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PATENT APPLICATION FOR A PROCESS FOR THE DEHYDROGENATION OF GASEOUS HYDROCARBONS

It has been found that contrary to current opinion saturated hydrocarbons with three or four carbon atoms in the molecule, or mixtures of such hydrocarbons, can be catalytically dehydrogenated in a simple way with better yields than obtained up to now if they are passed through tubes packed with metal oxides not easily reduced, these tubes being heated from the outside and the temperature kept at 842°F. 1,112°F., the preferred temperature being between 932 and 1,076°F. The catalyst is regenerated by treatment with gases containing oxygen. This way of operation makes it possible to introduce the heat required for the reaction in such a way that it corresponds to the activity of the catalyst at any given time. The use of tubular reaction spaces makes it possible to regulate the temperature in each individual operating period in such a way that the portion of the catalyst which is next to the gas inlet is heated less that the portion near the outlet so that the reaction velocity during the entire period remains approximately constant. Temperature control is obtained advantageously by introducing heat by means of a hot gas. The reaction tubes should have a diameter of 0.79 - 5.9 inches, preferably between 1.97 and 3.94 inches. The length should not exceed 33 feet and be preferably 16½ feet. It was found that with wider and longer tubes the introduction of heat into the catalyst is considerably more difficult and superheating of the reactor wall is not easy to avoid. The tubes are preferably manufactured from a special steel, e.g. chromium steel, preferably chromium steel containing silica.

The catalyst is regenerated after an operating period not exceeding 20 hours, preferably 4 - 8 hours. The dehydrogenation periods are chosen so short in order to permit the catalyst to become inactive only to such an extent that it can be regenerated at a temperature which does not exceed by much the temperature during the dehydrogenation period. As a rule, it is advantageous to work at lower temperatures. Air and other oxygen-containing gases are used as regenerating gas. By changing the oxygen content or the flow velocity, it is easy to control the temperature. It is not necessary to completely burn off the carbon deposited on the catalyst. It is sufficient to heat to such an extent that about 1/4 - 2/3, preferably 1/3 - 1/2, of the deposited carbon remains on the catalyst. This residual carbon may be distributed over the entire catalyst or regeneration can be carried out in such a way that the carbon is burned off completely in the first third or the first half of the catalyst (in the direction of gas flow), whereas it is left on the remaining part of the catalyst.

The process can be carried out at ordinary pressure, slightly elevated pressure or reduced pressure. Metal oxides which are difficult to reduce serve as catalysts, especially activated alumina which is further activated by addition of one or several catalytic materials. The catalyst should be as free from water as possible. Several catalysts of this kind can be used simultaneously and they should be arranged in reaction tubes in such a way that the most active one is placed at the gas outlet. In this case it is unnecessary to increase the temperature within the reaction tubes; it can be kept constant or it can decrease in the direction of the gas flow.

The advantages to be obtained with the new process can be shown in the following comparison. If n-butane is dehydrogenated using an alumina-chromium oxide-potassium oxide catalyst in accordance with the invention with periodic change of dehydrogenation and regeneration using a temperature which slowly increases from

968° - 1,040°F. a conversion of 27½% is obtained over the entire dehydrogenation period of 550 hours and the yield of n-butylene is 85 - 88% based on the butane reacted.

If, however, the reaction is carried out as practiced up to now by moving the catalyst through the reaction space, using otherwise the same conditions as in the previous experiment, the conversion after 44 hours has decreased 15 to 16% with a yield of 80 - 83% of butylene (based on the butane reacted). Dehydrogenation in a shell-type reactor with introduction of heat by superheating of the feed gases gives considerably lower yields than those obtained in accordance with the invention. Using the best possible temperature control conversion under otherwise equal conditions amounts to 11% for 150 hours of operation with a yield of butylene of 86%.

Claims

1. Method for the catalytic dehydrogenation of saturated hydrocarbons with three or four carbon atoms or mixtures of those hydrocarbons yielding olefins with the same number of carbon atoms by the use of metal oxides which are difficult to reduce. The process operates at temperatures between 842°F. and 1,112°F. and is carried out in tubes which are heated from the outside and contain a solid-bed catalyst. The catalyst can be regenerated by treating with gases containing oxygen and the length of the dehydrogenation period is chosen so that the catalyst is inactivated only to such an extent that its regeneration can be carried out at a temperature substantially equal to the dehydrogenation temperature.

2. Process according to Claim 1 characterized by increasing the temperature in the catalyst during dehydrogenation in the direction of gas flow.

3. Process according to Claim 1 characterized by using catalysts with increasing activity in the direction of the gas flow.

4. Process according to Claims 1 - 3 characterized by carrying out the regeneration of the catalyst only to such an extent that part of the carbon deposited is burned off.

5. Process according to Claims 1 - 4 characterized by using a catalyst which is as free from water as possible.