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DEHYDROGENATION OF SATURATED HYDROCARBONS

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The present invention relates to the dehydrogenation of saturated hydrocarbons. More particularly the present invention relates to a process for the catalytic dehydrogenation of higher molecular weight, non-gaseous paraffin hydrocarbons.

The dehydrogenation of hydrocarbons per se is well known and the prior art abounds in both thermal and catalytic processes as well as catalysts for the dehydrogenation and partial dehydrogenation of saturated and unsaturated, cyclic and non-cyclic, straight-chain and branched-chain hydrocarbons. Much of the prior art is specific in its application in the respect that specific catalysts and/or conditions are specific for certain hydrocarbons or hydrocarbon types. However, in spite of the great amount of art in the field of dehydrogenation, several deficiencies yet exist. One of these is in the dehydrogenation of higher molecular weight paraffin hydrocarbons. Several catalysts and processes have been advanced for the dehydrogenation of saturated hydrocarbons having greater than 6 carbon atoms per molecule, however, most of these have left much to be desired. Most dehydrogenation catalysts and processes thus far advanced give relatively good conversions of paraffin hydrocarbons to mono-olefin hydrocarbons but unfortunately do not stop there. In addition to causing dehydrogenation, they also cause considerable cyclization, thereby producing more aromatics than mono-olefin hydrocarbons. Further they promote isomerization of the dehydrogenated paraffin hydrocarbons to branched-chain olefins rather than straight-chain mono-olefin hydrocarbons. When aromatics are produced it becomes necessary to separate the mono-olefin hydrocarbons from the aromatic hydrocarbons and this is a rather tedious process within itself. Few relatively efficient methods of separating corresponding aromatic hydrocarbons and mono-olefin hydrocarbons are known and these methods are generally outside the scope of commercial use. It is then readily apparent that processes for the dehydrogenation of paraffin hydrocarbons capable of cyclization, e.g., hexane, heptane, etc., must be developed which will cause dehydrogenation of the paraffin hydrocarbons without also causing the further reaction of cyclization of the olefin hydrocarbons.

It is therefore an object of the present invention to provide a new process for the dehydrogenation of paraffin hydrocarbons having six carbon atoms or greater. A more particular object of the present invention is to provide a process for the catalytic dehydrogenation of paraffin hydrocarbons of 10 to 20 carbon atoms whereby relatively good yields of mono-olefin hydrocarbons are obtained with very little or no aromatic hydrocarbons being formed. Additional objects will become apparent from the following description of the invention herein disclosed.

In fulfillment of these and other objects, it has been found that when paraffin hydrocarbons of 10 to 20 carbon atoms are contacted with a catalyst comprising alumina containing from 1 to 25 percent by weight of copper as an oxide of copper, deposited thereon, at a temperature of 450 to 600° C. and a pressure of 0.01 to 30.0 atmospheres and at a space velocity of 1 to 20 liquid volumes of feed hydrocarbons per hour per volume of catalyst, mono-olefin hydrocarbons are formed with very little or no formation of aromatic hydrocarbons.

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To further describe and to illustrate the present invention the following examples are presented. These examples are not to be construed in any manner as limiting the objects, conditions or applications of the present invention.

Example I

A feed consisting essentially of n-dodecane was brought into contact with a catalyst containing 90 weight percent alumina and 10 weight percent copper. The alumina was one having 225 square meters per gram of surface area and pore diameters of 87 angstroms. The contact between the n-dodecane and the catalyst was at a space velocity of 6 liquid volumes of feed per hour per volume of catalyst and at a temperature of 540° C. with the pressure being approximately atmospheric. The resulting dehydrogenation products represented an olefin yield of 10.2 percent based on amount of paraffin hydrocarbon charged. The olefins produced were C₁₀ to C₁₂ olefins. The aromatic yield based on paraffin hydrocarbon charge was only 0.4 percent.

Example II

The feed, catalyst, space velocity and pressure were the same as in Example I. The temperature, however, was lowered to 500° C. The dehydrogenation products represented a yield of 7.2 percent C₁₀ to C₁₂ olefins with no aromatics being formed.

Example III

The n-dodecane feed of Examples I and II was brought into contact with a catalyst consisting of 80 weight percent alumina of the same type as described in Example I and 20 weight percent copper. The temperature of contact was 525° C. and the pressure atmospheric. The space velocity at which contact occurred was 10 liquid volumes of feed per hour per volume of catalyst. The dehydrogenation products represented a yield of 8.9 percent of C₁₀ to C₁₂ olefins with an aromatic yield of approximately 0.4 percent.

The catalyst which is used in the present invention is one consisting of copper, as an oxide of copper, and alumina. The amount of copper which may be present in the catalyst may range from 0.5 to 30 percent by weight of the catalyst with a more preferred range being from 5 to 25 percent by weight. The aluminas which may be used in the present invention are those having surface areas of 50 to 300 square meters per gram and having average pore diameters of 40 to 400 angstroms. More preferred, however, are those aluminas having surface areas of 200 to 250 square meters per gram and pore diameters of 75 to 100 angstroms.

The catalyst used in the present invention may be prepared by any of the conventional methods such as impregnation, precipitation, etc. An example of one of such methods comprises calcining the desired alumina support at approximately 550° C. for 16 hours. The support is then cooled and thoroughly wetted with a solution containing Cu(NO₃)₂·3H₂O. This is followed by filtering off the liquid and drying at approximately 130 to 160° C. for about 16 hours. The catalyst may then be calcined at 550° C. for approximately 16 additional hours and then reduced for approximately 1½ hours. The catalyst will then be ready for use. It is to be understood, of course, that the present invention is not to be limited by the method of preparation of the catalyst, since any method of preparation may be used as long as it will place the desired amounts of copper upon the alumina support.

In practicing the present invention the temperature of contact between the paraffin hydrocarbon feed and the catalyst may range from 450 to 600° C. It is, however, more preferred that the temperature be within the range

of 500 to 575° C. A still more preferred temperature range is that of 520 to 560° C.

The pressures at which the present invention is operable is preferred to be approximately atmospheric. However, pressures ranging from 0.01 atmosphere to 30 atmospheres may be used since the invention is operable within this range.

With respect to the space velocity at which contact between the hydrocarbon feed and the catalyst may be carried out, it may range from 1.0 to 20 liquid volumes of feed per hour per volume of catalyst. However, it is somewhat more preferred that space velocities ranging from approximately 4 to 8 liquid volumes of feed per hour per volume of catalyst be used.

The feedstocks to which the present invention are applicable are those containing substantial amounts of n-paraffin hydrocarbons having 6 or more carbon atoms. In its preferred embodiment, however, the hydrocarbon feed is one containing n-paraffin hydrocarbons of 10 to 20 carbon atoms. It is obvious that the feed should contain no aromatic materials since one of the primary purposes of the present invention is to provide a product containing relatively insignificant amounts of aromatic hydrocarbons. Further, it is desired that no diolefin or acetylenic hydrocarbons be present in the feedstock. However, such impurities may be present to a very limited extent in the feedstock without unduly adversely affecting the reaction. In addition to the minor amounts of unsaturated impurities permissible in the feedstocks to the present process, small amounts of branched-chain paraffin hydrocarbons may be present. Naphthenic hydrocarbons, however, should be avoided since their dehydrogenation may form aromatics thereby defeating one of the aims and advantages of the present invention, that is, to produce olefinic products substantially free of aromatic impurities.

The method of contacting the catalyst with the feed

may involve either adiabatic or isothermal operations in a fixed, moving or fluidized bed. The fluidized bed may be of the single vessel contained or multi-vessel circulating type. Those skilled in the art will see that a wide variety of mechanical designs of each of these types may serve to carry out the desired olefin production.

What is claimed is:

1. A process for the dehydrogenation of C_{10} to C_{20} n-paraffin hydrocarbons comprising contacting a feed containing at least one of such hydrocarbons with a catalyst consisting of 0.5 to 30 percent by weight of copper, as its oxide, and 70 to 99.5 percent by weight of an alumina having a surface area of 50 to 300 square meters per gram and pore diameters of 40 to 400 angstroms, the contact being carried out at a space velocity of 1.0 to 20.0 liquid volumes of hydrocarbon feed per hour per volume of catalyst and at a temperature of 450 to 600° C. and at a pressure of approximately 0.01 to 30 atmospheres.

2. The process of claim 1 wherein the catalyst consists of 5 to 25 percent by weight of copper and 75 to 95 percent by weight of alumina.

3. The process of claim 1 wherein the alumina support has a surface area of 200 to 250 square meters per gram and a pore diameter of 75 to 100 angstroms.

4. The process of claim 1 wherein the space velocity is 4 to 8 liquid volumes of hydrocarbon feed per hour per volume of catalyst.

5. The process of claim 1 wherein the temperature is 500 to 575° C.

6. The process of claim 1 wherein the pressure is approximately atmospheric.

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