Fig. I

Fig. II
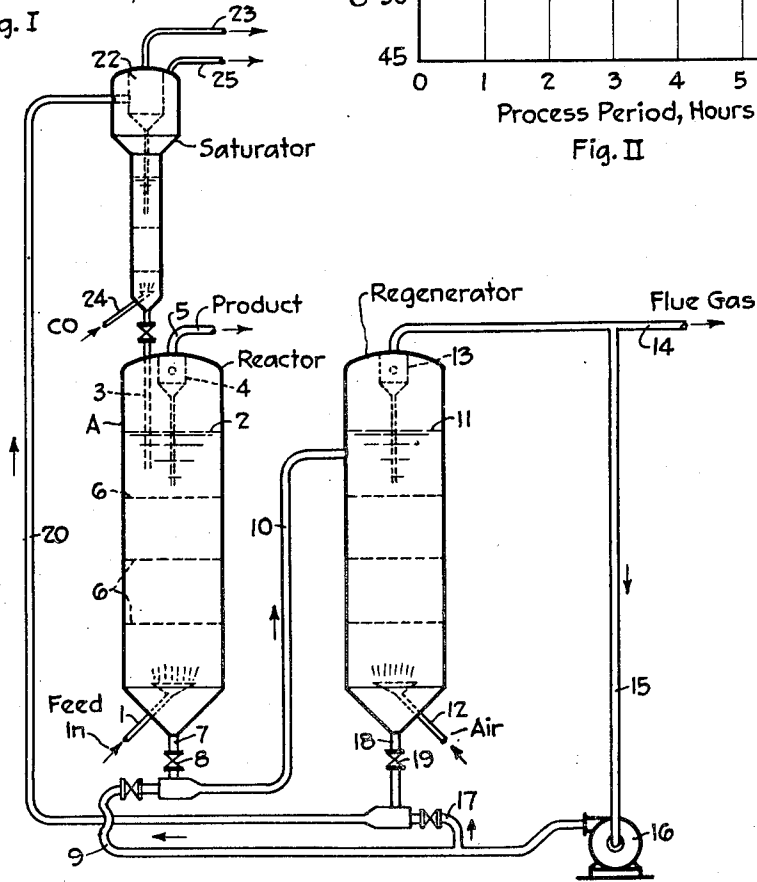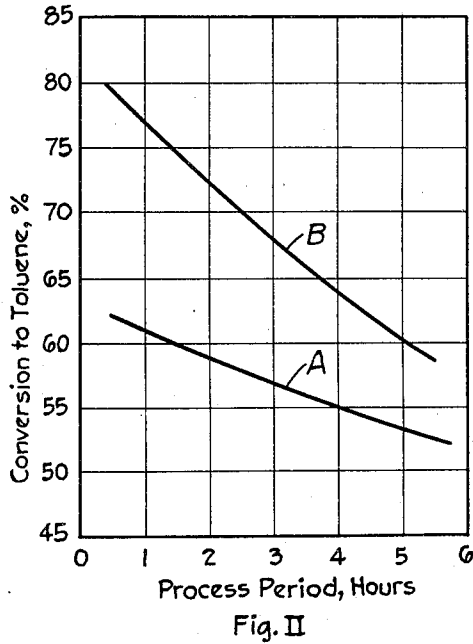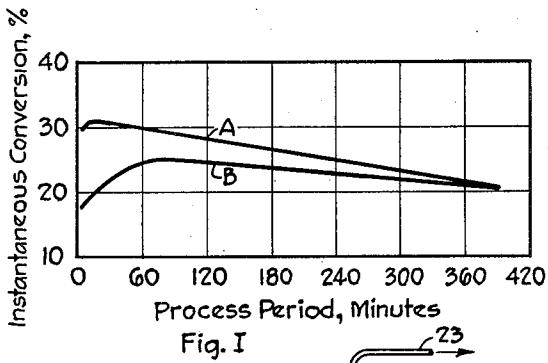
Fig. III

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By his Attorney:

UNITED STATES PATENT OFFICE

2,500,482

CATALYTIC DEHYDROGENATION

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4 Claims. (Cl. 260—668)

This invention relates to catalytic dehydrogenation with metal oxide dehydrogenation catalysts which are periodically regenerated by burning carbonaceous deposits therefrom. The term "catalytic dehydrogenation" as used throughout the present description and the appended claims, is used to denote a process or reaction in which one or more atoms of hydrogen is split and removed from a dehydrogenatable dehydrogen-containing compound by the catalytic action of a catalyzer. In dehydrogenation the splitting of the C—H bond generally requires relatively severe conditions which closely approach those causing cracking or the breaking of C—C bonds. As a consequence, the dehydrogenation of dehydrogenatable organic compounds is generally accompanied by a minor amount of such degradation or cracking reactions which lead to the formation of some tarry carbonaceous material. This tarry carbonaceous material deposits on the surface of the catalyst and soon renders it ineffective.

It is known that the formation and deposition of such tarry material can be appreciably repressed by the application of a sufficient partial pressure of hydrogen in the dehydrogenation zone. Thus, in some cases it is recommended to recycle a large amount of hydrogen (product gas) through the reaction zone, preferably under considerable pressure. Since, however, hydrogen is a product of reaction in dehydrogenation and since, furthermore, dehydrogenation is a reaction which results in an increase in volume, the use of added hydrogen under pressure has the material disadvantage of considerably curtailing the rate of dehydrogenation and extent of dehydrogenation possible. Consequently, it is preferable in many dehydrogenation processes to forego the use of added hydrogen.

When added hydrogen is not used under sufficient pressure, it is necessary to remove the carbonaceous deposits from the catalysts at frequent intervals. This process is known as regeneration and is carried out by carefully burning the carbonaceous deposits from the catalysts with a suitable regeneration gas, such as, for example, as air diluted with flue gas. The period during which dehydrogenation is carried out between the successive regeneration is called the process period. This process period may vary anywhere from about 10 minutes up to several hours, depending upon the particular catalyst used, the particular conditions, and the particular material being dehydrogenated. A process that is carried out in this manner with frequent regeneration of the catalyst may be called a regenerative process to distinguish it from non-regenerative or continuous processes where regeneration, if carried out at all, is carried out only at very infrequent intervals. The regenerative manner of operation requires a plant provided with adequate facilities for periodic regeneration of the catalyst. On the other hand this method of operation has the advantages that it usually requires lower temperatures and pressures, and a considerable portion of the heat liberated in the regeneration can be stored in the catalyst and utilized in the subsequent dehydrogenation period. For this latter reason it is often desirable to use quite short process periods. Short process periods down to about 10 minutes may be used with fixed beds of catalysts. However, for operation with short process periods a system in which the catalyst is continuously recycled through the dehydrogenation zone and the regeneration zone is more advantageous.

In spite of the advantages of the regenerative method of operation at low pressure over operation at higher temperatures and pressures in the presence of added hydrogen, this method has had very little commercial success. This is due largely to the fact that the efficiency of the process drops off as the process period is shortened; thus, as the process period is shortened the dehydrogenation declines and the amount of the feed treated that is converted to tarry deposits is increased.

Since in the regenerative method of operation the catalyst is subjected to frequent regeneration, this type of operation is limited to the use of metal oxide dehydrogenation catalysts. Examples of a few applicable metal oxide dehydrogenation catalysts are the oxides of zinc, aluminum, titanium, thorium, chromium, molybdenum, tungsten, iron, nickel and cobalt and mixtures and combinations of these. While the use of dehydrogenating sulfides, halides, etc., is often suggested these can not be regenerated in the simple manner described and are not suitable for practical operation with this type of process. The various applicable metal oxide dehydrogenation catalysts may be prepared by any of the conventional methods. For example, in the preparation of multi-compound catalysts the powdered ingredients may be simply mixed and then formed into pellets by piling or by extruding the moistened mixture. In many cases the oxide catalysts may be prepared by the decomposition of a compound of the metal or metals, as the nitrate, acetate, ammonium salts, or the like, by heating, reduction, oxidation, or the like. Also

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the metal oxide may in some cases be prepared by burning the powdered metal or the metal carbonyl. Many excellent catalysts of this type are prepared by precipitating the hydrous oxides. These various metal oxides or mixtures or compounds thereof, may be used per se or in combination with an inert diluent or other less active substance such, for example, as magnesia, kieselguhr, silica gel, zirconia, clay, silicon, silicon carbide, pumice, asbestos, bauxite or any one of the various forms of alumina. Particularly effective catalysts are prepared by impregnating a suitable support or carrier substance, such as one of the porous forms of alumina, with the dehydrogenating metal oxide or oxides.

The catalyst may be prepared in a powdered form or in the form of lumps or granules, or in the form of cast or shaped particles of any desired size and shape, such as cylinders, balls, saddles and the like. In general after combining the desired ingredients of the catalyst and forming into particles of the desired size and shape for the particular reactor in question, the catalyst is heated up to a temperature approaching the temperature to be used in the dehydrogenation process, or even a little higher, to strengthen the particles and allow any shrinkage to take place before packing the reactor. It is also frequently the practice to treat the catalyst with hydrogen or natural gas for a time at such temperature to reduce it to its active state. The catalyst is then placed in the reactor and the process is started. In general a single batch of catalyst is used for a considerable time before it is replaced. Various applicable metal oxides, their preparation, and their use in dehydrogenation are described in United States Patent No. 2,184,235, to which reference may be had.

It has now been found that the dehydrogenation of various dehydrogenatable organic hydrogen-containing materials with metal oxide dehydrogenation catalysts in a regenerative process may be unexpectedly and materially improved if the catalyst is saturated with carbon monoxide prior to contacting it with the material to be dehydrogenated, and the material to be dehydrogenated is contacted with the catalyst so saturated with carbon monoxide. Thus, when operating such a process in accordance with the present invention the catalyst, after each regeneration, is treated with carbon monoxide in the absence of any appreciable amount of hydrogen for a period until it is substantially saturated with carbon monoxide; then the material to be dehydrogenated is contacted with the catalyst so saturated with the carbon monoxide. This result in a considerably improved dehydrogenation activity which is particularly advantageous for short-cycle operation.

The treatment with carbon monoxide is carried out at an elevated temperature between about 350° C. and about 590° C. It is preferably carried out at a temperature between that prevailing at the end of regeneration, for example 550° C., and that prevailing during the dehydrogenation. This not only allows the treatment to be effected without change or adjustment of the temperature of the catalyst, but is also advantageous since when the treatment is carried out at approximately the dehydrogenation temperature the maximum amount of carbon monoxide that can be retained under the dehydrogenation conditions is absorbed. The treatment with carbon monoxide may be carried out at any pressure from somewhat below atmospheric pressure up to several hundred atmospheres; however, the treatment is preferably carried out at atmospheric pressure or a pressure slightly above atmospheric pressure, for example 1.5 to 3 atmospheres.

The surface of the catalyst upon completion of the regeneration treatment is saturated with nitrogen, oxygen and carbon dioxide; however, these materials are relatively weakly adsorbed and are easily displaced by any one of a number of more strongly adsorbed materials. Thus, if the catalyst at this stage is contacted with a material which is more strongly adsorbed, this latter material displaces the less strongly adsorbed material. When this displacement takes place to its maximum extent under the conditions prevailing, the surface of the catalyst is substantially covered with the more strongly adsorbed material and the catalyst is then said to be saturated with the latter material. If the catalyst is then treated with an even more strongly adsorbed material, this covers the catalyst by displacement, and the catalyst is then saturated with this latter material. It will be understood that the adsorption referred to is not limited to simple Van der Waals adsorption. At the temperatures under consideration activated adsorption and chemi-sorption may take place. According to the present invention the catalyst is saturated with carbon monoxide. This gas is only weakly adsorbed.

As the carbon monoxide is adsorbed on the surface of the catalyst a small temperature rise will be noted. The time required for substantially complete saturation is only a matter of a few minutes. Thirty minutes is ample.

The carbon monoxide may contain a minor amount of carbon dioxide or nitrogen or any other material which is less strongly adsorbed than carbon monoxide; however, such materials as hydrogen and water vapor which are more strongly adsorbed than carbon monoxide should not be present in any substantial amount. Even relatively small amounts of water vapor are particularly detrimental. The carbon monoxide should, therefore, be substantially dry, i. e. contains not more than about 3% water vapor and preferably less than 2% water vapor.

During the treatment with carbon monoxide some reduction of the catalyst may take place. However, since treatment of the catalyst with hydrogen does not give the improvement in question, it appears that the improvement is not due to any reduction which may take place.

As pointed out above the catalyst is not only saturated with carbon monoxide after the regeneration and prior to contacting it with the material to be dehydrogenated, but the material to be dehydrogenated is contacted with the catalyst saturated with carbon monoxide. In other words, if the catalyst is treated with hydrogen or any other gas which is more strongly adsorbed than carbon monoxide, it can not be saturated with carbon monoxide, and, on the other hand, if the catalyst is treated with hydrogen or any other gas more strongly adsorbed than carbon monoxide after treating it with carbon monoxide and before contacting it with the material to be dehydrogenated, the beneficial effect of the carbon monoxide treatment is lost.

As will be explained further, the beneficial results obtained by having the catalyst saturated with carbon monoxide at the start of the process period is not permanent, but gradually diminishes, becoming substantially lost in about 5 to 6 hours. This is due to the displacement of the adsorbed carbon monoxide from the catalyst by

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the hydrogen liberated in the course of the dehydrogenation. Since the partial pressure of product hydrogen under dehydrogenation conditions is relatively low, it requires about 5 to 6 hours for the hydrogen to destroy the effect of the carbon monoxide. If a higher partial pressure of hydrogen were present, as in operation with added hydrogen under pressure, the beneficial effect of the treatment with carbon monoxide would be lost in a much shorter time. It is for this reason that the use of any appreciable pressure of added hydrogen in the dehydrogenation is not recommended when operating in accordance with the process of the present invention. The partial pressure of added hydrogen, if this is used during the dehydrogenation, should be less than one atmosphere.

Certain aspects of the invention will be illustrated in the following examples:

Example I.—Isobutane was dehydrogenated under the following conditions:

Temperature _____ 550° C.
Pressure _____ 1 atm.
Space velocity _____ 16 vol. per min.
Process period _____ 6½ hours

The catalyst (Cr–183) was prepared by impregnating ⅛ inch pellets of gamma alumina with chromium oxide (7.9% Cr) and magnesium oxide (1.4% Mg). Prior to use the catalyst was reduced with hydrogen for about one hour at about 550° C.

After each regeneration of the catalyst and before contacting it with the isobutane in the subsequent process period, the catalyst was saturated with carbon monoxide by passing a stream of carbon monoxide through the catalyst bed under the following conditions:

Temperature_____ 550° C.
Pressure_____ 1 atm.
Time[1]_____ 30 min.

[1] This time was chosen to insure thorough saturation. As indicated by the temperature rise, the absorption of carbon monoxide was substantially complete in a much shorter time.

For comparison, the catalyst was treated with hydrogen instead of carbon monoxide in the same manner.

The results obtained during a typical process period are shown graphically in the attached drawing, Figure I. The curves A and B show the instantaneous conversions to olefins in per cent at various times throughout the entire process period for the carbon monoxide treated catalyst and hydrogen treated catalyst, respectively. The substantial improvement obtained by the method of the invention is evident.

The two types of curves could be alternately obtained in successive process periods by alternately treating with carbon monoxide and hydrogen. This is shown in the following Table I:

Table I

Time, Minutes	Conversion To Isobutane, Catalyst Saturated With—			
	H₂ 3rd cycle	CO 4th cycle	H₂ 5th cycle	CO 6th cycle
5	20.8	30.9	14.9	------
15	22.4	31.8	17.7	30.0
30	24.2	31.5	18.9	29.2
60	24.7	30.0	20.8	28.5
90	25.6	------	21.5	27.0
120	26.2	28.8	17.6	27.1
180	24.8	27.4	23.0	25.5
240	------	25.5	21.7	21.0
300	24.2	23.2	21.4	22.0
360	21.6	22.8	22.4	21.6

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Example II.—Isobutane was dehydrogenated under the following conditions:

Temperature_____ 550° C.
Pressure_____ 1 atm.
Space velocity_____ 16 vol. per min.
Process period_____ 70 min.

The catalyst (207-w-10) contained iron oxide (5.8% Fe) and chromium oxide (17.5% Cr) incorporated by impregnation on the surface of an activated alumina. Prior to use, the catalyst was calcined at about 550° C. for about 2 hours and then treated with hydrogen at about 550° C. for about 1 hour. After each regeneration of the catalyst and before contacting the regenerated catalyst with isobutane in the subsequent process period, the catalyst was substantially saturated with carbon monoxide by passing a stream of carbon monoxide through catalyst bed under the following conditions:

Temperature_____ 550° C.
Pressure_____ 1 atm.
Time_____ 30 min.

For comparison, the catalyst was treated with hydrogen instead of carbon monoxide in the same manner.

In this case also the improvement was very marked and very similar to that shown in Example I.

It was thought that the improvement might possibly be due to the presence of the carbon monoxide liberated from the catalyst during the process. To check this possibility, comparable runs were made in which small amounts of carbon monoxide were added with the isobutane. This added carbon monoxide, however, did not exert any beneficial effect.

Example III.—Methylcyclohexane was dehydrogenated under the following conditions:

Temperature_____ 490° C.
Pressure_____ 1 atm.
Liquid hourly space velocity_____ 0.36
Process period_____ 6 hours
Hydrogen/feed, mol ratio_____ 1:1

The catalyst (2507-HF-6) was prepared by incorporating chromium oxide (10.6% Cr) on the surface of pelleted gamma alumina. Prior to use, the catalyst was heated at about 600° C. for about two hours, and finally reduced with hydrogen for about one hour at about 490° C. The regenerations were carried out at about 600° C.

After regeneration, and before contacting the catalyst with the methylcyclohexane in the next process period, the catalyst was saturated with hydrogen by passing a stream of hydrogen through the catalyst at about 490° C. for about thirty minutes. The per cent toluene in the product and the per cent conversion during a typical process period are shown in the following Table II:

Table II

Time, Hours	Per Cent Toluene In Product	Per Cent Conversion
0–1	59.5	62.0
1–2	59.8	59.8
2–3	56.4	56.8
3–4	56.1	56.5
4–5	54.5	54.9
5–6	52.4	52.0

Following the process period, the conversions of which are given in the above table, the catalyst

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was regenerated in the usual manner and then saturated with carbon monoxide by passing a stream of carbon monoxide through the catalyst bed at about 490° C. for about thirty minutes. The results obtained in the following process period are shown in the following Table III:

Table III

Time, Hours	Per Cent Toluene In Product	Per Cent Conversion
0–1	82.7	79.5
1–2	75.7	73.5
2–3	73.3	71.0
3–4	70.4	67.7
4–5	62.3	60.0
5–6	60.6	58.4

The results shown in Tables II and III are shown graphically in the attached drawing Figure II as curves A and B respectively.

Merely for the sake of comparison, the results obtained during a typical process period when operating under the following conditions:

Temperature _____ 490° C.
Pressure _____ 20 atm.
Liquid hourly space velocity _____ 0.24
Hydrogen/feed, mol ratio _____ 5

are shown in the following Table IV:

Table IV

Time, Hours	Per Cent Toluene In Product	Per Cent Conversion
0–1	27.0	25.3
1–2	31.4	29.6
2–3	28.2	26.6
3–4	30.4	29.2
4–5	29.3	28.2
5–6	28.8	27.4

It will be seen that the conversions are very much lower in spite of the lower liquid hourly space velocity. The rate of decline of the activity of the catalyst is materially decreased, in fact at this low temperature level the deposition of carbonaceous deposits is substantially eliminated. In order to obtain comparable conversions the temperature would have to be materially increased and the deposition of carbonaceous deposits would then again become appreciable. This method, of using a substantial pressure of hydrogen, is therefore not suitable for short cycle operation, as, for example, when using the fluidized catalyst technique.

Example IV.—Isobutane was dehydrogenated under the following conditions:

Temperature _____ 500° C.
Pressure _____ 1 atm.
Space velocity _____ 16 vol. per min.
Process period _____ 6 hours

using different catalysts having different structures as well as compositions. The regenerations were carried out in the usual manner with air. Following the regeneration of the catalyst, and just prior to contacting it with the isobutane in the subsequent process period, the catalyst was saturated with carbon monoxide in the manner described in Example I. Comparable runs were made in which the catalyst was treated with hydrogen. (Treatment with hydrogen gives a slight improvement over no treatment at all between the regeneration and the subsequent process pe-

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riod, and consequently, treatment with hydrogen has been used as a comparison.) The comparative results are shown below in Table V:

Table V

Time, Min.	Conversion, percent					
	Catalyst 1 Pretreatment		Catalyst 2 Pretreatment		Catalyst 3 Pretreatment	
	H₂	CO	H₂	CO	H₂	CO
5	10.0	--------	25.5	37.5	18.8	30.9
15	14.2	24.0	28.8	38.1	20.3	31.8
30	16.3	23.8	32.0	37.4	22.8	31.5
60	18.0	--------	32.5	34.8	24.6	30.0
90	18.6	--------	31.0	32.2	--------	--------
120	19.4	22.8	29.6	30.2	24.9	28.8
180	19.8	--------	26.5	27.1	23.8	27.4
240	19.7	20.8	23.5	24.2	--------	--------
300	19.5	--------	20.2	--------	23.3	23.2
360	18.8	--------	17.2	17.4	--------	--------

After discovering the described unexpected effect of saturating the catalyst with carbon monoxide prior to contacting the feed to be dehydrogenated with it, tests were made in which the catalyst was pretreated with other agents, including nitrogen, water vapor and carbon dioxide. None of the agents or combinations thereof were comparable in effect to carbon monoxide. In combination with carbon monoxide the other agents gave different effects which could be correlated with their tendency to be adsorbed by the catalyst. Thus, for example, a treatment with nitrogen either before or after, or before and after, treating the catalyst with carbon monoxide had very little effect. On the other hand treatment of the catalyst with hydrogen either before or after treating the catalyst with carbon monoxide destroyed the described and illustrated effect of the carbon monoxide.

The beneficial effect of the described treatment of the catalyst with carbon monoxide is greatest at the start of the process period and gradually diminishes as the process period is continued. If the process period were made sufficiently long, the beneficial effect would be substantially reduced. The process is of most practical advantage when the process period is less than about 10 hours. It becomes more advantageous as the process period is shortened. It is generally impractical to operate with process periods shorter than a minimum of about one hour with a fixed bed of catalyst, although shorter process periods have been used in exceptional cases. This is due primarily to the fact that shorter process periods require very rapid temperature changes, and to the fact that as the process period is decreased the percentage of time used in nonprofitable temperature adjustment, flushing, etc., becomes inordinately large. When using moving catalyst beds or the fluidized catalyst technique, however, the residence time of the catalyst in the dehydrogenation zone (which is equivalent to the process period) may easily be maintained in the range of thirty minutes down to even one minute. This fluidized catalyst type of operation, while particularly suitable for catalytic cracking to produce gasoline, has not found any commercial application for dehydrogenation, because when using the usual type of catalyst under the usual conditions no advantage is gained in decreasing the effective process period. In fact it is seen that under the usual conditions, it is generally distinctly disadvantageous to decrease the process period to below two or three hours. The fluidized catalyst tech-

nique has, however, certain other advantages and considerable attention has been given to the possibility of its profitable application in this type of process. In applying the fluidized catalyst technique to this type of process, however, it has been necessary to increase the residence time of the catalyst in the reaction zone between successive regenerations by recycling the catalyst through the reaction zone while withdrawing only a small slip stream for regeneration. This is simply a means of increasing the process period (note U. S. Patent Nos. 2,325,516 and 2,303,083).

While this expedient allows the fluidized catalyst technique to be applied without the adverse effect of shortening the process period, it has the disadvantage that it precludes one of the chief advantages of this technique. Thus, when the process period is lengthened by this expedient, the amount of catalyst cycled through the regeneration zone is small and consequently the heat supplied to the reaction zone with the regenerated catalyst is likewise small. It has been suggested to overcome this difficulty by mixing a large amount of inert heat carrier material with the catalyst. This, however, greatly increases the cost of circulation and has other disadvantages which so far have precluded its commercial application.

The process of the present invention allows the fluidized catalyst technique to be applied to catalytic dehydrogenation of this type without these disadvantages inherent in the previously suggested processes. On the other hand, the short process periods in the order of one to thirty minutes which can be most easily maintained using this technique can be employed to great advantage when operating according to the processes of the present invention. Thus, the conversion may be considerably increased and at the same time all of the considerable heat required for the reaction can be supplied by the hot regenerated catalyst cycled to the reaction zone without reducing the catalyst with inert heat carrier material. A suitable application of the process of the invention using the fluidized catalyst technique is illustrated diagrammatically in Figure III of the drawing. Referring to Figure III, the feed to be dehydrogenated, for example, butane or propane, is introduced via line 1 into the bottom of reactor 2. Reactor 1 is filled up to about the level indicated by A with a finely divided dehydrogenation catalyst in the pseudo liquid state. The catalyst may be any one of the various applicable metal oxide dehydrogenation catalysts, for example, a chromium oxide—alumina—magnesia catalyst or molybdenum oxide impregnated on a spinel base. The catalyst is ground to a sufficiently fine state that it may be fluidized. A catalyst ground to pass a 100 mesh sieve is suitable. Another particularly suitable catalyst is one prepared by impregnating the dehydrogenating metal oxide or oxides on the surface of microspheres of porous alumina having diameters in the order of 100 microns. The regenerated catalyst, after being saturated with carbon monoxide, is introduced into the reactor at the top via line 3. The catalyst passes downward countercurrent to the ascending reactant vapors which are withdrawn through the centrifugal separator 4 and line 5. Baffles 6 in the reactor tend to diminish end-over-end mixing of the catalyst and reactant in the reaction zone, thus providing a more nearly perfect countercurrent operation. The temperature in the reaction zone is, for example, 550° C. and the pres-

sure is substantially atmospheric. The partially spent and partially cooled catalyst leaves the reactor via line 7 and valve 8. This catalyst is picked up by a stream of gas entering via line 9 and is carried via line 10 to the top of the regenerator 11. This gas not only serves to transport the catalyst from the reactor to the regenerator, but also serves to flush or strip the catalyst of volatile combustible material. The line 10 is, therefore, not only a transfer line but also serves as a catalyst stripper. The flue gas usually contains a small amount of non-reacted oxygen and this also helps in freeing the catalyst of volatile material. The partially spent catalyst passes downward through the regenerator countercurrent to the regeneration gas, such as air or oxygen, introduced near the bottom via line 12. The spent regeneration gas (flue gas) leaves the regenerator through centrifugal separator 13 and line 14. Part of the flue gas is withdrawn via line 15 and forced by blower 16 to line 9. Another portion is passed via line 17 to pick up the hot regenerated catalyst (withdrawn via line 18 and valve 19) and carry it via 20 to the saturator 21. The hot regenerated catalyst and carrier gas are introduced into centrifugal separator 22 within the saturator 21. The carrier gas is removed via line 23. Carbon monoxide is introduced into the bottom of the saturator 21 via line 24 and passes up through the descending catalyst. The temperature within the saturator may be, for example, 590–600° C. The hot catalyst substantially saturated with carbon monoxide is then passed directly to the reactor via line 3 as described.

The amount of carbon monoxide required is not large, consequently there is little or no tendency to carry catalyst out of the saturator via line 25 with the exit gas. The rate of addition of carbon monoxide should, however, be sufficient to maintain the catalyst within the saturator in a free flowing condition. Excess carbon monoxide issuing via line 25 may, if desired, be reused. However, the gas issuing via line 25 will be considerably contaminated and for this reason it is preferred to restrict the flow of carbon monoxide to such an extent that little carbon monoxide passes out via line 25 and to forego recycling.

Other arrangements of apparatus and flow may be used with the fluidized catalyst technique. Also the invention is applicable and advantageous when using the so-called moving-bed technique in which the catalyst is used as a solid moving bed rather than in the fluidized state. While the invention is particularly advantageous in the systems where the catalyst is cycled through a reaction zone and a separate regeneration zone, it is to be understood that it can also be advantageously employed using the conventional fixed bed technique.

I claim as my invention:

1. In the dehydrogenation of a saturated hydrocarbon with a chromium oxide catalyst in the absence of added hydrogen wherein the catalyst is periodically regenerated by burning carbonaceous deposits therefrom, the improvement which comprises saturating the catalyst with substantially dry carbon monoxide after said regeneration and prior to contacting it with the material to be dehydrogenated, said saturation of the catalyst being effected without preheating the catalyst after regeneration to a temperature higher than the conversion temperature by treating the unpreheated catalyst with substantially dry carbon monoxide at substantially the temperature

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at which the catalyst is used in the dehydrogenation, and then contacting the catalyst saturated with carbon monoxide with the material to be dehydrogenated.

2. In the dehydrogenation of a saturated hydrocarbon with a chromia-alumina catalyst in the absence of added hydrogen wherein the catalyst is periodically regenerated by burning carbonaceous deposits therefrom, the improvement which comprises saturating the catalyst with substantially dry carbon monoxide after said regeneration and prior to contacting it with the material to be dehydrogenated, said saturation of the catalyst being effected without preheating the catalyst after regeneration to a temperature higher than the conversion temperature by treating the unpreheated catalyst with substantially dry carbon monoxide at substantially the temperature at which the catalyst is used in the dehydrogenation, and then contacting the catalyst saturated with carbon monoxide with the material to be dehydrogenated.

3. In the dehydrogenation of a saturated hydrocarbon with a chromium oxide catalyst in the absence of added hydrogen wherein the catalyst is periodically regenerated by burning carbonaceous deposits therefrom, the improvement which comprises saturating the catalyst with substantially dry carbon monoxide after each regeneration and prior to contacting it with the material to be dehydrogenated, said saturation of the catalyst being effected without preheating the catalyst after regeneration to a temperature higher than the conversion temperature by treat-

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ing the unpreheated catalyst with substantially dry carbon monoxide at substantially the temperature at which the catalyst is used in the dehydrogenation, and then contacting the catalyst saturated with carbon monoxide with the material to be dehydrogenated.

4. In the continuous dehydrogenation of a saturated hydrocarbon with a chromium oxide catalyst in the absence of added hydrogen wherein the catalyst is continuously recycled through a regeneration zone wherein carbonaceous deposits are burned therefrom and through a dehydrogenation zone wherein it is contacted with the material to be dehydrogenated, the improvement which comprises treating the catalyst with substantially dry carbon monoxide during transfer from said regeneration zone to said dehydrogenation zone, said treatment being effected without preheating the catalyst after regeneration to a temperature higher than the conversion temperature and at substantially the temperature at which the catalyst is introduced into the dehydrogenation zone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,274,988	Matuszak	Mar. 3, 1942
2,366,531	Ipatieff et al.	Jan. 2, 1945
2,406,112	Schulze	Aug. 20, 1946