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PROCESS FOR SPLITTING HYDROCARBONS

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It is already known that hydrogenated aromatic hydrocarbons such for instance as cyclohexane, tetrahydrobenzene and the like can be split by heating, the chief reaction products thus obtained being olefines and diolefines. The operation has hitherto been performed in quartz vessels, or in the presence of quartz, platinum, charcoal or aluminium silicate.

We have now found that all kinds of hydrocarbons having a higher molecular weight than the desired products may be split, in a very advantageous manner, resulting in the formation of olefines and diolefines, by bringing them into contact in the form of vapor at an elevated temperature, with contact masses which consist of or contain one or more difficultly reducible metallic oxids. Generally speaking those oxids and combinations of several oxids, whether they are compounds or mixtures, which readily emit electrons such as the known strontium oxid-barium oxid combinations either alone or on a platinum substratum give the most favorable results. As is well known, the difficultly reducible oxids of such elements as are situated on the maxima of the curve of atomic volumes, or their dependent branches, are particularly suitable for the emission of electrons. Hence, the oxids of the alkali metals or their hydroxids and salts, especially the aluminates, chromates, tungstates, vanadates, uranates, phosphates, and also alkaline-earth metal oxids such for example as oxids of calcium, strontium, barium, magnesium, glucinium or salts of the alkaline-earth metals, for example, aluminates, and also the oxids of the elements scandium, titanium, yttrium, zirconium, lanthanum, tungsten, molybdenum, thorium and uranium, and the like, or mixtures of the same, or their compounds are suitable for use according to the present invention. The difficultly reducible oxids of the elements, which are situated on or near the minima of the curve of atomic volume, such as aluminium, chromium and zinc are less suitable, especially for the production of butadiene hydrocarbons inasmuch as they effect an extensive decomposition of the hydrocarbon molecules, though, on the other hand, they may be employed in the form of their salts, such as phosphates, chromates, vanadates and the like. Thus for example good results are obtained with aluminates of metals forming difficulty reducible oxids, such as calcium, zinc, and the like, and also with other compounds of the difficultly reducible metallic oxids with each other, such as the vanadates, chromates and tungstates of calcium, zinc and aluminium.

The said contact masses may be used either in the lump form, or may be deposited on carriers, for which purpose carriers composed for example of the silicates of magnesium and aluminium are suitable. Metals may also be present in the contact masses, for example metals, such as copper, platinum, molybdenum and tungsten, which have only a weak dehydrogenating action. When metals, such as iron, nickel and the like which have a powerful dehydrogenating action are used, they are beneficial only if added in small quantities, but harmful if added in large amounts, because in the latter case they effect extensive decomposition of the hydrocarbons with the formation of carbon and hydrogen.

The employment of the hereinbefore described contact masses facilitates the formation of olefines and diolefines, and by their means it is possible to obtain good yields of for example butadienes even from completely hydrogenated benzene hydrocarbons. Other cyclic and non-cyclic hydrocarbons may also be converted into olefines and the like with good yields, by means of the said catalysts. The employment of the said contact masses also enables the splitting temperature to be lowered in comparison with that hitherto in use for such processes, thereby diminishing the formation of carbon and improving the yield in olefines and diolefines.

The process according to the present invention may be applied both to the pure high-molecular hydrocarbons and to their mixtures, such as occur in Rumanian, Galician, Russian or American petroleum. It may even be applied for converting butylene into butadiene and lower olefines. It may be carried out under reduced pressure or in the presence or absence of other gases, such as hydrogen,

nitrogen, carbon dioxid, water vapor and the like and the operation may be carried on in a cycle by separating the unsaturated hydrocarbons formed from the reaction mixture and passing the residual gases again over the contact mass. The temperature employed for the reaction should be at least 500° C. and will generally range between about 550° and 750° C. The most suitable temperature depends on the nature of the catalyst, the kind of initial material and on the desired product.

Good yields of ethylene hydrocarbons and butadienes may be produced in a simple manner according to the said process from readily and cheaply available initial materials and the process is therefore of high industrial importance.

The following examples will further illustrate how the said invention may be carried into practical effect, but the invention is not limited to these examples.

Example 1

Tetrahydrobenzene vapor is passed through a contact furnace, constructed of inert materials, for example of porcelain, clay, noble metals, or other metals not giving rise to deposition of carbon and charged with coarse lumps of calcium oxid, at a temperature of 625° C. and at such velocity that about 30 per cent of the tetrahydrobenzene is split up. The gases issuing from the furnace are fractionally cooled, for example by passing them first through an ice-cooled receiver, and then through one cooled with a mixture of toluene and solid carbon dioxid. The bulk of the unaltered tetrahydrobenzene separates out in the first receiver, whilst butadiene, besides propylene, butylene and the remainder of the tetrahydrobenzene and small amounts of impurities are collected in the second receiver. The gaseous constituents formed consist chiefly of ethylene, methane and hydrogen. In most cases the gases leaving the second receiver contain further considerable amounts of butadienes which may be recovered by stronger cooling. Instead of separating the butadines merely by cooling, they may also be recovered by compression with or without cooling; the yield of crude butadienes amounts then to about 85 per cent of the theoretical, whilst that of ethylene is approximately quantitative. The unaltered tetrahydrobenzene is preferably used over again, after having, if necessary, been purified by fractional distillation.

Example 2

Hexahydrobenzene is passed, at about 600° C., through a contact apparatus constructed of, or lined with, quartz or clay and charged with calcium aluminate moulded into the shape of cubes, the rate of flow being such that about 40 per cent of the hexahydrobenzene is split up. The principal decomposition products obtained are ethylene and butadiene, which are separated in the manner specified in Example 1. The yield of butadienes is good, and that of ethylene approximately quantitative.

Example 3

The vapor of Russian benzene with a boiling point of from 100° to 220° C. is passed, at a temperature of 625° C., through a metal contact apparatus enamelled inside and filled with coarse lumps of calcium oxid, the rate of flow being such that the contents of the contact space, at that temperature, are renewed about 20 times per hour. The reaction product consists of liquid, partly unsaturated hydrocarbons, of substantially lower boiling point than the initial material. The gaseous products contain a large proportion of olefines.

In the foregoing examples the catalysts mentioned may be replaced by other contact masses of the kind specified, and both the temperature and rate of flow may also be modified. The hydrocarbon vapors may also be used in association with other gases, such as hydrogen, nitrogen, carbon dioxid, water vapor and the like.

Example 4

A mixture of 1 part, by volume, of beta-butylene (boiling point 1° C.) and at least 5 parts, by volume, of nitrogen is passed at 700° C. over coarse granules of strontium uranate, at a rate of about 10 grams of butylene per hour and per square centimetre of the cross-sectional area of the contact vessel. Hydrogen is split off and a good yield of butadiene besides unaltered initial material is obtained. The reaction may also be carried out under reduced pressure without the addition of nitrogen or other gases.

What we claim is:

1. The process of splitting hydrocarbons having a higher molecular weight than the desired products to olefines and diolefines which consists in bringing the hydrocarbon vapors into contact, at temperatures above 500° C., with a contact mass comprising a difficultly reducible metal oxid.

2. The process of splitting hydrocarbons having a higher molecular weight than the desired products to olefines and diolefines which consists in bringing the hydrocarbon vapors into contact, at temperatures above 500° C., with a contact mass comprising a difficultly reducible metal oxid capable of readily emitting electrons.

3. The process of splitting hydrocarbons having a higher molecular weight than the desired products to olefines and diolefines which consists in bringing the hydrocarbon vapors into contact, at temperatures between about 550° and 750° C., with a contact mass comprising a difficultly reducible metal oxid.

4. The process of splitting hydrocarbons having a higher molecular weight than the desired products to olefines and diolefines which consists in bringing the hydrocarbon vapors into contact, at temperatures above 500° C., with a contact mass comprising an alkaline earth metal oxid.

In testimony whereof we have hereunto set our hands.

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