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CATALYTIC PROCESS FOR DEHYDROGENATION OF HYDROCARBONS

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This invention relates to the dehydrogenation of hydrocarbons, and more particularly to dehydrogenation employing gadolinium oxide as a catalyst.

It is another object of the invention to provide a process and catalyst for the cracking of hydrocarbons that will give higher yields.

Other objects and advantages of the invention will be apparent as the description proceeds.

To the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claim, the following descriptions setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention relates to a process for dehydrogenation which comprises subjecting hydrocarbons to the action of gadolinium oxide supported on a carrier. The invention is also directed to an improved catalyst containing gadolinium oxide on a carrier.

More particularly, this invention relates to the process for dehydrogenation which comprises subjecting hydrocarbons to the action of a catalyst containing from about ninety-nine percent to about fifty percent by weight of a carrier, for example, aluminum oxide, and from about one percent to about fifty percent by weight of gadolinium oxide at a temperature within the range from about 430° C. to 650° C. at a space velocity of not more than 2.0.

The hydrocarbons which may be dehydrogenated in the process of the invention include both the gaseous and liquid compounds and may be either the aliphatic or cycloaliphatic structures. Ordinarily the hydrocarbons which are employed in the process contain from 2 to 12 carbon atoms; however, those containing from 7 to 9 carbon atoms are preferred. The acyclic hydrocarbons may be straight or branched chain compounds; for example, the alkanes, such as, ethane, propane, iso-propane, butane, iso-butane, pentane, hexane, 3-methyl-pentane, n-heptane, octane, nonane, decane, dodecane; and the alkenes, such as, propene, heptene, dodecene. Examples of cycloaliphatic hydrocarbons include cyclopentane, cyclohexane, cycloheptane, cyclooctane, and cyclononane. The naturally occurring mixtures of hydrocarbons, for example, the various fractions of petroleum and natural gas, are particularly applicable in the process.

The catalyst employed in the dehydrogenation reaction is a composition of a carrier and gadolinium oxide. The carrier may be present in amounts from about ninety-nine percent to about fifty percent (99% to 50%) by weight. The gadolinium oxide is present in amounts from about one percent to about fifty percent (1% to 50%) by weight.

The gadolinium oxide (Gd_2O_3) may be prepared by precipitation of the hydroxide from a solution of gadolinium nitrate by treatment with caustic soda, washing the precipitate with water, and drying the hydroxide precipitate at elevated temperatures, for example, within the range from about 100° C. to 650° C. in an atmosphere of inert gas.

A number of different types of carriers may be employed for supporting gadolinium oxide for promoting the dehydrogenation reactions. These carriers desirably are capable of withstanding severe use during service and regeneration. Examples of materials which may be employed in granular form as supports for the gadolinium oxide are: aluminum oxide, magnesium oxide, silica gel, mixtures of silica and alumina, bauxite, bentonite clays, and the like, with special preference given to aluminum oxide. By using these different types of carriers for supporting gadolinium oxide, the preparation of a number of catalyst compositions is possible, although they obviously will not exert the exact equivalent effects in dehydrogenation.

In making up the catalyst composites of the character and composition which, according to the present invention, have been found especially well suited for catalyzing hydrocarbon dehydrogenation reactions, the following procedures may be used. The carrier material is ground into granules of relatively small mesh of the approximate order of from four to twenty (4 to 20) and these are caused to absorb compounds which will ultimately yield compounds of gadolinium on heating to a proper temperature by stirring them with warm aqueous solutions of soluble gadolinium compounds such as, for example, gadolinium nitrate. While substantially all the compounds of gadolinium will have an appreciable catalytic action in further dehydrogenation reactions, some will be considerably better than others and it is not intended to imply that the compounds which may be employed alternatively are in any sense exact improvements.

The composite catalyst of gadolinium oxide supported by a carrier, such as, aluminum oxide, may be prepared by coprecipitation of aluminum hydroxide and gadolinium hydroxide from their respective nitrate solutions by treatment with caustic soda. The composite catalyst may also be prepared by dissolving gadolinium oxide in nitric acid, pouring the nitric acid solution over particles of aluminum oxide, filtering, and drying at temperatures above 100° C. in an atmosphere of inert gas.

In carrying out the dehydrogenation of the hydrocarbons according to the present process a solid composite catalyst prepared according to the foregoing briefly outlined methods was used as a fill-in in a reaction tube chamber in the form of particles of graded size of small pellets in the approximate order of from 4 to 20 mesh, although usually from 8 to 10 mesh. The hydrocarbon gas or vapor to be dehydrogenated is passed through a stationary mass of the composite catalyst particles after being heated to the proper temperature, usually within the range from about 430° C. to 650° C., depending upon the hydrocarbon or mixtures of hydrocarbons undergoing treatment. The most commonly used temperatures, however, are approximately 450° C. to 540° C. The catalyst tube is usually heated exteriorly to maintain the proper reaction temperature. The pressure employed may be super-atmospheric or sub-atmospheric. The super-atmospheric pressures may be within the order of some fifty pounds to 100 pounds per square inch (50 lbs. to 100 lbs. p.s.i.). Super-atmospheric pressures may be empolyed but atmospheric pressures are generally preferred.

The space velocity needed for the desired reaction is generally within the range of 0.1 to 2.0, and usually not more than 2.0. By the space velocity is meant that a unit volume of the liquid is vaporized and passed through a unit volume of catalyst for a unit of time. A space velocity of one is equal to passing 100 ml. of liquid in vapor form through 100 ml. of catalyst for one hour.

When the activity of the catalyst begins to diminish, it is readily regenerated by the simple expedient of oxidizing with air or other oxidizing gas in a moderately elevated temperature, usually within the range employed in the dehydrogenation action. This oxidation effectively removes traces of carbon deposits which contaminate the surface of the particles and decrease their efficiency. It is a characteristic of the present types of catalysts that

they may be repeatedly regenerated without substantial loss of catalytic potency.

In order to more clearly illustrate our invention, the preferred modes of carrying out the following examples are given:

Example 1

7.1 grams of gadolinium oxide were dissolved in 6.4 ml. of concentrated nitric acid. 4.6 grams of aluminum oxide granules were placed in an evacuated flask and the nitric acid solution poured thereover. The granules were dried overnight at 110° C. The so dried granules were placed in a catalytic tube and activated by gradually heating to 550° C. under an atmosphere of nitrogen.

Example II

n-Heptane was vaporized and passed through a chamber containing the catalyst prepared in Example I at a temperature of 525° C. and at a space velocity of from 0.15. The effluent product composition contained 8% by weight of heptene and 30% by weight of toluene.

Example III

8.0 grams of gadolinium oxide are dissolved in 16 ml. of concentrated nitric acid. 43 grams of aluminum oxide particles are placed over an evacuated flask and the nitric acid solution poured thereover. The particles are then dried overnight at 110° C. and activated in a catalytic tube by heating to a temperature of about 525° C. under a nitrogen atmosphere.

Example IV

n-Heptane is vaporized and passed through the tube containing catalysts prepared in Example III at 525° C. at a space velocity of 0.2. The composition of the exit products includes 8 percent by weight of olefins and 30 percent by weight of aromatics.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described provided the features stated in the following claim or the equivalent of such be employed.

I, therefore, particularly point out and distinctly claim as my invention:

The process of dehydrogenation which comprises subjecting aliphatic hydrocarbons having from 2 to 12 carbon atoms to the action of a catalyst consisting of ninety-nine percent to about fifty percent by weight of an aluminum oxide carrier supporting from about one percent to about fifty percent by weight of gadolinium oxide at a temperature within the range from about 430° C. to 650° C. at a space velocity of not more than 2.0 whereby the aliphatic hydrocarbons are dehydrogenated.

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