Patented Mar. 21, 1950

2,500,920

UNITED STATES PATENT OFFICE

2,500,920

PROCESS AND CATALYST FOR DEHYDROGENATION OF HYDROCARBONS

Alvie B. C. Dague and John W. Myers, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

No Drawing. Application July 16, 1946, Serial No. 683,996

8 Claims. (Cl. 260—683.3)

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This invention relates to the catalytic dehydrogenation of paraffin hydrocarbons to produce olefins and diolefins. In one of its more specific aspects it relates to an improved process for the dehydrogenation of aliphatic paraffin hydrocarbons to produce the corresponding olefins and diolefins and is particularly applicable to the production of olefins and diolefins from aliphatic paraffins containing from four to five carbon atoms per molecule. Another aspect of the present invention is the provision of novel catalysts for the catalytic dehydrogenation of paraffin hydrocarbons.

In the dehydrogenation of paraffins to the corresponding diolefins, two dehydrogenation steps are customarily employed. In the first step the paraffins are dehydrogenated to olefins which are then subjected in a second step to a separate dehydrogenation treatment to produce diolefins. The olefins may or may not be separated from the effluent of the first dehydrogenation step prior to dehydrogenation to diolefins.

The customary procedure for the production of diolefins by dehydrogenation of corresponding paraffins involves separate dehydrogenation of paraffins and olefins using somewhat different conditions for each dehydrogenation reaction. The paraffins are first dehydrogenated to olefins in the presence of a highly active dehydrogenation catalyst, the olefins are separated from the effluent of the paraffin dehydrogenation step, and separately converted to the corresponding diolefin at a temperature somewhat higher and in the presence of a less active dehydrogenation catalyst than employed for the paraffin dehydrogenation step. Chromium oxide is the active dehydrogenation catalyst conventionally used for the dehydrogenation of paraffin but it is much too severe for olefin dehydrogenation. Separate dehydrogenation of paraffins and olefins requires the use of difficult and relatively expensive separation steps to segregate the paraffin and olefin feed stocks, but the separation procedure is justified on the basis of improved yields and operation.

In the dehydrogenation of paraffins some diolefins are formed; however, the dehydrogenation of paraffins directly to diolefins is not practical by present dehydrogenation processes. Attempted combinations of concurrent dehydrogenation reactions involved in converting paraffins to diolefins in a single dehydrogenation step encounter serious difficulty due to the fact that optimum conditions for the conversion of paraffins to olefins are quite different from the

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optimum conditions for the conversion of olefins to diolefins.

For the dehydrogenation of paraffins, such as normal butane, the catalyst ordinarily employed comprises approximately 10 weight per cent chromium oxide (Cr_2O_3) deposited on a suitable carrier, such as aluminum oxide. As might be expected from the law of mass action, the dehydrogenation reaction is favored by low absolute or partial pressures. Low absolute pressures, i. e., below atmospheric pressure, while favorable to the dehydrogenation reactions, are undesirable in commercial operations due to the difficulty of preventing leakage of air into the system. For this reason it is customary to employ pressures somewhat above atmospheric pressure, generally in the neighborhood of about 30 pounds per square inch gage. A low partial pressure of the reactants, e. g., normal butane, may be obtained by dilution with an inert gas. It has been found that steam is undesirable as a diluent for the dehydrogenation of paraffins since it poisons or reduces the activity of the chromium oxide catalyst of the conventional type. While other gaseous diluents, such as propane and lighter hydrocarbons, are not subject to this disadvantage they are generally not employed because the handling and recycling of large amounts of gaseous diluents represents a large item in plant investment and operating cost. The dehydrogenation of paraffins containing four or five carbon atoms per molecule may be conducted in the absence of a diluent with an efficient separation of olefin products from the paraffin recycle stock.

From the standpoint of chemical and physical characteristics, the most desirable diluent for dehydrogenation is water vapor. This diluent may be cheaply provided in any desired amount and may be removed from the hydrocarbon stream by simple condensation, thereby eliminating a large part of the compression and fractionation equipment necessary when other diluents are used. Steam has been used as a feed diluent in several different types of catalytic and thermal processes for hydrocarbon conversion such as cracking and olefin dehydrogenation. In such processes, particularly those in which solid catalysts are used, the steam serves not only as a diluent, but also as a reagent for the removal of carbon that deposits on the catalyst.

As mentioned hereinbefore, the use of water vapor has previously been condemned in the art because of its deleterious effects on the activity of conventional catalysts employed for the dehydrogenation of paraffins. The catalysts now

used for the dehydrogenation of paraffins in commercial operations show poor conversion when steam is used as a diluent. Present practice is to dehydrogenate undiluted paraffins or to use a non-aqueous gaseous diluent. The feed stream is carefully dehydrated to eliminate all but traces of water vapor.

Steam dilution of feeds to dehydrogenation processes has been applied chiefly to olefins, from which diolefins are produced. The catalysts preferred for dehydrogenation of olefins are different from those preferred for dehydrogenation of paraffins; in fact, when steam-diluted olefinic feeds are treated under preferred conditions in the presence of preferred catalysts for the production of diolefins, any paraffins present in such feeds are, in many cases, substantially unreacted (see Schulze et al., U. S. 2,367,623).

We have now found that steam or water vapor may be employed as a diluent in the dehydrogenation of paraffins, particularly normal butane, effectively and efficiently with certain catalysts which are more fully disclosed hereinafter.

An object of this invention is to provide an improved process for the production of olefins and diolefins from corresponding parraffins. Another object of the present invention is to provide a process for the dehydrogenation of paraffins wherein steam or water vapor may be effectively and efficiently employed as the diluent. A more specific object is to provide a process which is particularly applicable to the dehydrogenation of butane to produce butylenes and butadiene. Still another object of the present invention is to provide catalysts which give efficient conversion of paraffins to olefins and diolefins in the presence of water vapor as a diluent. Other objects and advantages will become apparent to those skilled in the art from the following detailed disclosure of the invention.

We have found that paraffins may be advantageously dehydrogenated in the presence of steam as a diluent to produce olefins and diolefins. Advantages obtained by steam dilution are longer reaction cycles, obviation of the necessity for using reactors made of special heat and corrosion resistant alloys, and the feasibility of using comparatively large reactors. The longer reaction cycles result from the chemical reaction of steam on deposited carbon, known as the water gas reaction, which enables the catalyst to be used for long periods without regeneration with an oxygen-containing gas. Large reactors of the bed type, in contrast to reactors comprising complex heat exchange systems, may be employed in this process as a result of the heat-carrying capacity of steam. This represents a tremendous saving in investment and operating costs.

We have also found that catalysts that are satisfactory for the dehydrogenation of undiluted paraffins are relatively unsatisfactory for the dehydrogenation of paraffins diluted with steam; low yields and short process cycles are obtained. We have further found that a catalyst containing a major portion of alumina and a minor proportion of at least one oxide selected from the group consisting of molybdenum oxide, tungsten oxide, and vanadium oxide is satisfactory for dehydrogenating paraffins diluted with steam. Of these, vanadium oxide is preferred. The preferred content of the minor component is greater than 5 and less than 50 weight per cent of the catalyst. The catalyst may be further improved by the addition of from about 1 to about 15 weight per cent chromium oxide as an activator. Contrary

to expectations, the oxides of the alkali and alkaline earth metals as well as iron oxide, all of which are known promoters of the water gas reaction, decrease the effectiveness of the catalyst. Materials which promote the water gas reaction may, in some instances, be desirable as ingredients of the catalysts to increase the on-stream time or time between regeneration periods. The preferred catalysts are mixtures of aluminum oxide with a plurality of the oxides selected from the group consisting of molybdenum oxide, tungsten oxide, and vanadium oxide, and aluminum oxide admixed with chromium oxide and at least one of the oxides selected from the group consisting of molybdenum oxide, tungsten oxide, and vanadium oxide. Examples of preferred catalysts for use in the process of this invention are:

	Weight per cent
1	
Al_2O_3	60-90
MoO_3	10-40
2	
Al_2O_3	60-80
MoO_3	10-30
V_2O_5	10-30
3	
Al_2O_3	60-80
Cr_2O_3	5-15
V_2O_5	10-30

The catalysts of this invention may be prepared by any of the methods of preparing solid porous oxide catalysts known in the art. Such methods include mixing of the powdered nongel components, coprecipitation of the components as gel, and inpregnation of the carrier material, i. e., aluminum oxide, with an aqueous solution of a salt of the other metal, with subsequent ignition to the oxide. An example of the latter method of preparation is the use of an aqueous solution of a molybdenum salt, preferaby ammonium molybdate, to impregnate a porous alumina carrier, suitably in the form of small pellets, followed by ignition to molybdenum oxide by passing an oxygen-containing gas over the catalyst at a moderately elevated temperature. The catalyst may be used in the form of granules of approximately 5 to 60 mesh size, in the form of pills or pellets, in the form of fluidized powder, or in the form of dust suspended in the feed.

In the operation of the present invention the paraffin feed, e. g., normal butane, is admixed with steam in the ratio of about 10 volumes of steam per volume of paraffin. The mixture is heated to the conversion temperature and passed into contact with the catalyst. The effluent from the dehydrogenation zone may be processed in known manner for the separation of substantially pure olefins and diolefins. The olefins may be separately dehydrogenated in a known manner for conversion to diolefins. Unconverted paraffins are recycled to the dehydrogenation step. If desired, the diolefins may be separated from the effluent and the olefins together with unreacted paraffins recycled to the dehydrogenation step.

Preferred conditions for dehydrogenation of steam diluted paraffins in accordance with this invention are: temperature, 1000–1400° F.; absolute pressure 1–3 atmospheres; volume ratio of steam to hydrocarbons, 1 to 20 volumes of steam per volume of hydrocarbon, preferably 5 to 15 volumes of steam per volume of hydrocarbon; hydrocarbon space velocity 200–700 gaseous volumes (S. T. P.) per volume of catalyst per hour. The hydrocarbon and the steam may be mixed

before charging to the reaction zone or the steam may be separately injected at a plurality of points along the reaction zone. The steam is preferably preheated to a temperature at least as high as the temperature employed in the reaction and in some cases it may be preferable to separately preheat the hydrocarbons and the steam before mixing. It is sometimes desirable to preheat the steam to a temperature somewhat above the desired conversion temperature and to admix the preheated steam with preheated paraffin at a temperature slightly below the desired reaction temperature such that the resulting mixture attains the reaction temperature. The effluent from the reaction zone is cooled to condense and remove steam, and the individual hydrocarbon components are separated by conventional methods such as fractionation, solvent extraction, and so forth. When the activity of the catalyst becomes undesirably low because of carbon deposition, the flow of hydrocarbons is interrupted, and steam is allowed to contact the catalyst until the carbon is removed. Air may be added to the steam during the regeneration period if desired.

While the prior art states that steam is detrimental to the yield of olefins and diolefins in the dehydrogenation of paraffins, we have discovered catalyst compositions that are water resistant and especially suited to dehydrogenation of paraffins admixed with steam. In fact, we have found that with specific catalysts disclosed herein, the ultimate yield of olefins and diolefins is in some cases increased rather than decreased by use of steam. We have also found that it is not possible to predict from data on the dehydrogenation of paraffins without steam which catalysts will show the best yield when the paraffin hydrocarbon is admixed with steam. The following examples illustrate the processes of the present invention and illustrate the superiority of catalysts disclosed herein for dehydrogenation of paraffins in admixture with steam.

The catalyst of Example I is one which is commonly used for the dehydrogenation of anhydrous normal butane. In the subsequent examples, the catalysts were prepared by impregnating alumina pellets one-eighth inch in diameter and one-eighth inch in length with the solutions of salts of the respective minor components, followed by conversion of the salts to the corresponding oxides by ignition. In the several runs the steam was admixed with normal butane, the mixture preheated to the conversion temperature and passed over the pelleted catalyst. The effluent was condensed and analyzed. The space velocity is expressed in terms of volumes of normal butane per volume of catalyst per hour. The total conversion per pass represents the percentage by volume of normal butane reacted in passing over the catalyst. The yield of normal butylenes and butadiene per pass represents the percentage by volume of the normal butane feed which was converted to these products in passing over the catalyst. The ultimate yield indicates the percentage by volume of normal butane reacted which was converted to these products and is a measure of the efficiency of the catalyst for conversion of the feed to the desired products.

Example I

An alumina-chromia-magnesia catalyst commonly used for commercial dehydrogenation of undiluted normal butane was used for the dehydrogenation of normal butane admixed with steam. The catalyst was in the form of pellets one-eighth inch in diameter and one-eighth inch in length with slightly rounded ends to prevent stacking. The composition of the catalyst in parts by weight (weight per cent) follows:

Al_2O_3	86
Cr_2O_3	12
MgO	2

Two runs were carried out with this catalyst with conditions and results shown below:

Run	Temp., °F.	Space Vel. of butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion per pass, percent	Yield $n\text{-}C_4H_8+C_4H_6$, mol percent	
					Per Pass	Ultimate
1	1,220	555	1.4	39.2	4.4	11.2
2	1,280	630	9.2	17.9	2.3	12.6

While the per pass conversion is lowered by the larger quantity of steam, the ultimate yield or efficiency of the catalyst is slightly improved. This catalyst is much less efficient for the dehydrogenation of normal butane in admixture with steam than it is for the dehydrogenation of undiluted normal butane as will be readily apparent to those skilled in the art.

Example II

A catalyst composed of aluminum and molybdenum oxides was used for dehydrogenation of normal butane both with and without steam. The catalyst contained 90 weight per cent aluminum oxide and 10 weight per cent molybdenum oxide Three comparative runs were carried out with this catalyst under the conditions and with the results shown below:

Run	Temp., °F.	Space Vel. of butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion per pass, percent	Yield of $n\text{-}C_4H_8+C_4H_6$, mol percent	
					Per Pass	Ultimate
3	1,100	490	0.0	43.1	9.8	22.6
4	1,235	445	1.3	44.9	11.5	25.6
5	1,235	495	9.4	20.2	8.3	41.2

The temperature of 1100° F employed in the dehydrogenation of undiluted normal butane was chosen for comparison as it represents approximately the optimum conversion temperature. At temperatures as high as 1200° F. excessive decomposition of undiluted normal butane takes place with poor yields of the desired products and poor catalyst efficiency. When steam is used as a diluent, higher temperatures are re-

quired for optimum conversion, other conditions being equal, than when undiluted normal butane is employed as feed.

The butadiene content of the butylene-butadiene yield for run 3 was 6.7 mol per cent.

These data show that higher ultimate yields are obtained with mixtures or normal butane and steam than with undiluted normal butane. This is contrary to the teachings of the prior art.

Example III

Normal butane was admixed with steam, the mixture preheated, and passed into contact with a mixture of the oxides of aluminum and tungsten. The catalyst contained 85 weight per cent aluminum oxide and 15 weight per cent tungsten oxide. The conditions and results were as follows:

Run	Temp., °F.	Space Vel. of butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion per pass, percent	Yield of n-C_4H_8+ C_4H_6, mol percent	
					Per Pass	Ultimate
6	1,240	455	1.5	37.3	7.5	20.1
7	1,240	520	11.7	7.7	1.7	21.8

This catalyst shows much higher yields than the chromia-alumina catalyst of Example I, but showed little increase in efficiency (as shown by the ultimate yield) with increased steam dilution.

Example IV

Paraffin hydrocarbons were dehydrogenated by contacting them in admixture with steam with a catalytic mixture of the oxides of aluminum and vanadium. The catalyst contained 90 weight per cent aluminum oxide and 10 weight per cent vanadium oxide. Successive runs were made using different steam to hydrocarbon ratios. The conditions and results for n-butene are shown below:

Run	Temp., °F.	Space Vel. of Butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion per pass, percent	Yield of n-C_4H_8+ C_4H_6, mol percent	
					Per Pass	Ultimate
8	1,240	670	0.7	26.7	5.6	20.8
9	1,240	680	9.5	6.5	1.4	21.1

This example illustrates the superiority of this catalyst over the chromia-alumina catalyst of Example I. Like the catalyst of Example III, this catalyst shows little increase of efficiency with increased steam dilution.

From the foregoing examples it is evident that steam to hydrocarbon ratios of about 10 volumes of steam per volume of hydrocarbon give somewhat higher ultimate yields than mixtures with a lower steam to hydrocarbon ratio. In the subsequent examples steam to hydrocarbon ratios within the range of 7 to 12 volumes of steam per volume of hydrocarbon were employed.

Example V

To show the effect of increasing the quantity of molybdenum oxide in the aluminum oxide-molybdenum oxide catalyst normal butane was dehydrogenated in the presence of a catalyst containing 60 weight per cent aluminum oxide and 40 weight per cent molybdenum oxide. In this run (Run 10) a mixture of 11.1 volumes of steam per volume of normal butane was heated to 1255° F. and passed into contact with the catalyst with a butane space velocity of 560. The total conversion per pass was 16.7 per cent with a per pass yield of butylenes and butadiene of 6.3 per cent and an ultimate yield of 38.0 per cent. The mixture of butylenes and butadiene contained 21.0 mol per cent butadiene.

This example shows that little, if any, advantage is obtained in using more than about 10 weight per cent molybdenum oxide in the catalyst.

Example VI

To determine the effect of chromium oxide in admixture with molybdenum and aluminum oxides, ternary mixtures of these oxides were made up. Mixtures of normal butane and steam were dehydrogenated under the conditions and with the results shown below:

Run	Temp., °F.	Butane Space vel., vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion, per Pass, percent	Yield of N-C_4H_8+ C_4H_6, mol percent		C_4H_8 in C_4H_8+ n-C_4H_8 mol percent
					Per Pass	Ultimate	
11	1,255	575	10.5	17.6	9.5	53.8	35.3
12	1,250	645	10.5	19.6	9.4	47.8	26.6

The catalyst of Run 11 contained 60 weight per cent aluminum oxide, 30 weight per cent molybdenum oxide, and 10 weight chromium oxide; that of Run 12, 50 weight per cent aluminum oxide, 25 weight per cent molybdenum oxide and 25 weight per cent chromium oxide. From the foregoing it appears that little advantage is gained by the use of the higher proportions of chromium oxide. This example illustrates the beneficial effect of molybdenum oxide in a chromia-alumina catalyst for dehydrogenation of paraffins in admixture with steam.

Example VII

The catalyst of Example I was dipped in a solution of ammonium molybdate and calcined to convert the ammonium molybdate to molybdenum oxide. In the dehydrogenation of nor-

mal butane over this catalyst (Run 13) under conditions comparable to those of Example I, using 9.5 volumes of steam per volume of butane, the total per pass conversion obtained was 16.6, yield of butylenes and butadiene per pass 8.5, and ultimate yield of butylenes and butadiene 51.4. The butylene-butadiene mixture contained 10.2 mol per cent butadiene. This example further illustrates the value of molybdenum oxide in a chromia-alumina catalyst for dehydrogenation of paraffins in the presence of steam. This example also shows that magnesium oxide suppresses the production of butadiene.

Example VIII

Mixtures of the oxides of aluminum, chromium, vanadium and molybdenum were prepared. Mixtures of steam and normal butane were passed over the catalysts with the conditions and results indicated below:

Run	Temp., °F	Space Vel. of Butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion, per pass, percent	Yield of $n\text{-}C_4H_8+C_4H_6$, mol percent		C_4H_6 in $C_4H_8+n\text{-}C_4H_8$, mol percent
					Per Pass	Ultimate	
14	1,250	575	11.3	11.8	6.4	53.9	11.9
15	1,254	570	12.0	13.8	8.3	60.3	20.7
16	1,250	610	7.2	16.6	8.7	52.3	21.4

The compositions of the catalyst in the weight per cent were as follows:

Run	Aluminum Oxide	Chromium Oxide	Vanadium Oxide	Molybdenum Oxide
14	60	10	30	----
15	60	----	20	20
16	50	10	20	20

The strikingly high yields and high efficiency of the catalysts of this invention for the dehydrogenation of paraffins diluted with steam are brought out by this example.

Example IX

The catalyst of Run 11 of Example VI containing the oxides of aluminum, chromium, and molybdenum was modified by the incorporation of various materials known to promote the water gas reaction. In one run the catalyst was modified by dipping the pellets in a solution of barium chloride and calcining to convert the barium chloride to barium oxide. The conditions used and results obtained are shown in Run 17 of the following table. The catalyst composition was also modified by the incorporation of iron oxide in a similar manner with the conditions and results shown in Run 18 of the following table:

Run	Temp., °F	Space Vel. of Butane, vol./vol./hr.	Vol. Ratio Steam to n-Butane	Total Conversion, per pass, percent	Yield of $n\text{-}C_4H_8+C_4H_6$, mol percent		C_4H_6 in $C_4H_8+n\text{-}C_4H_8$, mol percent
					Per Pass	Ultimate	
17	1,265	560	11.4	13.0	6.2	47.4	19.9
18	1,245	570	11.6	15.7	6.8	43.1	22.5

This example shows that contrary to the teachings of the prior art, oxides which are known to promote the water gas reaction do not increase the efficiency of the catalyst, but on the other hand, tend to decrease the efficiency to some extent. From the standpoint of catalyst life, it may be found economical in some instances to incorporate in the catalyst used in the process of our invention a minor proportion of a catalytic material known for promotion of the water gas reaction.

From the foregoing it is believed that many advantages obtainable from the practice of the present invention will be readily apparent to persons skilled in the art. However, since certain changes may be made in carrying out the above method without departing from the scope of the invention as defined by the appended claims, it is intended that all matter contained herein shall be interpreted as illustrative and explanatory, rather than in a limiting sense.

We claim:

1. A process for the dehydrogenation of an aliphatic paraffin hydrocarbon containing four to five carbon atoms per molecule which comprises contacting said hydrocarbon diluted with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F. with a catalyst consisting essentially of a major proportion of aluminum oxide and a minor proportion of at least one oxide selected from the group consisting of molybdenum oxide, tungsten oxide and vanadium oxide, and a minor proportion of an activator comprising chromium oxide.

2. A process for the catalytic dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises contacting said hydrocarbon diluted with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F. with a catalyst consisting essentially of a major proportion of aluminum oxide and a minor proportion of at least one oxide selected from the group consisting of molybdenum oxide, tungsten oxide, and vanadium oxide.

3. A process for the catalytic dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises contacting said hydrocarbon diluted with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 100° F. to about 1400° F. with a catalyst consisting essentially of a major proportion of aluminum oxide and minor proportions of a plurality of the metal oxides selected

from the group consisting of molybdenum oxide, tungsten oxide and vanadium oxide.

4. A process as defined in claim 1 wherein said paraffin hydrocarbon is normal butane.

5. A process for the dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises passing said hydrocarbon in admixture with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F. into contact with a catalyst consisting essentially of a major proportion of aluminum oxide and a minor proportion of molybdenum oxide.

6. A process for the catalytic dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises contacting said hydrocarbon diluted with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F. with a catalyst consisting essentially of a major proportion of aluminum oxide and minor proportions of chromium oxide and molybdenum oxide.

7. A process for the catalytic dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises contacting said hydrocarbon diluted with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F.

with a catalyst consisting essentially of a major proportion of aluminum oxide and minor proportions of the oxides of molybdenum and vanadium.

8. A process for the dehydrogenation of an aliphatic paraffin hydrocarbon containing from four to five carbon atoms per molecule which comprises passing said hydrocarbon in admixture with from 1 to 20 volumes of steam per volume of hydrocarbon at a temperature within the range of from about 1000° F. to about 1400° F. into contact with a catalyst consisting essentially of a major proportion of aluminum oxide and minor proportions of chromium oxide and vanadium oxide.

ALVIE B. C. DAGUE.
JOHN W. MYERS.

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Certificate of Correction

Patent No. 2,500,920 March 21, 1950

ALVIE B. C. DAGUE ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 10, line 72, for "100° F." read *1000° F.*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of July, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.