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DEHYDROGENATION CATALYST

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This application is a continuation-in-part of co-pending application, Serial Number 516,971, filed January 4, 1944.

This invention relates to a new and improved iron oxide catalysts for dehydrogenation and more particularly for the production of diolefins by the catalytic dehydrogenation of the corresponding mono-olefins at high temperatures in the presence of steam.

Primary objects of the invention are to provide an improved process and improved catalysts for the production of diolefins, and particularly butadiene, by catalytic dehydrogenation affording excellent conversions per pass and excellent selectivity (i. e. conversion efficiency) while allowing the dehydrogenation to be effected substantially continuously and at ordinary or moderate pressures.

According to the process of the invention, suitable mono-olefins are converted in good yields and more or less selectively to the corresponding diolefins by catalytic dehydrogenation at temperatures above about 580° C. in the presence of at least 2 mols of steam per mol of olefin with alkalinized iron oxide or cobalt oxide catalysts provided with at least 1 mol per cent of chromium oxide (calculated as Cr₂O₃).

The process of the invention is particularly advantageous for the production of butadiene from butene-1 and/or butene-2. It is, however, also applicable and advantageous for the production of other diolefins, and particularly conjugated diolefins, such as piperylene, isoprene, the various hexadienes, etc. from the corresponding mono-olefins. Thus, the process may generally be applied for the production of diolefins from the corresponding mono-olefins having at least four non-quaternary carbon atoms in a straight chain. The process of the invention involves the treatment of the olefins in the vapor phase at temperatures above about 580° C. In order to produce the corresponding diolefins more or less selectively, the olefin treated is therefore one which may be heated to temperatures above about 580° C. without substantial decomposition. Since the tendency for the various olefins to undergo thermal cracking increases with their molecular weights, preferred olefins to be treated are the lower olefins having from 4 to about 6 non-quaternary carbon atoms in a straight chain. The olefin to be dehydrogenated may be a single hydrocarbon or, if desired, a mixture of olefins may be dehydrogenated to produce a mixture of diolefins. Also, in some cases a single diolefin may be produced from a

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mixture of isomeric olefins. For example, butadiene may be produced from either butene-1 or butene-2 or a mixture of the two, and isoprene may be produced from methyl ethyl ethylene, trimethyl ethylene, or isopropyl ethylene, or a mixture of these olefins.

In order to facilitate the recovery of the diolefin and unconverted mono-olefin from the product, and for various other practical reasons, it is usually desirable that the feed consist essentially of the desired olefin or olefins. This is, however, not essential and in some cases it may be more advantageous to use olefin fractions comprising appreciable amounts of relatively inert diluents. Thus, for example, in the production of butadiene, a so-called butane-butylene fraction containing, for instance, 50% butane may be used. The paraffin hydrocarbons are substantially unaffected in the process of the invention and may be considered as inert diluents. In this respect the process of the invention differs fundamentally from most of the known dehydrogenation processes which are much more suited for the dehydrogenation of paraffins than for the dehydrogenation of olefins and are totally incapable of selectively dehydrogenating olefins in the presence of paraffins.

The dehydrogenation of olefins to the corresponding diolefins differs from most other dehydrogenation processes in requiring a low partial pressure of reactants in the reaction zone. Thus, in all known processes for the production of diolefins by dehydrogenation, it is necessary either to carry out the dehydrogenation under a substantial vacuum or to employ large quantities of a diluent. Operation under a vacuum is very costly. The use of inert diluents to decrease the partial pressure of the reactants usually makes the efficient separation and recovery of the diolefin from the product very difficult and is a serious disadvantage. Steam is an ideal diluent but, unfortunately, many of the most active dehydrogenation catalysts are not suited for use in the presence of steam. Also, most of the known catalysts are not sufficiently selective in their action and, if steam is used as a diluent, they catalyze the oxidation of the reactants by the steam, thus giving low yields.

The above-described olefins are dehydrogenated, according to the process of the invention, in the presence of a substantial mol excess of steam with catalysts which are designed to selectively dehydrogenate olefins in the presence of steam over long periods of time with relatively infrequent regeneration without losing activity.

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In the process of the invention the use of steam is not merely permissible, it is essential. Thus, in the present process the olefin to be dehydrogenated is contacted with the catalyst in the presence of at least two and preferably at least seven mol proportions of steam. In the dehydrogenation of butylene to butadiene, for example, the best results have been obtained when using between about 7 and 30 mols of steam per mol of butylene. The use of such amounts of steam allows the process to be carried out at atmospheric pressure or, if desired, even at moderately superatmospheric pressures.

The catalysts used in the process of the invention are special iron oxide or cobalt oxide catalysts which are highly active and retain their activity with little or no regeneration over long periods of use in the presence of steam. Under the described conditions they dehydrogenate olefins selectively in the presence of paraffins and catalyze to a minimum extent the oxidation of the reactants by the steam. Cobalt oxide is somewhat more active than iron oxide and may be substituted for part or all of the iron oxide. However, in view of the relatively high cost of cobalt oxide, its practical application is probably limited to use in minor concentrations. In the following description the catalysts are referred to as iron oxide catalysts with the understanding that the iron oxide may be substituted in part by its equivalent, cobalt oxide.

Iron oxide has long been recognized to possess certain catalytic properties. Many catalysts containing iron oxide have been developed for special purposes and some of them are used commercially. As will be apparent from the comprehensive and detailed compilation of the catalysts mentioned in the literature and patents relating to dehydrogenation in Berkman, Morrell and Egloff, "Catalysis," pages 888-906, (1940), iron oxide is recommended for use in dehydrogenation catalysts only in a very few special cases. This is due, firstly, to certain undesirable properties of iron oxide catalysts for most dehydrogenations and, secondly, due to the availability of other more desirable catalysts for the usual dehydrogenation processes. The more objectionable properties of the hitherto-known iron oxide catalysts in dehydrogenation are, firstly, their pronounced tendency to produce large amounts of carbon and, secondly, their relatively short life. The first of these objectionable properties is partly due to the fact that under the reducing conditions usually prevailing in dehydrogenation the iron oxide tends to be converted at least in part to a lower oxide or metallic iron which catalyzes decomposition to carbon. The second of these objectionable properties, it is found, is due in part to the tendency of the iron oxide to react or combine with the carrier or support material used to provide a large catalyst surface. It has now been found that certain dehydrogenation reactions such, in particular, as the dehydrogenation of olefins to the corresponding diolefins may be much more effectively and economically accomplished using iron oxide catalysts provided that the iron oxide is promoted with an alkali and is used in the absence of substantial amounts of carriers or other materials which tend to react therewith, and provided that the dehydrogenation is carried out in the presence of a large excess of steam at temperatures above about 580° C.

Alkalized iron oxide per se is a fairly active catalyst but is very sensitive to the reaction conditions. Another disadvantage of alkalized iron

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oxide per se for the described dehydrogenation is that, although the ultimate life of the catalyst is suitable, the catalyst declines in activity during use and must be periodically regenerated. Thus, the maximum process period is in the order of 50 to 80 hours. It has been found, however, that if the iron oxide is combined with chromium oxide these disadvantages are avoided, and highly active and selective catalysts result. Thus, by providing the alkalized iron oxide catalyst with a suitable amount of chromium oxide the dehydrogenation may be carried out under conditions chosen to produce maximum conversions and yields of diolefins and the process may be carried out in an essentially continuous operation. Chromium oxide (Cr_2O_3) per se, when used under the described conditions, is somewhat less effective than iron oxide (Fe_2O_3) per se. When iron oxide is provided with suitable amounts of chromium oxide, however, the selective dehydrogenating activity under the described conditions is greater than that of either constituent alone. The more important advantage of the present catalysts is, however, that whereas both iron oxide per se and chromium oxide per se require frequent periodic regeneration, the present iron oxide catalysts provided with chromium oxide can be used essentially continuously, i. e. regeneration, if it is necessary at all, is required only after long periods of operation.

For the purposes of the present specification an operation in which the conversion and conversion efficiency remain with no appreciable drop for a period of continuous operation of at least 10 hours under a fixed set of conditions is considered to be an essentially continuous operation.

Iron oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) constitute a unique combination since these two oxides form solid solutions in all proportions. Also, as pointed out above, chromium oxide itself exerts a catalytic action which is comparable to that of iron oxide per se. Probably because of these facts, the concentration of chromium oxide is not extremely critical. Even small amounts of chromium oxide are quite effective. Thus, for example, catalysts consisting essentially of alkalized iron oxide and containing only one, three and five mol per cent of chromium oxide (Cr_2O_3) have been prepared and have given excellent conversions of butylenes to butadiene over periods of over 100 hours of continuous operation without any noticeable decline in activity or selectivity. However, very satisfactory catalysts have also been prepared containing 30 mol %, 50 mol % and 70 mol % of chromium oxide (the remainder being the alkalized iron oxide, calculated as Fe_2O_3). The iron oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) may form a solid solution; however, they cannot react under oxidizing conditions to form the chromite. Since the process of the invention is carried out in the presence of a large excess of steam, reaction to form the chromite is largely prevented. During long periods of use under severe conditions, and particularly if the catalyst is accidentally subjected to strongly reducing conditions (as by failure of the steam flow), some reaction to form the chromite may, however, take place. This is undesirable since tests have indicated the chromite to be much less efficient than the mixed oxides (or solid solution) and since reaction to form the chromite reduces the concentration of free iron oxide. Danger of loss of activity due to this cause is largely avoided by using a molecular excess of iron oxide (calcu-

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lated as Fe_2O_3) with respect to the chromium oxide (calculated as Cr_2O_3).

The best experimental evidence indicates that the state of oxidation of the iron oxide during the reaction and perhaps also the state of hydration are extremely critical. The exact states of oxidation and hydration are difficult to determine and are not known. It is known, however, that whatever these states may be they are established and maintained by the described reaction conditions. Since the state of the iron oxide is established by the reaction conditions and since furthermore the crystal types of the iron oxides can quickly come to equilibrium through the medium of solid solutions, suitable catalysts may be prepared starting with various iron oxides from various sources. Various commercial iron oxides such as the iron oxide pigments, the iron oxide produced as a by-product in the production of alumina (Luxmass) may be used. Suitable iron oxides may be also prepared, for instance, by the thermal decomposition of iron compounds such as ferric nitrate, ferric oxalate, ferric ammonium oxalate, etc., by precipitation from solutions of iron salts such as ferric nitrate, ferric sulfate, etc. followed by dehydration.

It is essential that the iron oxide be alkalinized by the incorporation of a suitable alkali. All of the common alkalis appear to be suitable. Thus, any of the oxides, hydroxides and salts of the alkali or alkaline earth metals may be used. The halides may be used but are less preferred. Particularly suitable alkalis are the compounds, for example, the hydroxide, nitrate, sulfate and carbonate of potassium. These various materials are probably converted at least in part into the corresponding oxides or hydroxides during the preparation and/or use of the catalyst.

The concentration of alkali, calculated as the oxide, should be at least 0.2% by weight of the catalyst and is preferably somewhat higher, for instance between about 0.5% and 5%. During extended use of the catalyst the alkali used, particularly if it is potassium, may be partly lost from the catalyst by volatilization and this may cause a decline in the activity of the catalyst. If this happens the activity of the catalyst may be restored by simply adding additional alkali, for instance by impregnation or by adding a small amount of potassium carbonate with the steam.

The inclusion of additional agents in the catalysts is not precluded; however, the major active constituent should be the described alkalinized iron oxide-chromium oxide and any other components which tend to react with the iron oxide under the process conditions, for instance to form a spinel, if present at all are present in minor amounts with respect to the iron oxide. For this reason such materials as alumina, magnesia and the like, if present at all, are present in minor concentrations and these and similar materials cannot be used as supports or carriers. Totally inert materials (with respect to the iron oxide), may, if desired, be used as supports, carriers, diluents or strengthening agents and may be present in any concentration. Since, however, the activity of the catalyst is proportional to the concentration of the major active agent, i. e. the alkalinized iron oxide-chromium oxide, such diluents or extenders, if used at all, are preferably used in their minimum effective concentrations. In the present description and in the claims the expression "consisting essentially of" is not meant to exclude such totally inert materials which do not affect the catalytic properties of the catalyst.

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The catalyst may be prepared by a variety of methods. The iron oxide and chromium oxide can be combined, for example, by mixing or co-grinding the powders, by thermally decomposing a mixture of the nitrates, by co-precipitating the hydrous oxides, by mixing the hydrous gels or sols, by calcination of a mixture of iron oxide powder and a decomposable chromium compound, or in general by any method providing an intimate contact between the components and preferably affording an essentially homogeneous mass. One particularly suitable method, for example, is to thoroughly mix as by co-grinding or ball milling a mixture of powdered iron oxide and powdered chromium oxide, form a paste of the mixture with a solution containing the desired amount of potassium salt, extrude or pellet and dry. In most cases and in particular when the iron oxide and chromium oxide are combined by co-precipitation and similar methods, the catalysts have a fairly large available surface, for instance above about 30 square meters per gram. In most dehydrogenation catalysts this is desirable. In the present catalysts, however, a large available surface is undesirable since catalysts having a large available surface are insufficiently selective in their action in catalytic dehydrogenation at elevated temperatures in the presence of steam. In such cases, therefore, where the catalysts produced, for example, by co-precipitation show relatively poor activity or selectivity they may be materially improved by subjecting them to a fairly drastic calcination in air for a time to decrease their available surface to below about 30 square meters per gram. The calcination may be effected at temperatures between about 700° C. and 1000° C. and preferably between about 800° C. and 950° C. A suitable treatment, for example, may be a calcination at a temperature of about 900° C. for about 5 to 10 hours.

The catalysts may be in any of the conventional forms such as powder, pills, spheres, saddles, extrudates, or irregular fragments of a shape and size adapted for the reaction system to be used. These catalysts, it is found, are unusually sensitive to changes in the particle size. Thus, their effectiveness increases markedly with decrease in the size of the catalyst particles. For this reason, it is desirable to use the catalysts in the smallest size consistent with an allowable pressure drop through the converter. For example, in the production of butadiene from butylene markedly improved results are obtained merely by decreasing the particle size of the catalyst particles from $\frac{1}{8}$ -inch pellets (average volume of about 0.113 cc.) to $\frac{1}{16}$ -inch pellets (average volume of about 0.038 cc.).

The above-described catalysts are exceptionally rugged and may be heated to temperatures up to about 900° C. to 1000° C. in the presence of steam without loss of efficiency. They are particularly adapted for use at high temperatures in the presence of steam, and as pointed out above, steam is essential for their use. If during use they become relatively inefficient due to lack of sufficient steam, they may be restored to essentially their original activity by simply steaming them for a few hours, preferably at a temperature between about 600° C. and 800° C. The described catalysts are not only exceptionally suited for the selective dehydrogenation of olefins to diolefins under the described conditions but can be used for a few other reactions for which these conditions are favorable. Thus, for

example, the catalysts are also particularly suitable for the dehydrogenation of alkyl aromatics, for instance, the dehydrogenation of ethyl benzene to styrene.

In the production of diolefins, according to the process of the invention, the contact time of the olefin with the catalyst affording the optimum results depends upon the particular olefin or mixture of olefins being dehydrogenated, and the particular conditions chosen and may best be determined for any given case by starting with a very short contact time and then gradually increasing the contact time until the desired conversion and conversion efficiency are obtained. Conversion is herein defined as the per cent of the reactant applied which undergoes reaction and is converted into a different product. Yield is defined as the per cent of the reactant applied which is converted to the desired product. Conversion efficiency is defined as the per cent of the material converted or reacted which is converted to the desired product; in this case, diolefins having the same number of carbon atoms as the parent material. In general, the conversion and conversion efficiency are interdependent, the conversion efficiency becoming lower as the conversion is increased. The optimum conversion and conversion efficiency for any given operation, therefore, depend upon the particular economic factors. In the production of butadiene by the present process, by way of example, conversions of about 30% are considered at present to be quite suitable. Suitable contact times for the dehydrogenation of butylenes to butadiene, by way of example, are of the order of 0.02 to 0.5 seconds. The process of the invention allows excellent conversions to diolefins to be obtained quite selectively over a considerable range of suitable space velocities. Suitable space velocities are, for example, between about 300 and 3000 volumes of gaseous reactant (N. T. P.) per volume of catalyst per hour. This is referred to as gaseous hourly space velocity (G. H. S. V.).

As pointed out above, the process of the invention is carried out at temperatures above about 580° C. at any desired pressure. In general, temperatures between about 580° C. and 750° C. are suitable. In the production of butadiene, for example, the best results have been obtained at temperatures between about 590° C. and 690° C. Although either subatmospheric pressure or superatmospheric pressure can be used, it is most advantageous for various practical reasons to operate the process at substantially atmospheric pressure, for instance, the slight pressure necessary to flow the reactant vapors and steam through the catalyst zone under the prescribed conditions.

If desired, the process may be carried out in a so-called dust catalyst, fluidized catalyst, or moving bed system. Excellent results may, however, be obtained by simply passing the preheated reactant vapors and preheated steam through a reaction chamber filled with the catalyst and maintained at the desired temperature and pressure. The steam in the product may be condensed and separated from the converted and unconverted material. The unconverted material may be separated from the product in conventional manners and recycled.

Example I

A catalyst designated 1322-C92, having the composition 70 mols Fe_2O_3 , 30 mols Cr_2O_3 , 1 mol CuSO_4 , 0.5 mol KNO_3 , was prepared as follows:

The hydrous oxides of iron and chromium were coprecipitated from mixed solutions of iron sulfate and chromium nitrate with ammonium hydroxide. The coprecipitated hydrous oxide mixture was washed, then mixed with the required amounts of copper sulfate and potassium nitrate, and finally dried at 100° C.-120° C. The resulting mass was broken up and screened to 6-14 mesh. Prior to use the catalyst was heated at 750° C. for 6 hours and then finally pretreated for one hour at about 600° C. with steam and hydrogen. This pretreatment is not essential but shortens the period during which the catalyst comes to equilibrium during use.

This catalyst was used for the production of butadiene from a typical normal butylene fraction consisting essentially of butene-1 and butene-2. The butylene was vaporized and preheated, and passed in admixture with steam through a stationary bed of the catalyst. The dehydrogenation conditions were as follows:

Temperature..... About 610° C.
Butylene, G.H.S.V. About 500
Steam, G.H.S.V. About 7000
Pressure (at exit) About 1 atmosphere absolute

The operation was carried out continuously. The conversion of butylene to butadiene increased during the first eight hours to about 25%-26% and then remained substantially constant. The conversion efficiency increased during the first eight hours to about 72%-74% and then remained substantially constant.

Example II

A quantity of powdered iron oxide (pigment grade) was mixed with 5% by weight of technical powdered chromium oxide for 10 minutes in a Clearfield mixer. A solution of potassium carbonate and tannic acid equivalent to 4% by weight potassium and 0.3% by weight of tannic acid was added to form a paste containing about 27% to 35% water. The paste was mixed for an additional 20 minutes and then extruded and cut into approximately $\frac{3}{4}$ -inch pellets. The pellets were placed in metal trays to a depth of about 2 inches and dried for 8 hours at about 150° C.-175° C. The pellets were then calcined at 900° C. for 12 hours.

This catalyst was used for the continuous dehydrogenation of butylene to butadiene under the following conditions:

Temperature..... About 620° C.
Butylene, G. H. S. V. About 300
Steam, G. H. S. V. About 3600
Pressure (at exit) About 1 atmosphere absolute

After an initial induction period the conversion and conversion efficiency remained substantially constant. After 415 hours of continuous operation the conversion of butylene to butadiene was about 22.4% and the conversion efficiency was about 77.2% with no indication of catalyst exhaustion.

I claim as my invention:

1. A catalyst particularly adapted for effecting dehydrogenation at temperatures above about 580° C. in the presence of steam consisting essentially of a major mol amount of iron oxide, a minor mol amount of an alkaline compound of potassium and a minor mol amount of at least one mol per cent of chromium oxide, the mixture having been calcined at a temperature between about 800° C. and about 950° C. in an atmosphere under which no appreciable formation of iron

chromite takes place and for a sufficient length of time to decrease the available surface of the catalyst to below 30 square meters per gram.

2. A method for the production of a dehydrogenation catalyst which comprises intimately mixing powdered iron oxide with a minor mol amount of powdered chromium oxide (Cr_2O_3), forming the mixture into an extrudable paste with an aqueous solution of a potassium salt, extruding the paste, drying the extruded pellets and calcining them at a temperature between about 800° C. and about 950° C. in an atmosphere under which no appreciable formation of iron chromite takes place and for a time sufficient to decrease the available surface of the catalyst to below 30 square meters per gram.

3. A catalyst particularly adapted for effecting dehydrogenation at temperatures above 580° C.

in the presence of steam consisting essentially of a major mol amount of iron oxide, a minor mol amount of an alkaline compound of potassium and a minor mol amount of at least one mol per cent of chromium oxide, the mixture having been calcined prior to use at a temperature of about 900° C. in an atmosphere under which no appreciable formation of iron chromite takes place and for a time between about 5 and about 10 hours sufficient to decrease the available surface of the catalyst to below 30 square meters per gram.

4. A catalyst as defined in claim 1 in which chromium oxide (Cr_2O_3) is about 5 mol per cent with respect to the iron oxide and the potassium, calculated as K_2O , is in mol excess with respect to the chromium oxide.

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