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TREATMENT OF HYDROCARBONS

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This invention relates to the isomerization of hydrocarbons and particularly to the catalytic isomerization of olefin hydrocarbons. By this process olefin hydrocarbons with straight and mildly-branched chain structures may be converted into more-branched chain olefins.

With the rapid development of hydrocarbon technology, isomerization of olefinic hydrocarbons assumes considerable importance. Frequently normal olefins are more readily available than iso-olefins and other olefins of branched-chain structure, and for some uses it becomes highly desirable to convert the less-branched into more-branched chain olefins. The present invention involves the conversion of normally liquid olefinic hydrocarbons in the presence of a specific type of catalytic material which functions under suitable conditions of operation to selectively isomerize normal or mildly-branched chain olefinic hydrocarbons into relatively high yields of more-highly branched chain olefins.

In one specific embodiment the present invention comprises a process for converting normally liquid straight and mildly branched chain olefinic hydrocarbons into substantial yields of more-branched chain olefinic hydrocarbons which comprises subjecting said normally liquid olefinic hydrocarbons to contact with alunite under isomerizing conditions of temperature and pressure.

In accordance with the present invention a catalyst comprising essentially alunite may be utilized in the isomerization of olefinic hydrocarbons. This mineral, preferably after heating for several hours at a temperature of the order of 300–400° C., may be employed as filling material in tubes or reactors in the form of small pellets or granules or it may be utilized as a powder to be mixed with the hydrocarbons and passed through suitable reactors. When using a fixed catalyst, the average particle size may be within the approximate range of 1–10 mesh, which may apply either to pellets of uniform size and short cylindrical shape or to particles of irregular size and shape produced by the grinding, consolidating, and sizing of the substantially anhydrous material comprising essentially alunite or a mixture of alunite and a carrier such as clay, diatomaceous earth, fuller's earth, silica, alumina, magnesia, etc.

While the simple procedure of preheating the olefinic hydrocarbon vapors, or vapors of a hydrocarbon mixture containing olefins, to a temperature suitable for olefin isomerization in contact with the catalyst, and then passing the vapors over a stationary section of catalyst particles may be employed in some cases, it may be preferable to pass the preheated vapors through or around a plurality of relatively small diameter tubes in multiple and parallel connection having the catalyst disposed in or around said tubes since this arrangement of apparatus is better adapted to permit heating and cooling of the catalyst and thus to compensate for heat absorbed in the isomerizing reactions and to dissipate heat in the reactivation.

Such reactivation of the catalyst may be carried out repeatedly by passing air or another oxygen-containing gas over the used catalyst particles to burn off deposits of carbonaceous material at approximately an isomerizing temperature to substantially restore the catalytic activity. After the passage of the hydrocarbon vapors over the catalyst, the products may be separated by fractionation and the insufficiently converted material may be returned to further catalytic treatment.

The process of this invention may be applied to mono-olefinic hydrocarbons of straight chain or mildly-branched chain structure generally within the approximate range of pentenes or dodecenes. With hydrocarbons of higher molecular weight, decomposition reactions occur to a substantially greater degree than has been observed with hydrocarbons containing less than 12 carbon atoms per molecule.

The preferred temperature at which an olefin-containing hydrocarbon fraction may be contacted with the catalyst is within the approximate range of 200–500° C. but generally about 300–400° C., and under substantially atmospheric pressure or under a moderately superatmospheric pressure generally not in excess of approximately 10 atmospheres, such pressures being somewhat governed by flow conditions through the vaporizing and converting zones and subsequent fractionating and collecting equipment.

The rate at which the olefinic hydrocarbon is passed over the catalyst may generally vary from 0.1 to 10 volumes of liquid charge per hour per volume of catalyst space. Continuous operation may be accomplished for several hours without appreciable decrease in catalyst activity; however, after a time, depending upon the nature of the charge, the conditions of operation, etc., it may be advantageous to remove adsorbed or deposited carbonaceous materials by oxidation in air or in an oxygen-containing gas in order to restore to the catalyst a substantial proportion of its original activity.

While the mineral alunite or alum stone, $K_2Al_6(OH)_{12}(SO_4)_4$, is generally preferred for isomerization of olefinic hydrocarbons as hereinabove set forth, other minerals may also be employed which comprise essentially double salts of aluminum sulfate with sulfates of alkali metals such as those of lithium, sodium, rubidium, and caesium. Alunite and other aluminum sulfate-containing double salts which may be employed alternatively although not on an equivalent basis, may be composited with substantially inert carriers or supports to produce composites of desired isomerizing activity.

The catalytic materials which may be employed in the present invention are characterized by their selectivity in accelerating the desired isomerization reaction with substantially no loss of hydrocarbons due to cracking, their ease and simplicity of production, their exact reproducibility, and their refractory nature, the latter enabling them to retain their catalytic properties over extended periods of time during use and reactivation at a relatively high temperature.

The following specific example is given to illustrate the process of the invention although without any intention of unduly limiting its generally broad scope.

Alunite was ground to pass through a 30-mesh screen and then heated in an oven at 300° C. for five hours. The calcined powder was mixed with 5% of a hydrogenated cocoanut oil (added as a lubricant for a pelleting machine) and formed into 3x3 mm. particles by a pelleting machine. The pelleting lubricant was burned off in a stream of air at 400° C. after which the resulting pellets were used as a filler in a tube through which normal heptene was passed at 400° C. under atmospheric pressure using a normal heptene charging rate corresponding to an hourly liquid space velocity of 1. During a processing period of one hour under the aforementined conditions, the recovery of liquid hydrocarbons was quantitative as there was no formation of gas or carbon. The recovered liquid hydrocarbon material was hydrogenated to a substantially saturated product at 100° C. under a pressure of 100 kg. per square centimeter. Distillation of the hydrogenated material separated 90% by volume of isomeric heptanes boiling lower than normal heptane obtainable by hydrogenating the untreated normal heptene.

The character of the present invention and the type of results obtainable by its use are evident from the preceding specification and example given, although they are not to be considered as imposing undue limitations upon the generally broad scope of the invention.

I claim as my invention:

1. A process for isomerizing substantially straight chain and mildly-branched chain olefinic hydrocarbons present in a hydrocarbon fraction into substantial yields of more-branched chain olefins which comprises subjecting said fraction to contact with a catalyst comprising essentially formed particles of alunite at a temperature within the approximate range of 200–500° C. under a pressure of from substantially atmospheric to approximately 10 atmospheres using an hourly liquid charging rate corresponding to 0.1–10 times the volume of the catalyst space.

2. A process for isomerizing substantially straight chain and mildly-branched chain olefinic hydrocarbons present in a hydrocarbon fraction into substantial yields of more-branched chain olefins which comprises subjecting said fraction to contact with a catalyst comprising essentially powdered alunite at a temperature within the approximate range of 200–500° C. under a pressure of from substantially atmospheric to approximately 10 atmospheres using an hourly liquid charging rate corresponding to 0.1–10 times the volume of the catalyst space.

3. A process for isomerizing normal heptene into a substantial yield of branched chain heptenes which comprises subjecting said normal heptene to contact at a temperature in the approximate range of 200–500° C. under a pressure of from substantially atmospheric to approximately 10 atmospheres with a catalyst comprising essentially alunite and at an hourly liquid charging rate corresponding to 0.1–10 times the volume of the catalyst space.

4. A process for isomerizing olefins which comprises contacting the same under isomerizing conditions with alunite.

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