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PROCESS OF DEHYDROGENATION

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This invention relates to a process for dehydrogenating organic compounds and relates more particularly to the dehydrogenation of hydrocarbons at elevated temperatures in the presence of oxygen and particular catalysts.

We have now discovered an improved process for the production of unsaturated hydrocarbons wherein hydrocarbons are dehydrogenated under certain specified conditions in the vapor phase at elevated temperatures in the presence of oxygen and a catalyst comprising certain mixed ferrites having iron combined with more than one metal selected from the group consisting of magnesium, zinc, nickel and cobalt. Oxygen will also be present in the crystalline lattice.

As a class, the ferrites are known commercial products. In the mixed ferrites used as catalysts in the present invention, the iron and the metals selected from the group consisting of magnesium, zinc, nickel and cobalt are combined in a crystalline structure together with oxygen. The preferred arrangement is the face-centered cubic structure. The exact arrangement of the atoms in the structure is difficult to determine. In some instances, the metallic atoms of magnesium, zinc, nickel and/or cobalt may be intetrahedral sites and the iron atoms in the octaherdral sites, or in some instances, the opposite is the case. Another possibility is that a portion of the iron atoms may be in the tetrahedral and a portion in the octahedral sites.

The particular ferrite catalysts of this invention produce high yields of unsaturated hydrocarbons at improved selectivities. The use of particular ferrites as catalysts for the oxidative dehydrogenation of organic compounds has been claimed in copending applications. We have now found according to the present invention that improved results may be obtained with mixed ferrites; that is, wherein the ferrite comprises, in addition to the iron, at least two of the metals selected from the group consisting of magnesium, zinc, nickel, cobalt and mixtures thereof. According to this invention, it has been found that the catalysts of this invention can operate at lower process temperatures than the unmodified ferrites containing only one divalent cation. There are numerous advantages to the operation at lower temperatures such as less exothermic heat of reaction to be dissipated, also higher selectivities may be achieved, and so forth. Another advantage may be longer catalyst life. These and other advantages constitute important advances in the process of dehydrogenation.

Hydrocarbons to be dehydrogenated according to the process of this invention are hydrocarbons of 4 to 7 carbon atoms and preferably are aliphatic hydrocarbons selected from the group consisting of saturated hydrocarbons, monoolefins, diolefins and mixtures thereof of 4 to 5 or 6 carbon atoms having a straight chain of at least four carbon atoms and cycloaliphatics. Examples of preferred feed materials are butene-1, cis-butene-2, transbutene-2, 2-methylbutene-1, 2-methylbutene-2, 2-methylbutene-3, n-butane, butadiene-1,3, methylbutane, 2-methylpentene-1, cyclohexene, 2-methylpentene-2 and mixtures thereof. For example, n-butane may be converted to a mixture of butene-1 and butene-2 or may be converted to a mixture of butene-1, butene-2 and/or

butadiene-1,3. A mixture of n-butane and butene-2 may be converted to butadiene-1,3 or to a mixture of butadiene-1,3 together with some butene-2 and butene-1. Vinyl acetylene may be present as a product, particularly when butadene-1,3 is used as a feedstock. Thus, the process of this invention is useful in converting hydrocarbons to less saturated hydrocarbons of the same number of carbon atoms. The major proportion of the hydrocarbon converted will be to less saturated hydrocarbons of the same number of carbon atoms. Particularly the preferred products are butadiene-1,3 and isoprene. Useful feeds may be mixed hydrocarbon streams such as refinery streams, or the olefin containing hydrocarbon mixture obtained as the product from the dehydrogenation of hydrocarbons. In the production of gasoline from higher hydrocarbons by either thermal or catalytic cracking a hydrocarbon stream containing predominantly hydrocarbons of 4 carbon atoms may be produced and may comprise a mixture of butenes together with butadiene, butane, isobutane, isobutylene and other ingredients in minor amounts. These and other refinery by-products which contain normal, ethylenically unsaturated hydrocarbons are useful as starting materials. Although various mixtures of hydrocarbons are useful, the preferred hydrocarbon feed contains at least 50 weight percent of hyrocarbon selected from the group consisting of butene-1, butene-2, n-butane, butadiene-1,3, 2-methylbutene-1, 2-methylbutene-2, 2-methylbutene-3 and mixtures thereof, and more preferably contains at least 70 weight percent of one or more of these hydrocarbons (with both of these percentages being based on the total weight of the organic compositions of the feed to the reactor). Any remainder may be, for example, essentially aliphatic hydrocarbons. This invention is particularly useful to provide a process whereby the major product of the hydrocarbon converted is a dehydrogenated hydrocarbon product having the same number of carbon atoms as the hydrocarbon fed.

Oxygen will be present in the reaction zone in an amount within the range of 0.2 to 2.5 mols of oxygen per mol of hydrocarbon to be dehydrogenated. Generally, better results may be obtained if the oxygen concentration is maintained between about 0.25 and about 1.6 mols of oxygen per mol of hydrocarbon to be dehydrogenated, such as between 0.35 and 1.2 mols of oxygen. The oxygen may be fed to the reactor as pure oxygen, as air, as oxygen-enriched air, oxygen mixed with diluents and so forth. Based on the total gaseous mixture entering the reactor, the oxygen ordinarily will be present in an amount from about 0.5 to 25 volume percent of the total gaseous mixture, and more usually will be present in an amount from about 1 to 15 volume percent of the total. The total amount of oxygen utilized may be introduced into the gaseous mixture entering the catalytic zone or sometimes it has been found desirable to add the oxygen in increments, such as to different sections of the reactor. The above described proportions of oxygen employed are based on the total amount of oxygen used. The oxygen may be added directly to the reactor or it may be premixed, for example, with a diluent or steam.

The temperature for the dehydrogenation reaction will be greater than 250° C., such as greater than about 300° C. or 375° C., and the maximum temperature in the reactor may be about 650° C. or 750° C. or perhaps higher under certain circumstances. However, excellent results are obtained within the range of or about 300° C. to 575° C. such as from or about 325° C. to or about 525° C. The temperatures are measured at the maximum temperature in the reactor. An advantage of this invention is that lower temperatures of dehydrogenation may be utilized than are possible in conventional

dehydrogenation processes. Another advantage is that large quantities of heat do not have to be added to the reaction as was previously required.

The dehydrogenation reaction may be carried out at atmospheric pressure, superatmonpheric pressure or at sub-atmospheric pressure. The total pressure of the system will normally be about or in excess of atmospheric pressure, although sub-atmospheric pressure may also desirably be used. Generally, the total pressure will be between about 4 p.s.i.a. and about 100 or 125 p.s.i.a. Preferably the total pressure will be less than about 75 p.s.i.a. and excellent results are obtained at about atmospheric pressure.

The initial partial pressure of the hydrocarbon to be dehydrogenated will preferably be equivalent to less than one-half atmosphere at a total pressure of one atmosphere. Generally the combined partial pressure of the hydrocarbon to be dehydrogenated together with the oxygen will also be equivalent to less than one-half atmosphere at a total pressure of one atmosphere. Preferably, the initial partial pressure of the hydrocarbon to be dehydrogenated will be equivalent to no greater than one-third atmosphere or no greater than one-fifth atmosphere at a total pressure of one atmosphere. Also, preferably, the initial partial pressure of the combined hydrocarbon to be dehydrogenated plus the oxygen will be equivalent to no greater than one-third or no greater than one-fifth atmosphere at a total pressure of one atmosphere. Reference to the initial partial pressure of the hydrocarbon to be dehydrogenated means the partial pressure of the hydrocarbon as it first contacts the catalytic particles. An equivalent partial pressure at a total pressure of one atmosphere means that one atmosphere total pressure is a reference point and does not imply that the total pressure of the reaction must be operated at atmospheric pressure. For example, in a mixture of one mol of butene, three mols of steam, and one mol of oxygen under a total pressure of one atmosphere, the butene would have an absolute pressure of one-fifth of the total pressure, or roughly six inches of mercury absolute pressure. Equivalent to this six inches of mercury butene absolute pressure at atmospheric pressure would be butene mixed with oxygen under a vacuum such that the partial pressure of the butene is 6 inches of mercury absolute. The combination of a diluent such as nitrogen, together with the use of a vacuum may be utilized to achieve the desired partial pressure of the hydrocarbon. For the purpose of this invention, also equivalent to the six inches of mercury butene absolute pressure at atmospheric pressure would be the same mixture of one mol of butene, three mols of steam and one mol of oxygen under a total pressure greater than atmospheric, for example, a total pressure of 20 p.s.i.a. Thus, when the total pressure in the reaction zone is greater than one atmosphere, the absolute values for the pressure of the hydrocarbon to be dehydrogenated will be increased in direct proportion to the increase in total pressure above one atmosphere.

The partial pressures described above may be maintained by the use of diluents such as nitrogen, helium or other gases. Conveniently, the oxygen may be added as air with the nitrogen acting as a diluent for the system. Mixtures of diluents may be employed. Volatile compounds which are not dehydrogenated or which are dehydrogenated only to a limited extent may be present as diluents.

Preferably the reaction mixture contains a quantity of steam, with the range generally being between about 2 and 40 mols of steam per mol of hydrocarbon to be dehydrogenated. Preferably steam will be present in an amount from about 3 to 35 mols per mol of hydrocarbon to be dehydrogenated and excellent results have been obtained within the range of about 5 to about 30 mols of steam per mol of hydrocarbon to be dehydrogenated. The functions of the steam are several-fold, and the steam does not merely act as a diluent. Diluents generally may be used in the same quantities as specified for the steam. Excellent results are obtained when the gaseous composition fed to the reactor consists essentially of hydrocarbons, inert diluents and oxygen as the sole oxidizing agent.

The gaseous reactants may be conducted through the reaction chamber at a fairly wide range of flow rates. The optimum flow rate will be dependent upon such variables as the temperature of reaction, pressure, particle size, and whether a fluid bed or fixed bed reactor is utilized. Desirable flow rates may be established by one skilled in the art. Generally, the flow rates will be within the range of about 0.10 to 25 liquid volumes of the hydrocarbon to be dehydrogenated per volume of reactor containing catalyst per hour (referred to as LHSV), wherein the volumes of hydrocarbon are calculated at standard conditions of 25° C. and 760 mm. of mercury. Usually, the LHSV will be between 0.15 and about 5 or 10. For calculation, the volume of reactor containing catalyst is that volume of reactor space excluding the volume displaced by the catalyst. For example, if a reactor has a particular volume of cubic feet of void space, when that void space is filled with catalyst particles, the original void space is the volume of reactor containing catalyst for the purpose of calculating the flow rate. The gaseous hourly space velocity (GHSV) is the volume of the hydrocarbon to be dehydrogenated in the form of vapor calculated under standard conditions of 25° C. and 760 mm. of mercury per volume of reactor space containing catalyst per hour. Generally, the GHSV will be between about 25 and 6400, and excellent results have been between about 38 and 3800. Suitable contact times are, for example, from about 0.001 or higher to about 5 or 10 seconds, with particularly good results being obtained between 0.01 and 3 seconds. The contact time is the calculated dwell time of the reaction mixture in the reaction zone, assuming the mols of product mixture are equivalent to the mols of feed mixture. For the purpose of calculation of residence times, the reaction zone is the portion of the reactor containing catalyst.

The catalytic surface described is the surface which is exposed in the dehydrogenation zone to the reactor, that is, if a catalyst carrier is used, the composition described as a catalyst refers to the composition of the surface and not to the total composition of the surface coating plus carrier. Catalyst binding agents or fillers may be used, but these will not ordinarily exceed about 50 percent or 60 percent by weight of the catalytic surface. These binding agents and fillers will preferably be essentially inert. The quantity of catalyst utilized will be dependent upon such variables as the temperature of reaction, the concentration of oxygen, the age of the catalyst, and the flow rates of the reactants. The catalyst will by definition be present in a catalystic amount and generally the mixed ferrite together with any atoms not combined as the defined mixed ferrite will be the main active constituents. The amount of catalyst will ordinarily be present in an amount greater than 10 square feet of catalyst surface per cubic foot of reaction zone containing catalyst. Of course, the amount of catalyst may be much greater, particularly when irregular surface catalysts are used. When the catalyst is in the form of particles, either supported or unsupported, the amount of catalyst surface may be expressed in terms of the surface area per unit weight of any particular volume of catalyst particles. The ratio of catalytic surface to weight will be dependent upon various factors, including the particle size, particle size distribution, apparent bulk density of the particles, amount of active coated on the carrier, density of the carrier, and so forth. Typical values for the surface to weight ratio are such as about one-half to 200 square meters per gram, although higher and lower values may be used. The catalyst is autoregenerative and the process is continuous.

The dehydrogenation reactor may be of the fixed bed or fluid bed type. Conventional reactors for the produc-

tion of unsaturated hydrocarbons are satisfactory. Excellent results have been obtained by packing the reactor with catalyst particles as the method of introducing the caalytic surface. The catalytic surface may be introduced as such or it may be deposited on a carrier by methods known in the art such as by preparing an aqueous solution or dispersion of a catalytic material and mixing the carrier with the solution or dispersion until the active ingredients are coated on the carrier. If a carrier is utilized, very useful carriers are silicon carbide, pumice and the like. When carriers are used, the amount of catalyst on the carrier will generally be between about 5 to 75 wt. percent of the total weight of the active catalytic material plus carrier. Another method for introducing the required surface is utilized as a reactor a small diameter tube wherein the tube wall is catalytic or is coated with catalytic material. Other methods may be utilized to introduce the catalytic surface such as by the use of rods, wires, mesh, or shreds and the like of catalytic material.

According to this invention, the catalyst is autoregenerative and the process is continuous. Moreover, small amounts of tars and polymers are formed as compared to some prior art processes.

In the following examples will be found specific embodiments of the invention and details employed in the practice of the invention. Percent conversion refers to the mols of hydrocarbon consumed per 100 mols of hydrocarbon fed to the reactor, percent selectivity refers to the mols of product formed per 100 mols of hydrocarbon consumed, and percent yield refers to the mols of product formed per mol of hydrocarbon fed.

Example 1

A catalyst was prepared as follows:

101 g. $Fe(NO_3)_3 \cdot 9H_2O$, 18.2 g. $Ni(NO_3)_2 \cdot 6H_2O$, and 18.6 g. $Zn(NO_3)_2 \cdot 6H_2O$

were each dissolved in 50 ml distilled water. The solutions were mixed and added to 90 g. of Houdry hard alumina pellets (5/32" dia.), under vacuum, in about 30 minutes. The impregnated pellets and the excess nitrate solution were transferred to a porcelain dish where the compounds were decomposed and reacted over an open flame. When evolution of the gas ceased, the pellets were allowed to cool to room temperature.

55 g. of the coated pellets were used to prepare a 4" high catalyst bed in a 36" long 1" I.D. Vycor glass tube. The catalyst bed, supported by a 1" layer of Vycor Raschig rings, was located within the lower 12" section of the tube. The reactor was heated by a two-unit electric furnace each unit being 12" long and having a separate manually operated powerstat.

Butene-2 and oxygen were introduced into the reactor through an inlet tube located between the steam generator and the reactor head. Steam was generated in an 11" long, 1" O.D., stainless steel tube, and the mixture of butene-2-oxygen-steam was preheated to about 275° C. prior to entering the catalyst bed.

The temperature of the reaction was measured by a Chromel vs. Alumel thermocouple placed in a ¼" O.D. stainless steel thermowell located in the center of the Vycor tube and extending 1" below the catalyst bed.

The reaction products were passed through a cold-water condenser to condense the steam. Samples of the products were withdrawn by a 1.0 ml. syringe through a sample tap sealed with a silicon rubber disc and located at the exit from the cold water condenser. All products were analyzed in a Perkin-Elmer vapor fractometer Model 154D using diethyl malonate as the liquid phase and helium as the carrier.

The liquid space velocity (LHSC) was maintained at 1.0, and the butene-2/oxygen/steam molar ratio was kept at 1.0/0.75/30. At a reactor temperature of 400° C. the conversion was 68 mol percent, the selectivity was 93 mol percent and the yield was 63 mol percent butadiene-1,3.

Example 2

A mixed iron, magnesium and nickel ferrite was prepared as follows: 7.5 g. NiO was slurried in 400 ml. distilled water in a quart size Waring Blendor. To this slurry was added 16.0 g. Mgo followed by 89 g. ferric oxide hydrate and slurrying was continued for 10 minutes at a speed obtained at 40 volts on Powerstat Type 3PN116. The slurry was suction filtered and the residue was dried 16 hours at 105° C. in an oven. The dried material was crushed and heated in a furnace kept at 900±10° C. for 1 hour. Material passing sieve No. 4 (U.S. Standard Series) but retained on sieve No. 10 was used for catalyst evaluation.

22 g. of the catalyst was used for a 4" high catalyst bed, and the catalytic performance was evaluated as in Example 1 except that the butene-2/oxygen/steam molar ratio was kept at 1/0.6/30.

The mol percent conversion was 72, the selectivity was 93, and the yield of butadiene was 67.

Example 3

A catalyst was prepared from a combination of zinc ferrite and magnesium ferrite. The zinc ferrite was Columbian Carbon Company, EG–2, having about 32.6 to 32.8 weight percent zinc, calculated as zinc oxide. The zinc ferrite had X-ray diffraction peaks at *d* spacings within 4.81 to 4.88, 2.96 to 3.00, 2.52 to 2.56, 2.41 to 2.45, 2.09 to 2.13, 1.70 to 1.74, 1.60 to 1.64 and 1.47 to 1.51, with the most intense peak falling within about 2.96 to 3.00. The magnesium ferrite used was Columbian Carbon Company EG–1, having about 18.7 to 19.2 weight percent magnesium calculated as MgO. The magnesium ferrite had X-ray diffraction peaks at *d* spacings within 4.81 to 4.85, 2.93 to 2.98, 2.50 to 2.54, 2.07 to 2.11, 1.69 to 1.72, 1.59 to 1.62 and 1.46 to 1.49, with the most intense peak falling within or about 2.50 to 2.54. The X-ray determinations on both the zinc ferrite and the magnesium ferrite were run with a cobalt tube.

The mixed catalyst was prepared as follows: 50 grams of 4 to 8 mesh AMC alumina catalyst support was added to a slurry consisting of 13 grams of the zinc ferrite, 13 grams of the magnesium ferrite, and 50 cc. of distilled water. The mixture was then evaporated to dryness. A catalyst containing 22 percent by weight of the combination of zinc ferrite and magnesium ferrite was obtained. Butene-2 was dehydrogenated by passing a reaction mixture of 0.5 mol of oxygen and 30 mols of steam per mol of butene-2 over the catalyst. The catalyst was present as a 50 cc. catalyst bed in a 30 mm. O.D. Vycor reactor. The flow rate was 0.5 liquid hourly space velocity (LHSV). At a reactor temperature of 413° C., butene was converted to butadiene at a selectivity of 97 mol percent of the butene converted.

Example 4

A mixed ferrite catalyst was prepared containing iron, magnesium and cobalt. The iron used was yellow Fe_2O_3 and the magnesium starting material was Baker and Adamson Powder, reagent grade MgO. A mixed ferrite catalyst was prepared from 50 parts of the Fe_2O_3, 40 parts of the MgO and 10 parts of ZnO. The dioxides were stirred in distilled water in a Waring Blender, filtered and dried at 105° C. for 16 hours. The mixtures were reacted to form the ferrite in a muffle furnace for 1 hour at 950° C. The reacted product was crushed, and material passing No. 4 but retained on No. 10 screen (U.S. Standard Series) was used for catalyst evaluation. Butene-2 was dehydrogenated to butadiene-1,3 by passing a mixture of 0.75 mol of oxygen and 30 mols of steam per mol of butene-2 through the catalyst. At a reactor temperature of 450° C. the selectivity to butadiene was 95 mol percent. At a reactor temperature of 500° C. selectivity to butadiene was 93 mol percent.

Example 5

The procedure of Example 4 was repeated with the exception that ZnO was substituted for the MgO. A high selectivity of butadiene-1,3 was obtained at 425° C. Similar results were obtained when nickelous oxide was substituted for the magnesium oxide of Example 4.

The catalysts are not limited to those illustrated in the examples. Other methods of preparation and other compositions may be employed. The atoms of iron will preferably be present in an amount from about 20 to 95 weight percent, based on the total weight of the atoms of iron and the metals selected from the group consisting of magnesium, zinc, nickel and cobalt in the catalyst surface, but generally will be between 40 and 90 and a preferred ratio is from 50 to 85 weight percent iron. Particularly preferred are catalysts having a weight percent of iron from or about 55 to 80 percent by weight iron based on the total weight of atoms of iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt. Valuable catalysts were produced comprising as the main active constituents iron and at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt and oxygen in the catalytic surface exposed to the reaction gases. High yields of product are obtained with catalysts having iron as the predominant metal in the catalytic surface. The catalysts will contain at least three weight percent each of at least two metals of the group magnesium, zinc, nickel and cobalt, based on the total weight of these metals and iron. Generally there will be at least 10 weight percent of one or more of the metals magnesium, zinc and/or nickel based on the weight of the atoms of iron. Preferably at least about 50 and generally at least about 65 weight percent of the atoms of the described metals will be present as a ferrite. Included in the definition of ferrites are the active intermediate oxides and the reduced ferrites. The preferred mixed ferrite has a cubic face-centered crystal structure. Ordinarily the mixed ferrite will not be present in the most highly oriented crystalline structure, because it has been found that superior results may be obtained with catalysts wherein the mixed ferrite is relatively disordered, that is where there are defects in the crystalline structure. The desired catalyst may be obtained by conducting the reaction to form the active catalyst at relatively low temperatures, that is, at temperatures lower than some of the very high temperatures used for the formation of mixed ferrites prepared for semi-conductor applications. Generally the temperature of reaction for the formation of the catalyst comprising mixed ferrites will be less than 1300° C. and preferably less than 1150° C. Of course, under certain conditions momentary temperatures above these temperatures might also be permissible. The reaction time at the elevated temperature in the formation of the catalyst may preferably be from about five minutes to four hours at elevated temperatures high enough to cause formation of the ferrite but less than about 1150° C. Any iron not present in the form of ferrite will desirably be present predominantly as gamma iron oxide. The alpha iron oxide will preferably be present in an amount of no greater than 40 weight percent of the catalytic surface, such as no greater than about 30 weight percent.

Although excellent results are obtained with the catalysts of this invention with a feed containing only the hydrocarbon, oxygen and perhaps steam or a diluent, it is one of the advantages of this invention that halogen may also be added to the reaction gases to give excellent results. The addition of halogen to the feed is particularly effective when the hydrocarbon to be dehydrogenated is saturated.

The source of halogen fed to the dehydrogenation zone may be either elemental halogen or any compound of halogen which would liberate halogen under the conditions of reaction. Suitable sources of halogen are such as hydrogen iodide, hydrogen bromide and hydrogen chloride; aliphatic halides such as ethyl iodide, methyl bromide, 1,2-dibromoethane, ethyl bromide, amyl bromide and allyl bromide; cycloaliphatic halides such as cyclohexyl bromide; aromatic halides such as benzyl bromide; halohydrins such as ethylene bromohydrin; halogen substituted aliphatic acids such as bromoacetic acid; ammonium iodide; ammonium bromide; ammonium chloride; organic amine halide salts such as methyl amine hydrobromide; and the like. Mixtures of various sources of halogen may be used. The preferred sources of halogen are iodine, bromine and chlorine and compounds thereof such as hydrogen bromide, hydrogen iodide, hydrogen chloride, ammonium bromide, ammonium iodide, ammonium chloride, alkyl halides of one to six carbon atoms and mixtures thereof, with the iodine and bromine compounds being particularly preferred, and the best results having been obtained with ammonium iodide, bromide or chloride. When terms such as halogen liberating materials or halogen materials are used in the specification and claims, this includes any source of halogen such as elemental halogens, hydrogen halides or ammonium halides. The amount of halogen, calculated as elemental halogen, may be as little as about 0.0001 or less mol of halogen per mol of the hydrocarbon compound to be dehydrogenated to as high as 0.2 or 0.5 or higher. The preferred range is from about 0.001 to 0.09 mol of halogen per mol of the hydrocarbon to be dehydrogenated to as high as 0.2 or 0.5 or higher. The preferred range is from about 0.001 to 0.09 mol of halogen per mol of the hydrocarbon to be dehydrogenated.

Improved catalysts may be obtained by reducing the catalyst of the invention. The reduction of the catalyst may be accomplished prior to the initial dehydrogenation, or the catalyst may be reduced after the catalyst has been used. It has been found that a used catalyst may be regenerated by reduction and, thus, even longer catalyst life obtained. The reduction may be accomplished with any gas which is capable of reducing iron oxide to a lower valence such as hydrogen, carbon monoxide or hydrocarbons. Generally the flow of oxygen will be stopped during the reduction step. In these reduced ferfites the catalysts may contain a lower amount of oxygen than the original ferrite. The temperature of reduction may be varied but the process is most economical at temperatures of at least about 200° C., with the upper limit being about 750° C. or 900° C. or even higher under certain conditions.

We claim:

1. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite of iron with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

2. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite of iron with magnesium and zinc to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

3. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the

dehydrogenation comprising a mixed ferrite of iron with magnesium and nickel to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

4. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with magnesium and cobalt to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

5. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with zinc and cobalt to produce a dehydragenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

6. A process for the dehydrogenation of hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with zinc and nickel to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

7. A process for the dehydrogenation of aliphatic hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 325° C. a mixture of the said hydrocarbon to be dehydrogenated, from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon and from 2 to 40 mols of steam per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon.

8. A process for the dehydrogenation of a hydrocarbon selected from the group consisting of n-butene, n-butane and mixtures thereof which comprises contacting in the vapor phase at a temperature of from 375° C. to 525° C. and at a pressure of 4 p.s.i.a. to 125 p.s.i.a. a mixture of the said hydrocarbon to be dehydrogenated and from about 0.25 to about 1.6 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon, the initial partial pressure of the said hydrocarbon being equivalent to less than one-fifth atmosphere at a total pressure of one atmosphere.

9. A process for the dehydrogenation of butene to butadiene-1,3 which comprises contacting in the vapor phase at a temperature of from 375° C. to 575° C. and at a total pressure of less than 75 p.s.i.a. a mixture of the said butene, from 8 to about 35 mols of steam and from 0.35 to 1.2 mols of oxygen per mol of the said butene with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt wherein the atoms of iron are present in an amount of 40 to 90 weight percent based on the total weight of the atoms of said metals selected from the group consisting of magnesium, zinc, nickel and cobalt to produce butadiene-1,3.

10. A process for the dehydrogenation of aliphatic hydrocarbons having at least four carbon atoms which comprises contacting in the vapor phase at a temperature of greater than 250° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 2.5 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon, the initial partial pressure of the said hydrocarbon being equivalent to less than one-half atmosphere at a total pressure of one atmosphere, said catalyst having been reduced with a reducing gas.

11. A process for the preparation of butadiene-1,3 which comprises contacting in the vapor phase at a temperature of 375° C. to 525° C. and at a total pressure of about 4 p.s.i.a. to 100 p.s.i.a. a mixture of n-butene and from 0.35 to 1.2 mols of oxygen and from 8 to 35 mols of steam per mol of the said n-butene with an autoregenerative catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt wherein the atoms of iron are present in an amount of 40 to 90 weight percent based on the total weight of the atoms of iron and said metals selected from the group consisting of magnesium, zinc, nickel and cobalt with any iron not present in the form of ferrite being predominantly present as gamma iron oxide to produce butadiene-1,3.

12. A process for the preparation of butadiene-1,3 which comprises contacting in the vapor phase at a temperature of 375° C. to 525° C. and at a total pressure of about 4 p.s.i.a. to 100 p.s.i.a. a mixture of n-butene and from 0.35 to 1.2 mols of oxygen and from 8 to 35 mols of steam per mol of the said n-butene with an autoregenerative catalyst for the dehydrogenation comprising a mixed ferrite having iron combined with at least two metals selected from the group consisting of magnesium, zinc, nickel and cobalt wherein the atoms of iron are present in an amount of 55 to 80 weight percent based on the total weight of the atoms of iron and said metals selected from the group consisting of magnesium, zinc, nickel and cobalt with any iron not present in the form of ferrite being predominantly present as gamma iron oxide to produce butadiene-1,3, and after the yield of butadiene-1,3 has fallen off after continued use regenerating the catalyst by reducing the catalyst with hydrogen.

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