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3,284,536

DEHYDROGENATION WITH MAGNESIUM
FERRITE

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No Drawing. Filed Jan. 2, 1964, Ser. No. 335,352
20 Claims. (Cl. 260—683.3)

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

We have now discovered that greatly improved yields and high selectivities of unsaturated hydrocarbons are obtained by dehydrogenating under certain specified conditions hydrocarbons in the vapor phase at elevated temperatures in the presence of oxygen and a catalyst containing magnesium ferrite.

Magnesium ferrite is a known commercial product which has uses such as in the formulation of coatings suitable for high temperature applications. One method for the production of magnesium ferrite is by the addition of dry magnesium carbonate to an aqueous slurry of yellow iron oxide hydrate with the reaction mixture containing a small amount of the hydrate of magnesium chloride as a catalyst. This reaction composition is uniformly mixed and then heated at a relatively low temperature above 100° C. for a period of several hours. The composition is then reacted for about 30 minutes at a temperature of 925° C. The reaction product is then ground and pelleted into catalyst particles.

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 cycloaliphatic hydrocarbons. Examples of preferred feed materials are butene-1, cis-butene-2, trans-butene-2, 2-methylbutene-1, 2-methylbutene-2, 2-methylbutene-3, n-butane, butadiene-1,3, methyl butane, 2-methylpentene-1, 2-methylpentene-2, cyclohexene 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 butadiene-1,3 is used as a feed-stock. 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

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starting materials. Although various mixtures of hydrocarbons are useful, the preferred hydrocarbon feed contains at least 50 weight percent of a hydrocarbon 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 composition 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, superatmospheric 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 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

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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

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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 catalytic amount and generally the magnesium ferrite together with any magnesium and iron atoms not combined as magnesium 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 catalyst 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 dehydrogenation reactor may be of the fixed bed or fluid bed type. Conventional reactors for the production of unsaturated hydrocarbons are satisfactory. Excellent results have been obtained by packing the reactor with catalyst particles as the method of introducing the catalytic 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 weight percent of the total weight of the active catalytic material plus carrier. Another method for introducing the required surface is to utilize 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

200 gr. of Columbian Carbon Company magnesium ferrite EG-1 was slurred into a thick paste using 320 cc. of distilled water. The paste was dried in an oven at 140° C. for 1½ hours, and then broken into small granules. A 6 to 8 mesh fraction of this broken catalyst was used as the catalyst for this run. The reactor used was a 1-inch diameter I.P.S. 316 stainless steel reactor, which was 24 inches long. Into the bottom of the reactor was loaded 100 cc. of the 6 to 8 mesh magnesium ferrite catalyst particles, and on top of this catalyst was added 6 mm. x 6 mm. Vycor¹ Raschig rings to fill the remainder of the reactor and to act as a preheat zone. Butene-2 was dehydrogenated to butadiene by feeding a mixture of butene-2, steam and air over the magnesium ferrite catalyst at a flow rate of 1.0 liquid hourly space velocity. Air was present in the reaction mixture in an amount equivalent to 0.75 mol of oxygen per mol of butene. Steam was present in the reaction mixture in an amount of 30 mols of steam per mol of butene. The temperature in the reactor at the top of the catalyst bed was 315° C. and the maximum temperature in the reactor was 482° C. Under these conditions 69 mol percent of the butene-2 was converted with the selectivity to butadiene being 94 mol percent of the butene-2 converted for a yield of butadiene of 65 mol percent.

An X-ray diffraction pattern was made of the magnesium ferrite catalyst prior to use in Example 1. The powder diffraction patterns were made with a Norelco constant potential diffraction unit type No. 12215/0 equipped with a wide range goniometer type No. 42273/0, cobalt tube type No. 32119, proportional counter type No. 52250/1; all coupled to the Norelco circuit panel type No. 12206/53. The cobalt K alpha radiation was supplied by operating the tube at a constant potential of 30 kilovolts and a current of 10 milliamperes. An iron filter was used to remove K beta radiation. The detector voltage was 1660 volts and the pulse height analyzer was set to accept pulses with amplitudes between 10 and 20 volts only. Slits used were divergence 1°, receiving .006 inch and scatter 1°. Strip chart recordings for identification were made with a scanning speed of ¼" per minute, chart speed of ½ inch per minute, time constant of 4 seconds and a full scale at 10³ counts per second. Under these conditions, the following X-ray diffraction was obtained:

d:	I/I ₁
4.82 -----	9.
3.67 -----	Very weak.
2.96 -----	32.
2.69 -----	About 7.
2.53 -----	100.
2.21 -----	Very weak.
2.09 -----	28.
1.84 -----	Very weak.
1.71 -----	10.
1.69 -----	Very weak.
1.61 -----	30.
1.48 -----	60.

¹ Vycor is the trade name of Corning Glass Works, Corning, N.Y. and is composed of approximately 96 percent silica with the remainder being essentially B₂O₃.

Example 2

236 g. of Fe(NH₄)₂(SO₄)₂·6H₂O and 86 g.

Mg(NO₃)₂·6H₂O

were dissolved in 1000 ml. of distilled water.

142 g. of (NH₄)₂C₂O₄·H₂O were dissolved in 2000 ml. of distilled water.

The two solutions were mixed at 35° C. while stirring. The resulting yellow precipitate of ferrous and magnesium oxalate was filtered, washed, and dried 16 hours at 100° C. The dried precipitate was reacted by heating for 4 hours at 950° C. and thereafter ground to sub 325 mesh.

A supported catalyst was then made by coating this material on 6 to 8 mesh inert support (Carborundum Company's polysurface fused alumina). The catalyst had 30 weight percent actives. 20 cc. of this catalyst was loaded in a 1 inch O.D. stainless steel tube, 16 inches long. The catalyst bed was supported by 20 cc. of Alcoa ½" T-162 fused alumina spheres, and the remainder of the reactor tube was also filled with these spheres.

Butene-2 was dehydrogenated by feeding a mixture of butene-2 and air over the catalyst comprising magnesium ferrite at a flow rate of 1.0 liquid hourly space velocity. Air was present in the reaction mixture in an amount equivalent to 0.60 mol of oxygen per mol of butene. Steam was present in the reaction mixture in an amount of 30 mols of steam per mol of butene. The reaction temperature was approximately 450° C. Under these conditions 61 mol percent of butene-2 was converted with the selectivity to butadiene being 92 mol percent of the butene-2 converted for a yield of butadiene of 56 percent.

Example 3

89 gm. yellow iron oxide (Mapico yellow, light lemon 100, Columbian Carbon Company) and 42 gm. magnesium carbonate (basic BA Reagent grade) were mixed dry in a 600 ml. tall form jar with 3-blade stirrer for 2 hours.

1.4 gm. of magnesium chloride was dissolved in 125 ml. of distilled water in an evaporating dish. The iron oxide-magnesium carbonate mixture was gradually mixed into this solution by hand with a spatula in about 30 minutes. The product was a heavy paste which was dried in an electric oven without air circulation at 105° C. for 16 hours. The dried material was reacted in atmospheric conditions at 900° ± 10° C. for 30 minutes and then cut into pieces. For catalyst evaluation material passing No. 4 but retained on No. 10 screen (U.S. Standard Series) was used.

The reaction product was coated on ¼" x ¼" Vycor Raschig rings. Butene-2 was dehydrogenated at atmospheric pressure in a Vycor glass reactor (36" x 1" O.D.) having a 4" high catalyst bed supported on a 1" high layer of ¼" O.D. Vycor Raschig rings. The butene-2, oxygen, and steam were introduced into an adapter located on top of the glass reactor, and the effluent gases were passed through a cold-water condenser to remove most of the steam.

Samples of the effluent gases were withdrawn with a syringe at the exit from the condenser. They were analyzed in a Perkin-Elmer, model 154, vapor chromatograph.

The reaction temperature was measured with a Chromel vs. Alumel thermocouple in a centrally located stainless steel thermowell ¼" O.D. Heat was supplied by a three-section 1400 watt furnace, each section having separate powershaft, and the heat input was controlled manually.

The butene-2 used was C.P. grade, 99.0 mol percent min.; the oxygen was commercial grade, purity 99.5+, and steam was generated in a stainless steel tube (12" x 1" O.D.) using distilled water made in the laboratory.

A mixture of butene-2, oxygen and steam was fed to the reactor in an amount of 0.75 mol of oxygen per mol of butene-2 and 30 mols of steam per mol of butene-2. The butene-2 was fed at a rate of 1.0 LHSV (with calculation being based on the volume of the reactor containing catalyst, that is the 4 inch catalyst section). Under these conditions 68 mol percent of the butene-2 was converted at a selectivity of 92 mol percent to butadiene-1,3 for a yield of 63 mol percent butadiene-1,3 per pass.

Example 4

58.9 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 25.6 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 350 ml. distilled H_2O .

42. 7 g. of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was dissolved in 750 cc. distilled H_2O . The two solutions were mixed at 25° C. while stirring. The resultant yellow precipitate was filtered, washed and dried at 130° C. for 2 hours.

The dried precipitate was made into $\frac{5}{32}$ " x $\frac{5}{32}$ " cylindrical tablets. 20 cc. of these tablets were loaded in a reactor of 1 inch O.D. stainless steel tubing 16 inches long. The catalyst bed was supported by 20 cc. of Alcoa $\frac{1}{8}$ " T-162 fused alumina spheres, and the remainder of the reactor was filled with the same material.

The catalyst bed was heated to 600° C. in air for 2 hours and then cooled to 450° C. before starting the reactant flows in order to form the ferrite in situ. The catalyst was pretreated by reduction with undiluted hydrogen for 45 minutes at 450° C. prior to starting the dehydrogenation reaction. Butene-2 was dehydrogenated to butadiene by feeding a mixture of butene-2, steam and air over the magnesium ferrite catalyst at a flow rate of 1.0 liquid hourly space velocity. Air was present in the reaction mixture in an amount equivalent to 0.60 mol of oxygen per mol of butene. Steam was present in the reaction mixture in an amount of 30 mols of steam per mol of butene. The reaction temperature was approximately 450° C. Under these conditions 61 mol percent of the butene-2 was converted with the selectivity to butadiene being 92 mol percent of the butene-2 converted for a yield of butadiene of 56 percent.

Example 5

A catalyst was prepared from 45.5 grams of Baker Reagent magnesium carbonate (equivalent to 43 percent MgO), 91.5 grams of alpha $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (equivalent to 87 percent Fe_2O_3) and 10 cc. of a one mol solution of MgCl_2 in water. The components were first thoroughly mixed and then heated at 940° C. for 40 minutes to cause the formation of the magnesium ferrite. A paste was made of the magnesium ferrite with water and the paste was then dried and broken into lumps. The catalyst tested was in the form of 4 to 8 mesh pellets. The reactor described in Example 1 was used for the example for the evaluation. Butene-2 was dehydrogenated to butadiene-1,3 at a flow rate of 1.0 LHSV utilizing 30 mols of steam and 0.6 mol of oxygen per mol of butene fed. At a reactor temperature of 425° C. the yield of butadiene-1,3 was 63.

Example 6

A catalyst was prepared from 55 grams of Baker Reagent magnesium carbonate (equivalent to 43 percent MgO), 91.5 grams of alpha $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (equivalent to 87 percent Fe_2O_3) and 10 cc. of a one mol MgCl_2 solution in water. The components were first thoroughly mixed and then heated at 940° C. for 40 minutes to cause the formation of the magnesium ferrite. A paste was made of the magnesium ferrite with water and the paste was then dried and broken into lumps. The catalyst tested was in the form of 4 to 8 mesh pellets. The reactor described in Example 1 was used for the example for the evaluation. Butene-2 was dehydrogenated to butadiene-1,3 at a flow rate of 1.0 LHSV, utilizing 30 mols of steam and 0.6 mol of oxygen per mol of butene fed. At a reactor temperature of 450° C., the yield of butadiene-1,3 was 56.1.

Example 7

A catalyst was prepared from 41 grams of Baker Reagent magnesium carbonate (equivalent to 43 percent MgO), 91.5 grams of alpha $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (equivalent to 87 percent Fe_2O_3) and 10 cc. of a one mol solution of MgCl_2 in water. The components were first thoroughly mixed and then heated at 940° C. for 40 minutes to cause the formation of the magnesium ferrite. A paste was made of the magnesium ferrite with water and the paste was then dried and broken into lumps. The catalyst tested was in the form of 4 to 8 mesh pellets. The reactor described in Example 1 was used for the example for the evaluation. Butene-2 was dehydrogenated to butadiene-1,3 at a flow rate of 1.0 LHSV utilizing 30 mols of steam and 0.6 mol of oxygen per mol of butene fed. At a reactor temperature of 475° C., the yield of butadiene-1,3 was 59.

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 be present in an amount from or about 75 to 97 weight percent, based on the total weight of the atoms of iron and magnesium in the catalyst surface, but a preferred ratio is from 80 to 96 weight percent iron. Particularly preferred are catalysts having a weight percent of iron from about 83 to 95 percent by weight iron based on the total weight of atoms of iron and magnesium. Valuable catalysts were produced comprising as the main active constituents iron, magnesium 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. Suitable catalysts may contain less than 5 weight percent of sodium or potassium. Preferably at least about 65 and generally at least about 80 weight percent of the atoms of magnesium will be present combined as magnesium ferrite. The preferred magnesium ferrite is that having a face-centered cubic structure. Included in the definition of ferrites are the so-called active intermediate oxides. The magnesium 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 magnesium ferrite is relatively disordered, that is where there are crystal defects. 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 temperature used for the formation of magnesium ferrites prepared for semi-conductor applications. Generally the temperature of reaction for the formation of the catalyst comprising magnesium ferrite 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 be preferably be from about five minutes to four hours at elevated temperatures high enough to cause formation of magnesium ferrite but less than about 1150° C. Any iron not present in the form of magnesium 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.

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. 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.

The preferred catalyst surface will generally have X-ray diffraction peaks at *d* spacings within or about 4.80 to 4.86, 2.93 to 2.99, 2.49 to 2.55, 2.06 to 2.12, 1.68 to 1.73, 1.58 to 1.63, and 1.45 to 1.50, with the most intense peak being between 2.49 to 2.55. Particularly preferred catalysts will have *d* spacings within or about 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. These X-ray determinations are suitably run with a cobalt tube.

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 from greater than 250° C. to about 750° 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 magnesium ferrite 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 from greater than 250° C. to about 750° 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 magnesium ferrite wherein the atoms of iron are present in an amount of about 75 to 97 weight percent based on the total weight of the atoms of iron and magnesium, 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 from 4 to 5 carbon atoms which comprises contacting in the vapor phase at a temperature of from greater than 250° C. to about 750° 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 magnesium ferrite wherein the atoms of iron are present in an amount of about 80 to 96 weight percent based on the total weight of the atoms of iron and magnesium, 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.

4. 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 greater than about 325° C. to about 750° C. 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 magnesium ferrite 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.

5. 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 from about 325° C. to 525° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.2 to 1.6 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising magnesium ferrite wherein the atoms of iron are present in an amount of 80 to 96 weight percent based on the total weight of the atoms of iron and magnesium, to produce a dehydro-

genated 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.

6. 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 from greater than 325° C. to about 750° 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 magnesium ferrite 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 from greater than 325° C. to about 750° 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 an autoregenerative catalyst for the dehydrogenation comprising magnesium ferrite wherein the atoms of iron are present in an amount of about 83 to 95 weight percent based on the total weight of the atoms of iron and magnesium, 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.

8. A process for the dehydrogenation of hydrocarbons having from 4 to 5 carbon atoms which comprises contacting in the vapor phase at a temperature of from at least about 375° C. to about 750° C. a mixture of the said hydrocarbon to be dehydrogenated and from 0.35 to 1.2 mols of oxygen per mol of the said hydrocarbon with a catalyst for the dehydrogenation comprising magnesium ferrite wherein the atoms of iron are present in an amount of about 83 to 95 weight percent based on the total weight of the atoms of iron and magnesium, 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-third atmosphere at a total pressure of one atmosphere.

9. 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 about 375° C. to 575° C. and at a pressure of about 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 magnesium ferrite 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.

10. 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 magnesium ferrite wherein the atoms of iron are present in an amount of 80 to 96 weight percent based on the total weight of the atoms of iron and magnesium, to produce butadiene-1,3.

11. 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 greater than about

325° C. to about 750° C. 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 magnesium ferrite to produce a dehydrogenated hydrocarbon product having the same number of carbon atoms as the said hydrocarbon, the said catalytic surface having X-ray diffraction peaks at *d* spacings within the ranges of about 4.80 to 4.86, 2.93 to 2.99, 2.49 to 2.55, 2.06 to 2.12, 1.68 to 1.73, 1.58 to 1.63 and 1.45 to 1.50, with the most intense peak being between about 2.49 to 2.55.

12. A process for the dehydrogenation of butene to butadiene-1,3 which comprises feeding to a reactor in the vapor phase at a temperature of from at least 250° C. to about 750° C. a gaseous mixture of the said butene and from 0.35 to 1.2 mols of oxygen per mol of the said butene with an autoregenerative catalyst for the dehydrogenation comprising magnesium ferrite wherein the atoms of iron are present in an amount of about 2.0 atoms of iron per atom of magnesium based on the total weight of the atoms of iron and magnesium, to produce butadiene-1,3, the initial partial pressure of the said butene being equivalent to less than one-fifth atmosphere at a total pressure of one atmosphere.

13. 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 from greater than 250° C. to about 750° 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 magnesium ferrite 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.

14. A process for the preparation of butadiene-1,3 which comprises contacting in the vapor phase at a temperature of 375° C. to 575° 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 mag-

nesium ferrite wherein the atoms of iron are present in an amount of 84 to 88 weight percent based on the total weight of the atoms of iron and magnesium with any iron not present in the form of magnesium ferrite being predominantly present as gamma iron oxide.

15. A process for the preparation of butadiene-1,3 which comprises contacting in the vapor phase at a temperature of 375° C. to 575° C. and at a total pressure of about 4 p.s.i.a. to 75 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 magnesium ferrite wherein the atoms of iron are present in an amount of from 80 to 96 weight percent based on the total weight of the atoms of iron and magnesium with any iron not present in the form of magnesium 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.

16. The method of claim 1 wherein at least about 80 weight percent of the atoms of magnesium are present as magnesium ferrite.

17. The method of claim 1 wherein the said catalyst contains less than 30 weight percent of alpha iron oxide.

18. The method of claim 1 wherein the said catalyst is reduced prior to dehydrogenation by contacting the catalyst with hydrogen.

19. The method of claim 1 wherein the said magnesium ferrite is formed at a temperature of less than 1150° C.

20. The method of claim 1 wherein iron is the predominant metal in the catalytic surface and the catalyst contains less than 5 weight percent of a member selected from the group consisting of sodium or potassium.

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