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**DEHYDROGENATION OF HYDROCARBONS****Jacque C. Morrell and Aristid V. Grosse, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware****No Drawing. Application May 11, 1936,  
Serial No. 79,218****9 Claims. (Cl. 260—683)**

The invention relates particularly to the dehydrogenation of paraffin hydrocarbons, both gaseous and liquid, although it is applicable also to the dehydrogenation of naphthenic hydrocarbons as well as to both gaseous and liquid hydrocarbon mixtures produced in the ordinary distillation or in cracking of petroleum and its fractions. It is particularly applicable to the treatment of gasoline fractions of inferior antiknock value to increase their antiknocking properties. The dehydrogenation reactions may involve isomerization and cyclization as well as the formation of olefins and unsaturated compounds generally.

More specifically, the invention is concerned with the application of particular types of catalysts to hydrocarbon dehydrogenation reactions generally, these catalysts, whose preparation, properties and uses will be described in detail in the succeeding specification being outstanding in the matter of accelerating selective dehydrogenation reactions to the practical exclusion of ordinary thermal conversion reactions under the preferred conditions of operation.

There is a large commercial production of gaseous paraffin hydrocarbons. They occur in very large quantities in natural gas, as well as in those gases associated with the production of crude oil and commonly known as casinghead gases, and this supply is further augmented by the gases produced in cracking oils for the production of gasoline, although this latter type of pyrolytically produced gas contains substantial quantities of olefins as well as paraffinic hydrocarbons.

The greater part of the paraffin gas production is used merely for domestic and industrial fuel purposes and not as a source of hydrocarbon derivatives, on account of the unreactive character of its components in comparison with their olefinic counterparts.

The normally liquid paraffin hydrocarbons which comprise those from the pentanes of 5 carbon atoms and higher are also available in considerable quantities as substantially pure compounds from the close fractionation of highly paraffinic crude petroleum fractions and are further available in mixtures representing products of less accurate fractionation. The lower boiling paraffin hydrocarbons, for example, those present in straight run gasoline and in natural gasoline are particularly amenable to treatment by the process. The present process is applicable to the production of the corresponding mono olefins and other compounds from any of the normally

liquid paraffin hydrocarbons under conditions of operation which obviously require some modification when dealing with the different compounds of this series. Cyclic compounds either of a completely saturated character such as the naphthenes or of a hydroaromatic character such as the terpenes may also be selectively dehydrogenated in whole or in part by the use of the present types of catalysts under suitably chosen conditions of temperature, pressure and time of contact.

It is more or less obvious from the foregoing statements as to the classes of hydrocarbons which can be dehydrogenated that the process is distinctly applicable to the hydrogenation of members of the same classes of hydrocarbons which occur in various percentage admixture in petroleum fractions. Thus the catalysts to be presently described are useful in the reforming of relatively low boiling naphtha fractions either from straight run distillation or cracking processes to increase the unsaturation thereof and render them less knocking in character.

In one specific embodiment the invention comprises the dehydrogenation of hydrocarbons at elevated temperatures in the presence of catalysts comprising essentially relatively inert solid granular carriers supporting minor amounts of compounds of neodymium.

According to the present invention, the catalysts which are preferred for selectively dehydrogenating hydrocarbons have been evolved as the result of a large amount of investigation with catalysts having a dehydrogenating action upon various types of hydrocarbons such as are encountered either in the gaseous or liquid fractions produced in the distillation and/or pyrolysis of petroleum and other naturally occurring hydrocarbon oil mixtures. The criterion of an acceptable dehydrogenating catalyst is that it shall split off hydrogen without inducing either scission of the bonds between carbon atoms or carbon separation. In the present invention catalyst mixtures comprising essentially major amounts of inert carriers and minor amounts of compounds of neodymium such as for example the oxides  $\text{NdO}_2$ ,  $\text{Nd}_4\text{O}_7$ , and particularly the sesquioxide  $\text{Nd}_2\text{O}_3$ , which results from the reduction of the two higher oxides are used. The oxides mentioned are particularly efficient as catalysts for the present types of reactions but the invention is not limited to their use but may employ other compounds of neodymium which may be either deposited upon the carriers from aqueous or other solutions in the course of the prepara-

tion of the composites or which may be mechanically admixed therewith either in the wet or the dry condition. As examples of neodymium compounds which are soluble in water and thus utilizable as primary sources of material which may be later reduced to the desired lower oxide may be mentioned the bromate, the chloride, the sulphate, and particularly the series of double nitrates of neodymium and the alkali metals, an example of a member of this series of compounds being neodymium rubidium nitrate having the formula  $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{RbNO}_3 \cdot 4\text{H}_2\text{O}$ . From any of these soluble compounds the hydroxide may be precipitated by the addition of alkali metal or ammonium carbonates or hydroxides, and the precipitated and adsorbed neodymium hydroxide then ignited to form either the dioxide  $\text{NdO}_2$  or in some cases the pale blue sesquioxide  $\text{Nd}_2\text{O}_3$ . This last named compound, which is one of the preferred catalysts proposed in the present invention, results from heating the hydroxide, the oxalate and the nitrate. It is to be understood that the various compounds which may be used will not have equivalent catalytic effectiveness and that some will have greater catalytic efficiency and be more practical to use than others.

Owing to the association in natural minerals of the elements neodymium and praseodymium and the practical difficulties encountered in the separation of these elements or their compounds, it is recognized as not likely that the compounds of neodymium which are available for catalytic purposes will be entirely free from praseodymium, but owing to the generally similar properties of these elements the presence of the praseodymium will have no deleterious influence in regard to the catalytic effectiveness of the present type of preferred composites, and apparently has some beneficial effects in some instances.

The invention contemplates the use of a number of different types of carriers for supporting the neodymium compounds which are in effect the active catalysts for promoting the more or less selective dehydrogenation reactions. These carriers are preferably of a rugged and refractory character capable of withstanding the severe use to which the catalysts are put in regard to temperature during service and in regeneration by means of air or other oxidizing gas mixtures after they have become fouled with carbonaceous deposits. As examples of materials which may be employed in granular form as supports for the preferred catalytic substances may be mentioned the following:

Magnesium oxide  
Aluminum oxide  
Bauxite  
Bentonite clays  
Montmorillonite clays  
Kieselguhr  
Crushed silica  
Crushed firebrick  
Glauconite (greensand)

Each of the above enumerated types of carriers will need some particular preparation before its use as a carrier. Magnesium oxide, for example, is best prepared by the controlled calcination of magnesite at temperatures of the order of  $1500^\circ$  to  $1600^\circ$  F. until substantially all of the carbonate has been converted to oxide. Aluminum oxide may be prepared by a similar calcining of the precipitated hydroxide or the minerals bauxite or diaspor which are naturally occurring hydrated oxides. The clays mentioned

may also require a careful calcination to preserve their structure as far as possible. In the case of silica and firebrick, these may be considered as igneous products and less sensitive to temperature effects, while glauconite should generally be ignited at a minimum temperature at least below the highest temperature of service before the neodymium compounds are added. By using these different types of carriers alternately with the different neodymium compounds already mentioned, the preparation of a considerable number of catalysts is made possible, although obviously they will not exert exactly equivalent effects.

Our investigations have also definitely demonstrated that the catalytic efficiency of such substances as alumina, magnesium oxide, and clays which may have some catalytic potency in themselves is greatly improved by the presence of compounds of neodymium in relatively minor amounts, usually of the order of less than 10% by weight of the carrier. It is most common practice to utilize catalysts comprising 2% to 5% by weight of neodymium compounds.

In making up catalyst composites of the character and composition which according to the present invention have been found specially well suited for catalyzing hydrocarbon dehydrogenation reactions, the following is the simplest and generally the preferred procedure. A properly prepared carrier is ground and sized to produce granules of relatively small mesh of the approximate order of from 4 to 20 and these are caused to absorb compounds which will ultimately yield compounds of neodymium on heating to a proper temperature by stirring them with warm aqueous solutions of soluble neodymium compounds, such as for example neodymium sulphate having the formula  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , which is sufficiently soluble in warm water to render it readily utilizable as a source of catalytic neodymium compounds. Other soluble compounds which may be used to form catalytic deposits containing neodymium are the various alkali metal double compounds. Other less soluble compounds of acids of neodymium, including compounds of the alkaline earth and heavy metals may be distributed upon the carriers by mechanical mixing either in the wet or the dry condition. While substantially all of the compounds of neodymium will have an appreciable catalytic action in furthering dehydrogenation reactions, some will be considerably better than others in this respect and it is not intended to infer that the compounds which may be employed alternately are in any sense exact equivalents. As a rule the lower oxides are the best catalysts.

Practically all of the carriers mentioned will have sufficiently high absorptive capacity for solutions of soluble neodymium compounds to take up the necessary quantities without leaving any excess of solution. Some of the salts of neodymium which are utilizable as a source of the dioxide or sesquioxide are, however, not extremely soluble in water and in order to get a sufficient quantity of the desired compounds deposited upon the carriers it may be necessary at times to add the aqueous solutions in successive portions with intermediate drying stages rather than to add the carriers to a dilute aqueous solution and depend upon the absorptive capacity of the carrier for the extraction of the salt.

The oxide resulting from the decomposition of such compounds as the nitrate and the hydroxide is for the most part the sesquioxide  $\text{Nd}_2\text{O}_3$ . Any

other oxides which may be present either in the original preparation of the catalyst or produced during regeneration of spent material are reduced by hydrogen or by the gases and vaporous products resulting from the decomposition of the hydrocarbons treated in the first stages of the dehydrogenation reactions so that the essential catalyst for the larger portion of the period of service is the sesquioxide  $\text{Nd}_2\text{O}_3$ .

In practicing the dehydrogenation of hydrocarbons according to the present process, a solid composite catalyst prepared according to the foregoing briefly outlined methods is used as a filler in a reaction tube or chamber in the form of particles of graded size or small pellets, and the hydrocarbon gas or vapor to be dehydrogenated is passed through a stationary mass of the catalyst particles after being heated to the proper temperature, usually within the range of from 800–1200° F., depending upon the hydrocarbon or mixtures of hydrocarbons undergoing treatment. The most commonly used temperatures, however, are around 900–1000° F. The catalyst tube is usually heated exteriorly to maintain the proper reaction temperature. The pressure employed may be subatmospheric, atmospheric or slightly superatmospheric of the order of from 50 to 100 pounds per square inch. While pressures up to 500 pounds per square inch may be employed in some cases, pressures of the order of atmospheric and below are generally preferred. The time during which the hydrocarbons are exposed to dehydrogenating conditions in the presence of the preferred catalysts is comparatively short, usually below twenty seconds, and preferably from 0.5 to 6 seconds.

It is an important feature of the present process that the vapors of hydrocarbons to be dehydrogenated should be free from all but traces of water vapor since the presence of any substantial amounts of steam reduces the catalytic effectiveness of the composite catalysts to a marked degree. In view of the empirical state of the catalytic art, it is not intended to submit a complete explanation of the reasons for the deleterious influence of water vapor in the present type of catalyzed reactions, but it may be suggested that the action of the steam may be to cause a partial hydration of such carriers as alumina and some of the neodymium compounds due to preferential adsorption, so that in effect the hydrocarbon vapors are prevented from reaching or being adsorbed by the catalytically active surface.

When the process is used to selectively dehydrogenate paraffinic hydrocarbons which are normally gaseous, the exit gases from the catalytic tube or chamber may be passed through selective adsorbents to combine with or absorb the olefin or olefin mixture produced, or the olefins may be selectively polymerized by suitable catalysts, caused to alkylate other hydrocarbons such as aromatics or paraffins or treated directly with chemical reagents to produce desirable and commercially valuable derivatives. After the olefins have been removed the residual gases may be recycled for further dehydrogenating treatment with or without removal of hydrogen.

In the case of the dehydrogenation of normally liquid starting materials such as, for example, liquid paraffinic hydrocarbons, naphthenes or the lower boiling naphthas or gasoline produced in petroleum refining, the products may be subjected to any suitable type of fractionation to produce a final product of desired characteristics. Obviously hydrogen released by the reactions

along with other light fixed gases in minor amounts may be led off from distillate receivers and the liquid products may be given any type of fractionation adequate to separate individual compounds or fractions of limited boiling range. As in the case of the olefins produced from normally gaseous paraffinic hydrocarbons, the products of the dehydrogenation of liquid hydrocarbons may be directly contacted with any type of chemical to produce derivatives if desired.

The present types of catalysts are selective in removing two hydrogen atoms from paraffin molecules to produce the corresponding olefins without furthering to any great degree undesirable side reactions, and because of this show an unusually selective conversion of paraffins into the corresponding mono olefins as will be shown in later examples. This selectivity is particularly in evidence when dealing with normally liquid paraffin hydrocarbons such as, for example, pentanes, hexanes, heptanes, octanes, etc. The present preferred types of catalysts also accelerate and direct the course of the reactions leading to simple loss of hydrogen from cyclic hydrocarbon molecules so that, for example, hexahydrobenzol may be converted substantially completely into benzol without the formation of any considerable amounts of by-products or the disruption of the ring.

The procedure when employing catalysts to dehydrogenate petroleum fractions such as low antiknock value gasoline is generally similar to that used when treating any normally liquid hydrocarbon and consists in first vaporizing the fraction, preheating it to a suitable temperature and then passing it through a stationary bed of catalyst of sufficient extent to cause the desired development of unsaturation and corresponding increase in antiknock value.

When the activity of the catalysts begins to diminish it is readily regenerated by the simple expedient of oxidizing with air or other oxidizing gas at a moderately elevated temperature, usually within the range employed in the dehydrogenating reactions. This oxidation effectively removes traces of carbon deposits which contaminate the surface of the particles and decrease their efficiency. It is characteristic of the present types of catalysts that they may be repeatedly regenerated without substantial loss of catalytic potency.

During oxidation with air or other oxidizing gas mixture in regenerating partly spent catalytic material there is evidence to indicate that the sesquioxide is to some extent oxidized to the dioxide  $\text{NdO}_2$  and the heptoxide  $\text{Nd}_4\text{O}_7$ , which may combine with such basic carriers as alumina or magnesium oxide to form a certain amount of various mixed compounds. The existence of several alkaline earth compounds with oxides of neodymium is known, but analyses have indicated that their composition is rather indefinite so that they may possibly be solid solutions or isomorphous oxide mixtures rather than definite chemical compounds. These compounds are later decomposed by contact with reducing gases in the first stages of service to reform the lower oxide and regenerate the real catalyst and hence the catalytic activity.

The following examples are introduced to indicate in a general way the results obtainable in practice by the use of the invention although it is not intended to limit its scope in exact correspondence with the figures presented.

## Example I

A catalyst was prepared for use in dehydrogenating butane as representing normally paraffinic gases. The general procedure was to dissolve neodymium magnesium nitrate in water and utilize this solution as a means of adding neodymium oxides to a carrier. 20 parts of weight of the double salt was dissolved in about 50 parts by weight of water and the solution subsequently diluted by the addition of approximately an equal volume of water. The solution was then added to about 250 parts by weight of activated alumina which had been produced by calcining bauxite at a temperature of about 1300° F. followed by grinding and sizing to produce particles of approximately 8-12 mesh. Using the proportions stated the alumina exactly absorbed the solution and the particles were first dried at 212° F. for about 2 hrs. and the temperature was then raised to 650° F. in a period of 8 hrs. After this calcining treatment the particles were placed in a reaction chamber and the neodymium oxides heated in a current of hydrogen at about 930° F., when they were then ready for service. After several hours reduction the bluish tint of the material indicated the presence of appreciable quantities of the sesquioxide. The residue of the non-reducible magnesium oxide acted both as spacing material and support for the active oxides.

In the present instance n-butane was passed through the catalyst chamber at a temperature of 1140° F. and at atmospheric pressure so that its total contact time was about 5 secs. The composition of the exit gases as shown below indicates the selectivity of the catalytic action.

## Composition of exit gases

|                             | Per cent |
|-----------------------------|----------|
| 40 Butenes.....             | 21.5     |
| Hydrogen.....               | 26.5     |
| Methane and ethane.....     | 2.5      |
| Propane.....                | 2.0      |
| Propene.....                | 1.0      |
| 45 Ethylene.....            | 0.5      |
| n-Butane (unconverted)..... | 46.5     |

The selectivity of the catalytic action is shown by the approximately equal percentages of butenes and hydrogen and the relatively low percentages of methane, ethane and propane.

## Example II

The catalyst used in this case was made by a process generally similar to that given in Example I, using, however, a burned magnesite consisting of over 90% magnesium oxide in place of the alumina, and a solution saturated in respect to neodymium oxalate and neodymium nitrate.

The catalyst was employed to dehydrogenate n- and i-pentanes. Using n-pentane at a temperature of 1050° F. and atmospheric pressure at a time of contact of 24 secs. it was found that the liquid products recovered after separation of hydrogen and a small percentage of light hydrocarbon gases contained over 55% of amylenes admixed with unconverted pentane. In the case of isopentane and a contact time of 22 secs. the recovered liquid consisted of 60% amylenes. The recovered liquids contained less than 3% diolefins in all instances and approximately 95% of material boiling within the range of the boiling points of 5 carbon atom straight chain hydrocarbons.

## Example III

This example is given to show the value of present types of catalysts in reforming low anti-knock value gasolines. The catalyst was prepared by uniformly incorporating neodymium molybdate with a bentonite clay adding enough water to make a mass which was definitely wet, this being then dried to evaporate excess water and heated to a temperature not exceeding 392° F. for several hours. The dried material was ground and sized to produce approximately 10 mesh particles which were used as filler in a vertical reaction chamber.

The vapors of a Michigan naphtha fraction having an initial boiling point of 190° F. and a final boiling point of 400° F. were passed downwardly through the catalyst mass at a temperature of 932° F. under atmospheric pressure and a contact time of six seconds. The recovered naphtha fraction, which constituted 92% of the starting material, had an octane number of 70 as compared with an original value of 38 on the untreated naphtha. The loss was entirely due to gas formation, the gas having an average molecular weight of 10 which shows the presence of relatively large percentages of hydrogen. The activity of the catalyst remained substantially constant for a period of 6 days after which it was restored to practically its original value by oxidizing with air at the temperature of treatment, after observing the precaution of steaming out the tower prior to the admission of air.

We claim as our invention:

1. A process for dehydrogenating paraffine which comprises subjecting the same to the action of a compound of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

2. A process for converting normally gaseous paraffins into their corresponding olefins which comprises dehydrogenating the paraffinic gas by subjection thereof to the action of a compound of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

3. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises subjecting the same to the action of a compound of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

4. A process for dehydrogenating paraffins which comprises subjecting the same to the action of an oxide of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

5. A process for converting normally gaseous paraffins into their corresponding olefins which comprises dehydrogenating the paraffinic gas by subjection thereof to the action of an oxide of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

6. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises subjecting the same to the action of an oxide of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

7. A process for dehydrogenating paraffins which comprises subjecting the same to the action of aluminum oxide supporting a relatively small amount of an oxide of neodymium at a tem-

perature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds.

5 8. A process for converting normally gaseous paraffins into their corresponding olefins which comprises dehydrogenating the paraffinic gas by subjection thereof to the action of aluminum oxide supporting a relatively small amount of an oxide of neodymium at a temperature of from about 800 to 1200° F. and for a time period of  
10 from about 0.5 to 20 seconds.

9. A process for increasing the anti-knock value of paraffinic gasoline fractions which comprises subjecting the same to the action of aluminum oxide supporting a relatively small amount of an oxide of neodymium at a temperature of from about 800 to 1200° F. and for a time period of from about 0.5 to 20 seconds. 5

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