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DEHYDROGENATION PROCESS

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The present invention relates to the catalytic dehydrogenation of hydrocarbon vapors at elevated temperatures in the presence of ferrous metals. A particular aspect of the invention relates to the catalytic dehydrogenation of hydrocarbon vapors at elevated temperatures, i. e. from about 750° F. to 1300° F., with dehydrogenation catalysts such, in particular, as those comprising an oxide of chromium, molybdenum, tungsten, vanadium, or manganese which are normally substantially free of iron and which are subject to poisoning by iron.

As is well known, one of the most practical and common methods for executing catalytic dehydrogenation reactions in the vapor phase is to provide a porous bed of catalyst in a suitable reaction tube, converter or catalyst case, and to pass the vapors of the reactant therethrough under appropriate conditions of temperature, pressure, etc. In most cases when treating carbonaceous materials at temperatures in the order of 750° F. to 1300° F., the catalyst gradually loses its activity due to the deposition thereon of carbon and tarry materials. This deactivation of the catalyst is temporary and may be indefinitely counteracted by periodically burning off the deposited materials in situ.

Many of the most effective dehydrogenation catalysts are susceptible to poisoning by iron. These various catalysts, when used for the vapor phase dehydrogenation of organic materials at these elevated temperatures in the presence of iron, steel or ferrous alloys, besides undergoing the above-mentioned temporary deactivation due to accumulation of carbon and tarry deposits, undergo a permanent deactivation due to an accumulation of iron or iron compounds formed by the oxidation or corrosion of the ferrous metal in contact therewith. Even traces of iron derived from various parts of the plant, such as preheating coils, etc., carried with the reactant vapors are often sufficient to cause a serious poisoning of these catalysts. Thus, as a general rule, it is found that the activity of these catalysts is decreased approximately linearly from 80% of their initial activity with an iron content of 0.7% to 40% when the iron content is increased to 1.3%. This deactivation of the catalyst, unlike that due to the deposition of tarry materials, is permanent and cannot be counteracted by any of the known regeneration processes. Since the dehydrogenations are often executed under diminished pressure and since, furthermore, they require the introduction of considerable quantities of heat to the reaction zone, usually through the confining walls, it is usually impractical in these processes to employ apparatus constructed of or lined with non-ferrous materials such as silicon, ceramic materials, and the like, and the use of iron, steel or ferrous alloy equipment is practically unavoidable.

The industry has searched diligently for some practical method whereby the transfer of iron to these catalysts could be avoided, while at the same time utilizing apparatus fabricated from ferrous metals. It has, for example, been proposed to employ apparatus plated with chromium, aluminum, copper, etc. Such apparatus sometimes works well for a short time. It is found, however, that these various linings invariably have minute pin holes or become scratched by the catalyst, and after a short period of operation the under-metal is attacked through these imperfections with the result that the lining becomes pitted or peels, and iron is transferred to the catalyst. The contamination of these catalysts by iron has also been minimized to a considerable extent by the use of certain alloy steels such, in particular, as the more or less corrosion-resistant steels containing chromium, molybdenum, vanadium, titanium, etc. It is found, for example, that whereas iron and plain carbon steels are practically useless, the tendency to contaminate the catalyst with iron is considerably decreased by the incorporation of chromium. However, even chrome steel containing 27% chromium, which is the highest chrome steel that can be fabricated, has not proved entirely satisfactory for the purpose. The reaction vessels fabricated from this material are both expensive and short-lived. After a relatively short period of use, they suddenly begin to contaminate the catalyst with iron and must be discarded. It has also been proposed to employ ferrous metals pretreated with hydrogen sulfide. This pretreatment is sometimes effective in preventing carbon formation in non-catalytic processes and when employing catalysts which are not susceptible to iron poisoning. It does not, however, avoid or decrease iron contamination, and, in fact, increases it.

In our copending application Serial No. 356,036 which matured January 6, 1942 into United States Patent 2,269,029 and in our copending application Serial No. 391,748 (filed May 3, 1941), of which applications the present application is a continuation-in-part, we have described a practical and effective method whereby the contamination of these catalysts with iron, when used in contact with ferrous metals, may be substantially obviated. By the use of the described method various processes may be executed in apparatus constructed of the more common, less expensive steels and ferrous alloys such as the KA2, KA2S, KA2MoT, KA2Cb, KA2Mo and KA2ST steels, while at the same time avoiding all substantial contamination of the catalyst by iron. This is effected by maintaining certain specific concentrations of certain sulfur compounds in the feed to the reaction zone.

It is generally known that when treating carbonaceous materials at these elevated tempera-

tures with these catalysts in the presence of ferrous metals in the absence of any substantial amount of sulfur, corrosion of the ferrous metal and iron poisoning of the catalyst take place. It is also generally known that the corrosion and iron poisoning are usually increased by the presence of sulfur in the feed. We have found by careful investigation, however, that the types and characters of the corrosions occurring with sulfur-free feeds and with sulfur-bearing feeds are different and that there is a region corresponding approximately to the transition of one type of corrosion to the other where corrosion of the ferrous metal and iron transfer to the catalyst are practically negligible. This region where corrosion and iron transfer practically do not take place corresponds to a low, specific and narrow range of sulfur concentrations. If the concentration of sulfur is increased beyond this range corrosion is greatly increased and large quantities of iron are transferred to the catalyst, and on the other hand, if the concentration of sulfur is reduced beyond this range, corrosion of the other type and iron transfer are again increased.

The existence of this region of minimum iron transfer to the catalyst may be easily seen from the following illustrative examples. These examples, for the sake of comparison, all relate to the dehydrogenation of propane vapors at a temperature of 1140° F. at a space velocity of 35 per minute and process period of 40 minutes. The catalyst in each case was an 8–14 mesh activated alumina impregnated with chromium oxide (11% Cr). The fresh catalyst contained 0.025% iron. The reaction in each experiment was executed in a new sand-blasted KA2S steel reaction tube.

Example I

Propane vapors substantially free of sulfur were treated under the above-described conditions. After only about 19 (and 38) process cycles the catalyst contained about 0.26% (and 0.35%) iron. In other words, in check runs during 19 and 38 process periods iron was transferred from the KA2S steel reaction tube to the catalyst to the extent of about 0.24% (and 0.33%) by weight of the catalyst. It is thus seen that in the absence of sulfur, contamination of the catalyst by iron is considerable.

Example II

A commercial propane fraction contaniing 0.0002% sulfur (principally as mercaptans) was treated under the above-described conditions. During about 120 (and 250) process cycles the catalyst was found to have gained 0.16% (and 0.18%) iron. From these experiments it is seen that 0.0002% mercaptan sulfur in the feed is insufficient to effectively prevent contamination of the catalyst with iron.

Example III

To a commercial sulfur-free propane fraction there was added sufficient carbonyl sulfide to raise the sulfur content to 0.006%. This material was treated under the conditions described above for 200 process cycles. During this time the conversion to propylene declined from 33.5% to 29.5%. The catalyst at the end of the 200 process cycles was not noticeably changed in iron content (initial iron content 0.025%. It is thus seen that in the presence of about 0.006% sulfur in the form of carbonyl sulfide, iron poisoning of the catalyst is almost completely eliminated and excellent conversions are obtained.

Example IV

A similar set of experiments was made in which dimethylsulfide was added to the propane to provide the desired sulfur content. The iron contents of the catalysts after 200 process cycles correspond to the following concentrations of sulfur:

Sulfur in feed	Iron in catalyst
Per cent	*Per cent*
0.0006	0.17
0.014	0.04
0.063	0.38

Similar series of experiments were made by adding various amounts of carbon disulfide thiophene, sulfur trioxide, sulfur dioxide, ethyl mercaptan and elemental sulfur. In each case it was found that within a limited range of sulfur concentrations the contamination of the catalyst by iron was substantially avoided whereas at both lower and higher concentrations considerable iron was transferred to the catalyst. The most effective concentration of sulfur varied somewhat with the individual sulfur compound but was, in general, between about 0.0002% and 0.05%. Preferred limits of sulfur concentrations for individual types of sulfur compounds were found to be:

S=0.0006–0.015
COS=0.0006–0.05
Thiophene=0.0006–0.05
R—S—R=0.005–0.038
R—S—H=0.0005–0.003
SO_3=0.002–0.025
SO_2=0.002–0.015
CS_2=0.002–0.02

The transfer of iron to the catalyst is prevented by the use of specific quantities of reducible sulfur. By the term "reducible sulfur compound" we mean elemental sulfur and such vaporizable sulfur compounds as are capable of being reacted or reduced with hydrogen. Hydrogen sulfide is incapable of further hydrogenation and is not included. Hydrogen sulfide, we have found, is relatively ineffective and is not equivalent to sulfur and reducible sulfur compounds for the present purpose.

Examples of suitable sulfur compounds are elemental sulfur, carbonyl sulfide, sulfur trioxide, thiophenic compounds, dialkyl sulfides, polysulfides, mercaptans and similar reducible sulfur compounds which are sufficiently vaporizable to afford the required concentrations of sulfur at the reaction temperatures. These various types of reducible sulfur compounds are not equally effective and therefore not equivalent. Thus, of the available sulfur compounds, one preferred group comprises volatile oxygenated sulfur compounds, i. e. those having at least one oxygen atom attached directly to the sulfur. A preferred sulfur compound of this class is carbonyl sulfide. Of the available reducible non-oxygenated sulfur-bearing materials, preferred agents are elemental sulfur and thiophenic compounds.

Elemental sulfur has the following advantages and is a particularly desirable agent:

1. Elemental sulfur is very efficient and when used in optimum amounts substantially completely obviates iron poisoning.

2. The effect-concentration curve for elemental sulfur in the optimum concentration

range is very flat, affording a relatively wide range of nearly optimum concentrations. Thus, when employing elemental sulfur a concentration within the desired optimum range may be easily maintained in large commercial scale operation.

3. Elemental sulfur, it is found, is quite stable under the reaction conditions and has substantially no tendency to react with and sulfurize the product.

4. When elemental sulfur is employed the problem of removing sulfur from the product is greatly simplified. Thus, by simply washing the product with a caustic solution the sulfur may be substantially completely removed.

Thiophene and its homologues, i. e. benzenoid compounds containing the characteristic grouping, =CH—SH=CH—, are also preferred non-oxygenated sulfur compounds. These compounds are exceedingly effective and can be used in a fairly wide range of concentrations. These compounds are also very stable under the reaction conditions.

The least desirable of the applicable reducible sulfur compounds are the mercaptans. Although mercaptans are fairly effective when used in optimum concentrations, the range of applicable concentrations is quite narrow and more difficult to maintain in practical application. Concentrations outside of the narrow applicable range greatly increase iron transfer and are quite detrimental. This is believed to be due to the fact that mercaptans are partly converted to the undesirable hydrogen sulfide under the reaction conditions.

Other metalloid compounds such as the corresponding reducible selenium and tellurium compounds function in the same manner as the sulfur compounds, although often not quite as efficiently. Since sulfur and its reducible compounds are the most practical agents to use, these other metalloid compounds are of much less practical interest. Their use, however, is considered to be within the scope of the invention.

The prevention of contamination of the catalyst by iron by the suitable application of these sulfur compounds is applicable to a wide variety of reactions. The present invention relates more particularly, however, to the dehydrogenation of hydrocarbons, and still more particularly to the catalytic dehydrogenation of hydrocarbons having from two to five carbon atoms. Suitable hydrocarbons which may be dehydrogenated according to the present process are, for example, ethane, propane, butane, isobutane, the pentanes, cyclopentane and the corresponding olefines. The saturated hydrocarbons may be dehydrogenated to the corresponding olefines or diolefines depending upon the particular hydrocarbons in question and the severity of the dehydrogenation conditions. The process is particularly applicable, for example, for the dehydrogenation of normal butane to butylene and/or butadiene, the dehydrogenation of isobutane to isobutylene, the dehydrogenation of cyclopentane to cyclopentadiene, etc.

These various lower boiling hydrocarbons, as obtained from commercial sources, normally contain appreciable quantities of water. The amount of water depends somewhat upon the treatment which they have undergone in their recovery, storage, etc. but varies in general between about 0.01% for dry feeds up to about 0.1% for fairly wet feeds. Butane, for example, which has been stored in the liquid phase at ordinary temperatures may contain 0.01% by weight of water. Butane vapor obtained from gasoline stabilizer units (which is one of the largest sources of supply) ordinarily contains considerably higher concentrations. Commercial ethane, propane and olefine fractions also contain, in general, still greater concentrations of water. In the conventional dehydrogenation of these materials these concentrations of water do no harm and no effort is made to dry the feed. In fact, it is generally believed that a certain amount of water is quite beneficial to the catalytic dehydrogenation and, in some cases, additional water is purposely added to the hydrocarbon feed to be dehydrogenated. See, for example, U. S. Patent 2,131,089. When dehydrogenating these commercial hydrocarbons and preventing the transfer of iron to the catalyst by the use of sulfur compounds as described above, excellent conversions are obtained. We have now found that when dehydrogenating these various commercial hydrocarbons and preventing the transfer of iron to the catalyst by the use of sulfur compounds as described above, even traces of water have a considerable influence. It was found that, contrary to expectations, the concentrations of water normally present in these feeds have a detrimental effect when the prescribed concentrations of sulfur are employed and that by substantially removing this water the conversions may be considerably increased. Of even more importance than the increased conversion is the decrease in the rate of decline of the catalyst activity with use. Thus, in a typical run, by drying a commercial butane feed to a water content of 0.001% by weight and employing 0.0007% sulfur, the decrease in the dehydrogenation conversion during 100 process cycles (40 minutes on-stream; space velocity, 35; temperature, 1100° F.; chromium-oxide-on-alumina catalyst) was only about 0.9%. We have found that the conversions are increased and the rate of catalyst decline decreased as the water content of the feed is reduced until a more or less critical concentration dependent somewhat upon the hydrocarbon feed is reached. According to the process of the present invention, the water content of the hydrocarbon feed to be dehydrogenated is therefore reduced to below the critical maximum allowable water concentration, usually to below about one-half of that normally present in the fairly dried commercial feed. Thus, in the dehydrogenation of normal butane and/or isobutane the feed is preferably dried to a water content below about 0.005%, for example to between about 0.001% and 0.005%. When dehydrogenating propane the allowable maximum water concentration is somewhat higher for example about 0.011%. When dehydrogenating ethane and olefines, concentrations of water up to about 0.015% may be employed. Reduction of the water content of the feed to concentrations below the above-given maximum concentrations allows some improvement over the maximum permissible concentrations. Exhaustive drying of the feed is, however, of no advantage. Thus, for example, substantially equally good results are obtained when the feed is dried to a water content of 0.001% as when dried to a water content of 0.00002%. Preferred ranges of water concentrations are as follows:

	Per cent
Butane	0.001–0.005
Propane	0.002–0.009
Ethane	0.003–0.011

We have also found that substantial drying of the feed when using the prescribed concentrations of sulfur as described is of particular advantage for effecting the dehydrogenation under conditions of high space velocity. Thus, the advantages of the above-described control of the water and sulfur concentrations in the feed are particularly pronounced when employing space velocities above about 30. Space velocity, as herein defined, is the number of volumes of vapor measured at standard conditions which is passed through a unit volume of the catalyst per minute.

The water content of the hydrocarbon feed may be reduced to below the above-defined maximum permissible concentrations by any one of several known methods. One suitable method which is practical in commercial operation is to pass the hydrocarbon, preferably in the vapor phase, through a bed of a suitable drying agent such as magnesium perchlorate, phosphorous pentoxide, or the like. Fresh activated alumina is also quite suitable and practical. The desired sulfur compound is preferably added to the predried material.

The process of the present invention is generally applicable in the dehydrogenation of the above-specified hydrocarbon materials in the vapor phase at elevated temperatures at least equal to 750° F. wherein the conversion is executed in ferrous metal equipment with the aid of regenerative catalysts which are affected by contamination by iron. By regenerative catalysts we mean, of course, catalysts which are periodically regenerated by the oxidation of combustible deposits therefrom. As examples of such catalysts there may be mentioned by way of illustration the many catalysts comprising one or more compounds such, in particular, as the oxides of the metals Ti, Zn, Ce, Th, V, Nb, Ta, Cr, Mo, W, U and Mn. These catalysts often contain minor percentages of these metals or compounds thereof such as, for example, the molybdates, tungstates, chromates, chromites, etc. in combination with major amounts of relatively inert materials such, for example, as activated alumina, activated magnesia, activated clays, activated carbon, alumina gel, zirconia gel, silica gel, bauxite, artificial aluminum silicates and the like. They are usually substantially free of iron, cobalt and nickel. They may, however, contain small amounts of the noble metals of group VIII such, for instance, as platinum and/or palladium. The process is particularly advantageous when the catalyst comprises chromium oxide and/or molybdenum oxide, and/or tungsten oxide and alumina. These catalysts are exceptionally suited for the dehydrogenation of hydrocarbons, but suffer considerably from iron contamination when used in ferrous metal equipment. The described catalysts are not generally detrimentally affected in their activities by sulfur. Obviously, such catalysts as nickel catalysts, platinum catalysts and the like which are poisoned by sulfur are not applicable in the present process.

The contamination of the catalyst by iron may be inhibited, according to the present process, in the presence of any of the steels and common ferrous alloys. Iron and mild steel are not usually employed in these processes due to their lesser ability to withstand the more or less severe conditions. Particularly suitable materials which may be used are the chrome steels such as KA2, KA2S, KA2ST, KA2Cb, KA2Mo, KA2MoT, etc. In the past these otherwise excellent steels have not been found entirely suitable due to their tendency to cause iron contamination of the catalyst after a short period of use and the industry has been forced to go to the more expensive and difficultly workable high-chrome steel such as 27–Cr. These latter materials, although definitely superior to most low-chrome steels, are nevertheless far from satisfactory and cause iron contamination after a relatively short time. By utilizing the process of the present invention, any of these steels may be used indefinitely without any appreciable tendency to cause iron contamination of the catalyst. Particularly excellent results are also obtained using nitrogen or aluminum-stabilized high-chrome steels. For example, a particularly excellent steel has the following composition:

	Per cent
C	0.14
Mn	0.40
S	0.012
P	0.021
Si	0.38
Cr	26.78
Ni	trace
N_2	0.17

Many commercial hydrocarbon feeds to be dehydrogenated according to the present process normally contain small to appreciable amounts of sulfur compounds. It will be appreciated, in view of the above, that in order to realize the advantages of the present method the sulfur contents of these materials must be adjusted prior to treatment to within the narrow limits of sulfur concentrations specified above. In such cases where the sulfur content is normally too low, it is merely necessary to add the required amounts of sulfur to bring the concentration within the specified limits. In such cases where the sulfur content is too high, the excess sulfur should be removed. This may be done by any of the conventional desulfurization treatments. Also, besides adjusting the concentration of sulfur to within the desired limits, it is desirable to take into consideration the type of sulfur compound present. In most cases it is found that sulfur-containing feed stocks contain the sulfur in the form of hydrogen sulfide and/or mercaptans. As pointed out above, mercaptans are the least desirable of the applicable sulfur compounds and hydrogen sulfide is usually quite detrimental. According to the preferred embodiment of the invention, these sulfur compounds are substantially removed and the correct amount of a preferred type of sulfur, such carbonyl sulfide, elemental sulfur or a thiophenic sulfur compound, is added.

Although the sulfur or sulfur compound may be added directly to the reaction zone or by any other convenient method, the most convenient and practical method for introducing the desired sulfur or sulfur compound into the reaction zone is in admixture with the reactant vapors. Thus, for instance, the correct amount of a desirable form of sulfur may be dissolved in the feed and the whole vaporized and passed into the reaction zone, or vapors of the sulfur compound may be mixed with the preheated reactant vapors entering the reaction zone. In certain cases a convenient means for dosing the desired sulfur into the feed is to vaporize the feed and pass a portion of the vapors through a bath or solution of the sulfur compound whereupon sulfur is taken up in proportion to its vapor pressure.

We claim as our invention:

1. In a dehydrogenation process wherein butane is contacted in the presence of a ferrous metal at

an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the butane to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

2. In a dehydrogenation process wherein isobutane is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the isobutane to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

3. In a dehydrogenation process wherein propane is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the propane to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

4. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

5. In a dehydrogenation process wherein a hydrocarbon having from two to five carbons atoms is contacted in a chrome steel reactor at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

6. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted at an elevated temperature of at least 750° F. with a chromium oxide dehydrogenation catalyst in the presence of a ferrous metal and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% of reducible sulfur.

7. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% sulfur in the form of a reducible oxygenated sulfur compound.

8. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0002% to 0.05% sulfur in the form of a reducible non-oxygenated sulfur compound.

9. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0006% to 0.05% sulfur in the form of a thiophenic compound.

10. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0006% to 0.05% sulfur in the form of carbonyl sulfide.

11. In a dehydrogenation process wherein a hydrocarbon having from two to five carbon atoms is contacted in the presence of a ferrous metal at an elevated temperature of at least 750° F. with a sulf-active dehydrogenation catalyst susceptible to contamination by iron and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the hydrocarbon to be dehydrogenated to a water content not greater than 0.005% by weight and maintaining in the predried feed from 0.0006% to .015% elemental sulfur.

12. In a dehydrogenation process wherein isobutane is contacted at an elevated temperature of at least 750° F. with a chromium oxide dehydrogenation catalyst in a chrome steel reactor and the catalyst is periodically regenerated by oxidation of carbonaceous deposits therefrom, the step of predrying the isobutane to be dehydrogenated to a water content between about 0.001% and 0.005% by weight and maintaining in the predried feed from 0.0006% to about 0.05% elemental sulfur.

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