoting the water gas reaction between steam and carbon during either the reaction or regeneration cycles. It is for this reason, that the catalyst bed has a much longer active life than would a single catalyst bed in which the amount of the basic oxide promoter content is distributed evenly.

The following example will illustrate the improvements to be achieved by the use of our process. Two reactors were filled with catalysts composed of magnesium oxide, iron oxide, copper oxide and potassium oxide. In the first reactor the potassium oxide content of the catalyst was 5 wt. per cent whereas in the second reactor the potassium oxide content of the catalyst was 10 weight per cent. The iron oxide and copper oxide contents of the two catalysts were identical. A mixture of steam and normal butylenes concentrate in a ratio of about 10:1 was passed through each catalyst bed during two-hour cycle operations. After each two-hour cycle, the catalyst was regenerated with steam and the reaction cycle was continued for another two hours. The products from each cycle were analyzed for butadiene content as well as for residual butylenes. From these data the butylenes conversion, selectivity, and yield of butadiene were determined. The data in the following table show a comparison of the results obtained after the two catalyst beds had been employed for a number of reaction cycles:

Table

Reactor Employed	1	2
Potassium oxide content of catalyst, weight per cent	5	10
Dehydrogenation cycles	69–72	142–153
Catalyst age, cycles	72	153
Reactor charge analyses, mole per cent:		
Iso and N-Butane and lighter	7.0	13.3
Isobutylene	5.5	6.0
N-Butylenes	86.9	79.7
Butadiene	0.6	1.0
Average catalyst temperature, ° F	1,146	1,146
Hydrocarbon space velocity, volumes of hydrocarbons per volume of catalyst per hour	391	399
Steam to hydrocarbon ratio	9.8	10.4
Reactor Outlet Pressure, lbs./sq. in. gauge	0.9	0.9
N-Butylenes conversion, mole per cent	31.6	31.6
Selectivity to Butadiene, mole per cent	76.9	81.0
Butadiene Yield, mole per cent	24.3	25.6

It will be noted that in the case of reactor 2 containing a high potassium oxide content catalyst, a higher selectivity and yield of butadiene were obtained after 153 reaction cycles than were obtained with the low potassium oxide content catalyst after only 72 reaction cycles. These data show, therefore, that the active life of the high potassium oxide content catalyst is greater than that of the lower potassium content catalyst. In continuing the above-mentioned runs, it was found that the temperature requirement for an average of 30% conversion of normal butylenes was about 20° to 25° F. lower for the high potassium oxide content catalyst than it was for the low potassium oxide content catalyst. It was also found that the rate of temperature increase for maintaining constant conversion for the high potassium oxide content catalyst is about 17° F. for 100 cycles as compared with about 20° F. per 100 cycles for the low potassium oxide content catalyst. In addition, it was found that the catalyst containing 10% potassium oxide would require a temperature of 1250° F. for 30% conversion of normal butylenes after about 960 two-hour cycles, whereas, the catalyst containing 5% potassium oxide would reach this temperature at a 30% conversion level after only 650 cycles.

In the practice of the present invention a catalyst containing a high potassium oxide content is employed in conjunction with one containing a low potassium oxide content and this procedure increases the active life of the entire catalyst bed.

The nature and objects of the present invention having been fully described and illustrated, what we desire to claim is:

1. A process for catalytically dehydrogenating a normal mono-olefin having more than three carbon atoms in the molecule to the corresponding diolefin in the presence of a dehydrogenating catalyst consisting of a major amount of magnesium oxide, a small amount of iron oxide, and a small amount of potassium oxide which consists of passing a mixture of said mono-olefin and steam at a reaction temperature through a bed consisting of a thin first layer of said dehydrogenating catalyst containing a relatively large amount of potassium oxide and a thick second layer of said dehydrogenating catalyst containing a relatively small amount of potassium oxide.

2. A process in accordance with claim 1 in which the ratio of the thicknesses of the first and second catalyst layers varies from 1/48:1 to ¼:1.

3. A process in accordance with claim 1 in which the potassium oxide content of the first catalyst layer varies from 5 to 20 weight per cent and that

of the second catalyst layer varies from 0.5 to 10 weight per cent.

4. A process in accordance with claim 1 in which the reaction temperature employed is within the range of 1150° to 1300° F. and the steam to hydrocarbon molal ratio in the catalyst zone is within the range of 10:1 to 30:1.

5. A process for catalytically dehydrogenating normal butylene to butadiene in the presence of a dehydrogenating catalyst consisting of a major amount of magnesium oxide, a small amount of iron oxide, and a small amount of potassium oxide which consists of passing a mixture of said monoolefin and steam at a reaction temperature through a bed consisting of a thin first layer of said dehydrogenating catalyst containing a relatively large amount of potassium oxide and a thick second layer of said dehydrogenating catalyst containing a relatively small amount of potassium oxide.

6. A process in accordance with claim 5 in which the ratio of the thicknesses of the first and second catalyst layers is within the range of 1/48:1 to 1/4:1.

7. A process in accordance with claim 5 in which the basic potassium oxide promoter content of the first catalyst layer is within the range of 5 to 10 weight per cent and that of the second catalyst layer is within the range of 0.5 to 10 weight per cent.

8. A process in accordance with claim 5 in which the reaction temperature employed is within the range of 1150° to 1300° F., and the steam to hydrocarbon molal ratio in the catalyst zone is within the range of 10:1 to 30:1.

9. A process for catalytically dehydrogenating normal butylenes to butadiene in the presence of a dehydrogenating catalyst consisting of a major amount of magnesium oxide, a small amount of iron oxide, and a small amount of potassium oxide which consists of providing a plurality of reactors each containing a thin first layer of said dehydrogenating catalyst containing a relatively large amount of potassium oxide and a thick second layer of said dehydrogenating catalyst containing a relatively small amount of potassium oxide, said first layer being deposited on said second layer, preheating the butylenes to a temperature below active dehydrogenating temperatures, admixing the preheated butylenes with steam heated to a temperature above active dehydrogenating temperatures, forming a mixture of said heated butylenes and steam, passing said mixture of butylenes and steam through each of said reactors containing said catalyst and in sequence through said first and second layers until said catalyst in the first of said reactors becomes fouled with carbonaceous matter, terminating the flow of mixture through the first of said reactors, and contacting said fouled catalyst including first and second layers of catalyst with heated steam to cause regeneration thereof, discontinuing the flow of steam to said reactor, resuming the flow of feed admixture to said reactor, and recovering a product including butadiene from said reactors while said feed admixture is being routed thereto.

10. A process for catalytically dehydrogenating normal butylenes to butadiene which comprises providing a pair of fluidly connected reactors, each containing a first thin layer of a dehydrogenation catalyst comprising a major portion of magnesium oxide, minor portions of iron and copper oxides and from 5 to 20 weight per cent potassium oxide and a second thick layer of a dehydrogenation catalyst comprising a major portion of magnesium oxide, minor portions of iron and copper oxides and from 0.3 to 10 weight per cent potassium oxide, said first layer being deposited on said second layer, the ratio of the thicknesses of the said first and second catalyst layers in each reactor being within the range of 1/48:1 to 1/4:1, preheating the normal butylenes to a temperature within the range of 1050° to 1150° F., preheating steam to a temperature within the range of 1250° to 1400° F., admixing the preheated steam and preheated hydrocarbons in a molal ratio within the range of 10:1 to 30:1, passing said mixture of butylenes and steam through the first and second of said reactors and in sequence through said first and second layers in each of said reactors until the catalyst in one of said reactors becomes fouled, terminating the flow of steam and hydrocarbon mixture to said reactor containing fouled catalyst, flowing heated steam over said fouled catalyst including first and second layers of catalyst until the fouled catalyst becomes regenerated, continuing flow of said mixture to the second of said reactors until said catalyst in said second reactor becomes fouled, resuming flow of steam and heated hydrocarbon to said regenerated catalyst, and recovering from said reactors while steam and hydrocarbons are being routed thereto a product including substantial quantities of butadiene.

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