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PROCESS FOR ISOMERIZATION OF OLEFIN HYDROCARBONS

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This invention relates to the catalytic isomerization of olefinic hydrocarbons.

The principal object of the invention is to provide a practical and economical process for the production of the commercially valuable branched or more highly branched olefins from the corresponding normal or less branched olefins.

The process of the invention is of great technical importance in that it provides a method for the conversion of the less valuable and less reactive secondary base olefins, such as the normal olefins and the iso-olefins of secondary character, to the corresponding tertiary olefins. The tertiary olefins, as is well known, are valuable starting materials in the production of tertiary alcohols, tertiary alcohol derivatives, unsaturated chlorides, unsaturated alcohols, unsaturated acids, etc., and they are extremely valuable as starting materials in the production of motor fuels of high anti-knock value.

The process of the invention comprises contacting the olefin to be isomerized, alone, or in admixture with one or more olefins which may or may not be capable of isomerization, and/or in the presence of one or more substantially inert diluent materials such as a saturated hydrocarbon, aromatic hydrocarbon, nitrogen, etc., with a solid catalyst consisting of or essentially comprising a hydrated aluminum silicate of the permutite or zeolite type at a temperature of from about 275° C. to about 500° C., the olefin or olefin-containing mixture being contacted with the heated catalyst at such a rate that the desired isomerization is effected while polymerization of the reactants and/or products and other undesirable side reactions such as cracking, dehydrogenation and the like are substantially obviated.

The process of the invention is applicable to the isomerization of any of the normally gaseous or normally liquid secondary olefins of either normal or branched chain structure to the corresponding tertiary olefins. For example, the normal butenes may be converted to tertiary butene; the normal pentenes and isopentene may be converted to tertiary pentenes; the secondary hexenes may be converted to tertiary hexenes; the secondary heptenes may be converted to tertiary heptenes; the secondary octenes may be converted to tertiary octenes; and the like.

The source of the olefins or mixtures of olefins isomerized in accordance with the process of the invention is immaterial. The pure olefins, or mixtures thereof, or mixtures of such olefins with one or more saturated or unsaturated hydrocarbons as well as other substantially inert materials, may be used as starting material. Thus, it is seen that the invention provides for the utilization of the normal olefin content of commercial hydrocarbon mixtures such as are obtained from the cracking of higher molecular weight hydrocarbons and hydrocarbon mixtures, such as petroleum oils, shale oils, petroleum products, animal and vegetable oils, coal, peat, waxes and the like. Normal olefin-containing mixtures resulting from the catalytic dehydrogenation of the normal paraffins or normal paraffin-containing mixtures are also suitable starting materials. A conveniently treated normal butene-containing mixture, for example, is the so-called butane-butene fraction which may contain, besides one or both normal butenes, isobutene, isobutane and normal butane in varying amounts. If desired, the tertiary olefins may be preliminarily removed, by any suitable method, from such a fraction. Mixtures of one or more of the desired olefins with one or more substantially inert materials as nitrogen, etc., may be treated. Substantially pure normal olefins or mixtures thereof may be obtained by effecting the dehydration of the corresponding primary or secondary alcohols, or mixtures thereof, or by other known means.

The process of the invention is executed in the presence of a solid catalyst consisting of or essentially comprising a hydrated aluminum silicate, preferably a hydrated aluminum silicate of the permutite or zeolite type. Both the zeolites and the permutites are suitable catalysts in the process. The zeolites comprise a group of hydrated aluminum and calcium or sodium silicates, which occur as natural mineral deposits. The permutities are of substantially the same constitution and structure and are nothing more than artificially prepared zeolites. Thus, it is seen that the invention comprehends the use of natural as well as prepared hydrated aluminum silicates. Suitable known zeolites are the following: analcine, chabazite, heulandite, natrolite, stilbite, and thomsonite. Suitable permutites include, among others, sodium permutite, "Doncil", "Decalso", "Dusarit", and the treated zeolites including neo-permutite, super neo-permutite, and the like. A particularly suitable group of hydrated aluminum silicates is the hydrated alkali metal aluminum silicates, such as sodium permutite and potassium permutite, of either the permutite or zeolite type. The principal constituents of the materials of this preferred group

are: Na_2O and/or K_2O, Al_2O_3, SiO_2, and water while a part of the alkali present is exchangeable for other metal ions. In general, the excellent catalytic isomerizing activity of the hydrated alkali metal aluminum silicates appears to be due to their high SiO_2 content bound up with great exchangeability of the alkali present.

The catalytic material in any suitable solid form as powder or pellets or granules of the desired size is employed in manners customary in the execution of catalytic processes of this type. The desired quantity of the catalytic material, preferably in the form of granules, may be packed into a reaction tube, chamber, or tower of the desired size and heated and maintained at the desired temperature by suitable heating means while the material to be treated is passed into contact with it, preferably in the vapor phase, at the desired space velocity and under the desired pressure of operation.

The process is preferably executed at temperatures at least equal to about 275° C. but not greater than about 500° C. At temperatures below 275° C., the isomerization generally proceeds too slowly. At temperatures greater than 500° C., losses due to cracking, dehydrogenation and polymerization may be prohibitive. These factors establish the preferred practical operating range of from 275° C. to 500° C., although it is to be understood that higher or lower temperatures may be used when necessary or desirable.

The process of the invention is preferably executed with the olefin or olefins to be isomerized in the vapor phase. In the case of the lower boiling olefins, such as the normal butenes, it is in most cases not desirable to operate at the high pressures which would be required to maintain such low-boiling olefins in the liquid phase at temperatures of 275° C. or higher.

The isomerization may be effected under pressure, if desired. However, since the use of excessively high pressures may result in losses due to polymerization, which is favored by pressure, the process is preferably executed at subatmospheric, about atmospheric, or at only moderately elevated pressures. In general, pressures below about 5 atmospheres are suitable and preferred.

The process of the invention may be successfully executed over a wide range of contact times of the treated material with the heated catalyst. The most suitable temperature as well as the most suitable contact time will depend to a certain extent upon the nature of the olefin, olefins, or olefin-containing mixture treated. In general, with the lower olefins, such as the normal butenes, higher temperatures may be used with less risk of cracking or dehydrogenation, and longer contact times can be used with less risk of polymerization, than is the case with the higher olefins, for example, the normal octenes. Thus, in the isomerization of the lower olefins, the best results may be obtained at temperatures of from 400° C. to 500° C. and with contact times of 120 seconds or greater. In the isomerization of the higher olefins, the best results may be obtained at temperatures below 400° C. and with contact times less than about 120 seconds.

In general, the process of the invention is preferably executed employing contact times in the practical operating range of from about 10 to 250 seconds; however, longer or shorter contact times may be employed when necessary or desirable. The contact time may be calculated from the macroscopic free space in the catalyst and the rate of feed of the gaseous mixture. It may, for example, be computed by dividing the macroscopic free space in the catalyst in c. c. by the gas feed in c. c. per second at the reaction temperature and atmospheric pressure. The result is the contact time in seconds.

The following examples illustrate suitable modes of executing the process of the invention. The invention is not to be regarded as restricted to the particular olefins, the particular catalysts, the particular methods of operation, or the particular conditions specified in the examples.

Example I

A suitable reaction tube was packed with granules (size of grain about 1 mm.) of a solid commercial sodium permutite. The tube was enclosed in a suitable heating device and the catalyst mass heated to a temperature of about 450° C. While the catalyst mass was maintained at this temperature, a butane-butene mixture consisting of about 50% by volume of normal butenes and about 50% by volume of normal butane was, at about atmospheric pressure, passed through the reaction tube at such a rate that the contact time was about 183 seconds.

Under the conditions of the operation, substantially no polymerization occurred. It was found that about 33% by volume of the olefin content of the effluent gas mixture was isobutene. The catalyst retained its initial activity for a period exceeding 80 hours of continuous use.

Example II

Normal octene was passed through a heated reaction tube packed with about 1 mm. granules of a sodium permutite catalyst. The operation was effected under about atmospheric pressure, with the catalyst maintained at a temperature of about 300° C., and with the normal octene passed through the tube at such a rate that the contact time was about 60 seconds.

The effluent material, after condensation, was found to consist of about 58% methyl-3 heptene, about 5% heptenes, and about 37% of unconverted normal octene.

Example III

Normal pentene was passed through a heated reaction tube packed with about 1 mm. granules of a commercial sodium permutite.

At a temperature of about 400° C. and a contact time of about 33 seconds, the effluent material, after hydrogenation, had an isopentane content of about 53% by volume.

At a temperature of about 450° C., and using a contact time of about 62 seconds, about 84% by weight of a reaction product was obtained which, after hydrogenation, had an isopentane content of about 56% by volume.

Example IV

2,2-dimethyl butene-3 was passed through a heated reaction tube packed with granules of a sodium permutite catalyst. At a temperature of about 310° C., under about atmospheric pressure, and employing a contact time of about 30 seconds, the 2,2-dimethyl butene-3 was converted almost quantitatively, with substantially no cracking or polymerization, to a mixture of 2,3-dimethyl butene-1 and 2,3-dimethyl butene-2.

The tertiary olefins or tertiary olefin-containing mixtures prepared in accordance with the process of the invention are useful starting materials in the production of a wide variety of products. In the case that tertiary olefins falling within the gasoline boiling range are obtained,

such tertiary olefins or mixtures of them may, preferably after hydrogenation, be used as such as motor fuels of high anti-knock value, or they may be added in appropriate amount to gasoline to increase its anti-knock value.

When the process is applied to the manufacture of isobutene from normal butenes, the resulting isobutene or isobutene-containing mixture may be treated with a polymerization agent under such conditions that the isobutene is polymerized to diisobutylene which may be separated and hydrogenated to iso-octane. If desired, the reaction products which contain isobutene as well as unchanged normal butenes may be treated under such conditions that the butenes of different orders of reactivity interpolymerize to yield higher molecular weight products which can be hydrogenated to valuable motor fuels of high octane number. If desired, the tertiary olefins may be hydrated to the corresponding tertiary alcohols, chlorinated to the corresponding unsaturated halides, or otherwise converted to valuable products.

While I have described my invention in a detailed manner and provided specific examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

I claim as my invention:

1. A process for the isomerization of open-chain olefin hydrocarbons which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with a hydrated aluminum silicate having base-exchange properties whereby isomerization is effected as the principal reaction in the process.

2. A process for effecting isomerization between open-chain tertiary olefins and their corresponding normal isomers which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with a hydrated aluminum silicate having base-exchange properties whereby isomerization is effected as the principal reaction in the process.

3. A process for effecting isomerization between tertiary butylene and its corresponding normal isomers which comprises contacting a butylene to be isomerized for from 120 to 250 seconds in the vapor phase at a temperature of from 400° C. to 500° C. with an artificially prepared hydrated aluminum silicate of the class known as permutites whereby isomerization is effected as the principal reaction in the process.

4. A process for effecting isomerization between tertiary butylene and its corresponding normal isomers which comprises contacting a butylene to be isomerized for from 120 to 250 seconds in the vapor phase at a temperature of from 400° C. to 500° C. with a hydrated aluminum silicate of the class known as zeolites whereby isomerization is effected as the principal reaction in the process.

5. A process for effecting isomerization between open-chain tertiary olefins and their corresponding normal isomers which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with an artificially prepared hydrated aluminum silicate of the class known as permutites whereby isomerization is effected as the principal reaction in the process.

6. A process for effecting isomerization between open-chain tertiary olefins and their corresponding normal isomers which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with a hydrated aluminum silicate of the class known as zeolites whereby isomerization is effected as the principal reaction in the process.

7. A process for the isomerization of open-chain olefin hydrocarbons which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with an artificially prepared hydrated aluminum silicate of the class known as permutites whereby isomerization is effected as the principal reaction in the process.

8. A process for the isomerization of open-chain olefin hydrocarbons which comprises contacting an open-chain olefin to be isomerized for from 10 to 250 seconds in the vapor phase at a temperature of from 275° C. to 500° C. with a hydrated aluminum silicate of the class known as zeolites whereby isomerization is effected as the principal reaction in the process.

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