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INHIBITING CARBON FORMATION IN
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This invention relates to a method of preventing or inhibiting undesirable side reactions resulting in excessive carbon formation which normally occur when endothermic chemical reactions involving one or more organic compounds are conducted at elevated temperatures in metal or metal-lined reaction vessels wherein the reactant or reactants is/are in contact with a heated metal surface at the temperature of operation.

When endothermic reactions involving organic reactants, such as the cracking of hydrocarbons, the dehydrogenation of hydrocarbons, the dealkylation of aralkyl hydrocarbons and substitution products thereof, the dehydrogenation of organic oxy-compounds as primary and secondary alcohols, the dehydration of alcohols, and the like are conducted in metal or metal-lined reaction vessels as retorts, tubes, etc., at the high temperatures necessary to effect such reactions at a practical rate, the heated metal surface in contact with the organic material being acted upon exerts an undesirable catalytic influence causing substantial decomposition of the organic material with the formation of prohibitively large quantities of carbon and hydrogen. These side reactions resulting in excessive carbon formation are very undesirable; they materially decrease the yield of the desired product or products; they may result in the formation of sufficient carbon to close up the reaction tube in a relatively short time; and when catalysts are used to accelerate the endothermic reaction, the formed carbon deposited upon the surface of the catalyst material may render it inactive in a relatively short time and require frequent mechanical removal or burning of the carbon therefrom.

The carbon formed in the endothermic reactions to which this invention relates is due to the catalytic effect of the heated walls of the reaction vessel material; it is usually of a fluffy, soot-like type but it may be coherent and of a lustrous or graphitic form. It is, however, distinguished from the entirely different type of carbon which is formed by the condensation of tarry or asphaltic material and subsequent coking of the condensate. It is not the purpose of the present invention to inhibit this latter type of carbon formation.

It has heretofore been impossible to prevent or inhibit the excessive formation of carbon which invariably occurs when endothermic reactions involving organic materials are conducted on a technical scale. This excessive carbon formation materially decreases the usefulness and practicality of the known endothermic processes which for reasons of economy and to provide adequate heating of the reaction material and temperature control are usually conducted in metal or metal-lined reaction vessels.

Prior investigators have attempted to solve the problem of inhibiting excessive carbon formation in organic cracking and dehydrogenation reactions by providing metal alloy tubes which could be used at the high temperatures required without the interior surface thereof catalyzing carbon formation. Numerous alloys consisting for the most part of iron or steel alloyed with one or more of the metals as vanadium, chromium, manganese, nickel and cobalt have been provided for this purpose. None of the alloys proposed have successfully solved the problem. So far no metallic tube materials have been found which will not catalyze carbon formation at high temperatures. Some of the alloy tube materials are relatively inactive as regards carbon formation when they are first put into use, but the effect is not lasting, and the catalytic effect of the tube material increases with its use. Certain alloy tubes used in the catalytic dehydrogenation of organic compounds may be employed with some success for considerable periods of time but eventually the catalyst loses its activity and must be regenerated. The loss of catalyst activity is in many cases, as when an activated alumina catalyst or similar catalyst is used, due to the deposition of carbon on the surface of the catalyst. The most practical way to reactivate a non-metal catalyst which has lost its activity in this manner is to burn out the carbon with an oxygen-containing gas while leaving the catalyst packed in the reaction tube. I have found that after such a reactivation treatment, even the alloy tubes proposed by the art will catalyze carbon formation to a prohibitive extent.

Now, I have found that metal reaction tubes and other types of metal reaction vessels can be used in high temperature endothermic chemical reactions involving organic compounds while carbon formation, due to the catalytic influence of the walls of the metal reaction vessel, is substantially avoided and in many cases entirely prevented.

In accordance with the invention, carbon formation in metal reaction vessels used in high temperature endothermic reactions of organic compounds is inhibited or substantially prevented by treating the metal surface of the reaction vessel which is exposed to the organic material under reaction conditions with substances which poison

the catalytic influence of the metal surface and thus render it substantially inactive as regards its tendency to decompose the organic material to carbon.

- 5 Suitable substances which have the desired poisoning effect on the reaction vessel material are the elements sulphur, phosphorus, selenium and tellurium and compounds of these elements which, under the conditions of the particular
10 endothermic reaction to which they are applied, have the desired poisoning influence on the surface of the reaction vessel. A particularly suitable group of substances for my purpose includes hydrogen sulphide, hydrogen selenide and hydrogen telluride and organic or inorganic compounds
15 capable of forming these hydrides under reaction conditions. The most frequently applied agent is sulphur in the form of hydrogen sulphide, although organic sulphur compounds as mercaptans, mercaptides, thioethers, polysulphides, etc., may be successfully employed if desired.

- The treatment of the interior surface of the reaction vessel may be carried out before it is put into use, or the treating agent may be added
25 to the organic material undergoing treatment in the required amount continuously or intermittently during the reaction. In some cases, it may be desirable to use both methods, that is, to pretreat the interior surface of the reaction vessel
30 prior to its use and then maintain the effect of the pretreatment by adding the required amount of the agent to the reaction mixture in the vessel during the execution of the process.

- When pretreatment of the reaction vessel is
35 resorted to, the reaction vessel may be treated with a suitable agent, as hydrogen sulphide, at an elevated temperature usually greater than about 200° C. and preferably at the same temperature at which the endothermic reaction is to be conducted therein. The time and temperature
40 of the pretreatment will be dependent upon the particular treating agent used, the concentration in which it is employed and the characteristics of the metal surface treated, such as its stability
45 to the treating agent. When the treating agent is hydrogen sulphide, the pretreatment generally requires from about 5 minutes to about 120 minutes depending upon the temperature employed. Care must be taken to avoid excessive corrosion
50 of the reaction vessel when the pretreatment is effected at high temperatures. For reasons of economy and to avoid excessive corrosion of the reaction vessel material, we prefer to effect the pretreatment with the minimum practical
55 amount or concentration of the treating agent.

- After the pretreatment, the treated reaction vessel is used for the reaction proper until the passivation or catalyst poisoning effect of the agent with which it was treated becomes ineffective and carbon formation is again catalyzed to an undesirable extent. This condition may be detected in a variety of ways: the reaction tube, for example, may start to become plugged with carbon; more hydrogen may be formed than
65 when the reaction is proceeding while carbon formation is being inhibited, and, when the endothermic reaction is effected in the presence of a catalyst, a decrease in activity of the catalyst may be noted due to deposition of carbon on the
70 surface thereof. When the effect of the pretreatment has worn off to the extent that carbon is formed in prohibitive amounts, the reaction vessel may be taken out of service and again pretreated as described. In some cases, successive pretreatment of the reaction vessel is un-

necessary. When the passivation of the reaction vessel surface becomes ineffective, the required degree of passivation may be restored and maintained by continuously or intermittently adding an effective amount of the tube poisoning agent
5 to the reaction mixture, usually in admixture with the organic material undergoing treatment. The length of time that the pretreated reaction vessel is ineffective to substantially catalyze carbon formation usually depends on the nature of the metal surface of the reaction vessel, upon the temperature at which the endothermic reaction is effected therein, and upon the nature of the reaction participants. Usually alloyed steels, lower temperatures and reaction mixtures substantially devoid of hydrogen allow the use of less of the carbon formation-inhibiting agent and cause a pretreatment to last longer.

In general, when carbon formation is inhibited by adding the agent which poisons the catalytic influence of the metal surface of the reaction vessel during the reaction, the amount of the effective agent which must be added to the reaction mixture or to the organic material treated will depend upon the nature of the metal reaction
25 vessel surface in contact with the reactants under reaction conditions, upon the temperature at which the endothermic reaction is effected, and upon the nature of the materials undergoing reaction. As when the reaction vessel is rendered
30 passive by pretreatment, the carbon formation-inhibiting agent is added to the reaction mixture in an amount just effective to substantially inhibit carbon formation. In other words, the minimum effective amount or concentration of such agent or material yielding it under reaction conditions is employed. The minimum effective amount is used for purposes of convenience and economy and also to avoid excessive corrosion of the reaction vessel.

My invention may be applied with excellent results to any endothermic chemical reaction involving organic materials which is conducted in metal reaction vessels at high temperatures, that is, temperatures at which excessive carbon formation is catalyzed by the reaction tube materials. Such reactions are usually executed at temperatures equal to or greater than about 400° C. The type of carbon formation which may be inhibited by the application of the process of my invention usually does not occur to any appreciable extent in endothermic reactions executed at temperatures below about 400° C. However, when such carbon formation does occur in endothermic reactions executed at lower temperatures, the invention is applicable to its inhibition.

My process is effective to substantially inhibit carbon formation regardless of the nature of the metal reaction vessel in which the endothermic reaction is effected. The reaction vessel may, for example, consist of or be lined with iron, steel, copper, silver, chromium, vanadium, nickel, cobalt, platinum, manganese and the like or alloys comprising a plurality of these as well as one or more other metals. The heated metal surface in contact with the reactants may consist of or comprise aluminum, for example, the endothermic reaction may be effected in a calorized reaction vessel, i. e., a steel or iron reaction vessel the interior surface of which has been coated with aluminum. The process is very effective in inhibiting carbon formation in iron and steel reaction tubes and also in nickel-iron-chromium, nickel-iron, nickel chromium, iron-chromium-vanadium, iron-chromium-molybdenum and other alloys commonly in

use as reaction tubes or retorts in high temperature cracking and dehydrogenation processes. I have tested a wide variety of the metal reaction vessel materials on the market and I find that they all catalyze carbon formation from organic materials at high temperatures. In general, it can be said that all metal and metal alloys which are capable of acting as dehydrogenation agents at low temperatures will catalyze carbon formation at higher temperatures.

The present invention, while it finds perhaps its most important field of usefulness in processes involving the thermal decomposition or cracking of organic compounds and in the catalytic dehydrogenation of organic compounds, is nevertheless generally applicable to all endothermic reactions requiring high temperatures and involving one or more organic compounds. The reaction or reactions involved may be in the liquid, vapor or liquid vapor phase and they may involve inorganic compounds in addition to one or more organic compounds. Regardless of the nature and specific conditions of the endothermic reaction, the general procedure to inhibit carbon formation in accordance with the principles of the invention is substantially the same.

My invention is applicable to the inhibition of carbon formation in a wide variety of commercial processes involving the endothermic reaction of organic materials. The following processes are typical illustrative examples:

Liquid and vapor phase cracking operations wherein carbonaceous materials as petroleum, petroleum products, shale oils, vegetable oils, animal oils, coal, tars, asphalts, pitches, etc., are thermally decomposed, in the presence or absence of catalysts, to saturated or unsaturated hydrocarbon materials of lower molecular weight. For example, cracking operations wherein petroleum oils or fractions thereof of a higher boiling range than gasoline are pyrolyzed or catalytically decomposed at high temperatures to lower boiling liquids of the gasoline type.

Cracking processes wherein paraffin or paraffin type hydrocarbons are cracked to products rich in olefines or to aromatic hydrocarbons and olefine-containing gases. Processes wherein olefines are cracked and converted to aromatic hydrocarbons as benzene, naphthalene, anthracene, toluene and the like. Processes wherein paraffin hydrocarbons and/or olefines are cracked, in the absence or presence of catalysts, to acetylene and/or acetylene type hydrocarbons.

Decomposition reactions of the class of which dealkylations are an example, that is, processes wherein aralkyl compounds are treated at high temperatures in the liquid or vapor phase and in the presence or absence of catalysts and converted to less alkylated products. For example, the cracking of toluene to benzene, cresol to phenol, alkyl quinolines to quinoline, etc.

Dehydration processes wherein organic compounds are dehydrated, usually in the vapor phase at high temperatures in the presence of dehydrating catalysts. For example, processes involving the dehydration of the aliphatic alcohols as ethyl, propyl, butyl, isobutyl, secondary butyl, tertiary butyl, amyl, hexyl and the like to olefines and/or diolefines at elevated temperatures in the presence of catalysts as alumina, ceria, thoria, acidic solid salts, etc.

Decarboxylation processes involving the pyrolytic or catalytic elimination of carbon dioxide from organic carboxy compounds as carboxylic acids and carboxylic acid esters. The process is also

applicable to the inhibition of carbon formation catalyzed by the heated interior metal surface in which endothermic reactions involving the formation or reaction of carbon monoxide are executed.

Dehydrogenation processes involving the pyrolytic or catalytic elimination of hydrogen from organic compounds. For example, processes wherein hydrocarbons of the paraffin series are dehydrogenated to the corresponding olefines, as ethane to ethylene, propane to propylene, normal butane to n-butylene, isobutane to isobutylene, cyclohexane to cyclohexene, ethyl benzene to styrene, etc., by contact with a metal or metal dehydrogenation catalyst at an elevated temperature.

Processes wherein primary or secondary alcohols are contacted at elevated temperatures with metallic or non-metallic catalysts and dehydrogenated to the corresponding aldehydes or ketones, respectively. For example, processes wherein ethyl alcohol is dehydrogenated to acetaldehyde, isopropyl alcohol to acetone, secondary butyl alcohol to methyl ethyl ketone, methallyl alcohol to methacrolein, borneol and isoborneol to camphor, cyclohexanol to cyclohexanone, fenchyl alcohol to fenchone, and the like.

When my invention is used to inhibit the excessive formation of carbon when hydrocarbon or hydrocarbon mixtures are cracked in metal tubes as steel or steel alloy tubes, I preferably pretreat the metal tube with hydrogen sulphide at about the temperature at which the cracking operation is to be conducted. The material subsequently treated in the pretreated metal tube may or may not contain a sufficient concentration of hydrogen sulphide or organic sulphur compounds capable of forming hydrogen sulphide under the conditions of the cracking process to substantially maintain the passivity of the metal tube surface. After the pretreatment accorded the metal cracking tube becomes ineffective to prevent substantial carbon formation as indicated by formation of more hydrogen than during the normal cracking period, the tube may be taken out of operation and again subjected to a treatment with hydrogen sulphide.

My invention may be applied to the inhibition of carbon formation in catalytic dehydrogenation reactions conducted in metal reaction tubes in a variety of manners depending upon the particular dehydrogenation reaction, the specific catalyst or catalyst composition used and, upon the nature of the reaction tube material.

The invention may be applied with excellent results to the inhibition of carbon formation in organic dehydrogenations carried out in metal tubes in the presence of catalysts which are not poisoned by the elements sulphur, phosphorus, selenium and tellurium and compounds thereof, or which have a certain tolerance for such elements and their compounds. The sulphactive catalysts as molybdenum sulphide are examples of catalysts which are not poisoned by sulphur and sulphur compounds as hydrogen sulphide, mercaptans, etc. There are numerous dehydrogenation catalysts which although not immune to poisoning by the carbon formation-inhibiting agents, as for example hydrogen sulphide, have a certain tolerance for such catalyst poisons. A group of such dehydrogenation catalysts includes among others activated alumina, activated charcoal, silica gel, magnesite, zinc oxide, chromium oxide, thorium oxide, alumina impregnated with chromium oxide, alumina im-

pregnated with chromium chromite, magnesite impregnated with chromium chromite, etc., and mixtures of such catalysts. With such catalysts, the presence of the carbon formation-inhibiting agent in an amount necessary to substantially inhibit carbon formation may even make the catalyst more active than in the absence of said agent.

When catalysts, as the above-named, which have a definite tolerance for the agent used to inhibit carbon formation are used, it is desirable that the catalyst be capable of tolerating a greater amount of the carbon formation-inhibiting agent without substantial loss of activity than is required to substantially obviate the tendency of the tube material to catalyze carbon formation. It is seen that the carbon formation-inhibiting agent may be added to the reaction mixture in a controlled amount sufficient to substantially inhibit carbon formation but insufficient to materially decrease the activity of the catalyst. For example, when using a brass catalyst packed in iron, steel or steel alloy tubes for the dehydrogenation of alcohols, I have found that the brass catalyst can tolerate up to about 0.0025% of sulphur in the alcohol treated without a substantial decrease in activity of the catalyst. In accordance with the present invention, I may add sufficient sulphur, preferably in the form of hydrogen sulphide, to the alcohol to be treated so as to maintain the concentration of sulphur in the reaction mixture not greater than about 0.0025% sulphur, and thus completely prevent carbon formation without deleteriously effecting the life and activity of the catalyst. The above is given for purposes of illustration only. A wide variety of other metal and metal alloy catalysts having a sufficient tolerance for the carbon formation-inhibiting agents may be used for the dehydrogenation of alcohols and other organic oxy-compounds as well as hydrocarbons. The tolerance of the catalyst for the particular carbon formation-inhibiting agent can be readily determined and the material of the reaction vessel so selected that carbon formation can be inhibited without deleteriously effecting the activity of the catalyst. The catalyst should be capable of tolerating a greater amount of the carbon formation-inhibiting agent than is required to render the metal reaction surface incapable of inhibiting substantial carbon formation.

My invention is applicable with excellent results to the inhibition of carbon formation in processes wherein hydrocarbons are dehydrogenated by contact with solid catalysts contained in metal reaction tubes at elevated temperatures generally in the range of from about 400° C. to about 900° C. and preferably from about 500° C. to 800° C. If the catalyst used can tolerate a concentration of the selected carbon formation-inhibiting agent, for example, hydrogen sulphide, greater than the minimum concentration of said agent effective to inhibit carbon formation to the desired extent, pretreatment of the metal tube alone may be resorted to, or the tube as well as the catalyst may be pretreated and the effect of the pretreatment maintained by providing an effective concentration of the carbon formation-inhibiting agent in the reaction mixture during the dehydrogenation reaction.

In the dehydrogenation of isobutane, normal butane and other hydrocarbons by contact with catalysts as activated alumina, impregnated activated alumina, activated charcoal, chromium

oxide, and the like packed in iron, steel or steel or iron alloy tubes, such as steel tubes containing from 4% to 6% chromium and 0.2% molybdenum, I have found that an amount of about 0.3% sulphur added to the material to be treated is effective to inhibit carbon formation for indefinite periods of continuous operation depending only on the life of the catalyst. For pretreatment, a 10 minute treatment of the interior surface of the catalyst tube with concentrated hydrogen sulphide at the temperature at which the dehydrogenation is to be effected, is usually effective to inhibit carbon formation during the complete life-time of the catalyst between regeneration treatments. With such pretreated tubes, carbon formation has been substantially prevented for a period of as long as one week of continuous operation, after which time the catalyst employed usually loses sufficient activity to require regeneration.

The following examples illustrate specific embodiments of my invention. It is to be understood that the examples are illustrative only and are not to be regarded as limiting the scope of the invention.

Example I

A steel reaction tube having an inside diameter of 0.95 cm. was heated over a length of about 57 cms. in a suitable furnace. Propane was passed through the heated tube at a velocity of 60 c. c./min. (space velocity of about 90).

At a temperature of about 800° C., decomposition of the hydrocarbon to carbon and hydrogen, catalyzed by the interior surface of the reaction tube, occurred to such an extent that the tube was almost completely choked with carbon in a few minutes, while substantially no aromatics were formed.

When propane to which about 2% of hydrogen sulphide had been added was passed through a clean reaction tube of the same material and size at about the same space velocity, the propane was cracked to methane and ethylene and good yields of aromatics were obtained at temperatures of from about 700° C. to 900° C. while substantially no carbon was formed even after the process had been operated for a long period of time.

Example II

A reaction tube of the material and size described in Example I was pretreated as follows: The tube was heated to a temperature of about 700° C. while a stream of hydrogen sulphide was passed through it slowly for about 30 minutes.

Following the pretreatment, the tube was heated to a temperature of from about 700° C. to 900° C. and propane was passed through it at a velocity of about 60 c. c./min. Cracking of the propane took place without carbon formation. At 850° C., about 20% by weight of the cracking stock was converted to a tar which consisted of aromatic hydrocarbons, principally benzene.

Example III

Substantially pure propylene was passed through a steel reaction tube heated to a temperature of from about 700° C. to 900° C. No aromatic hydrocarbons were formed but carbon formation occurred so rapidly and to such an extent that the tube was almost completely stopped up in a short time.

When propylene to which about 0.38% of hydrogen sulphide had been added was passed through the same clean reaction tube heated to

a temperature of about 800° C., conversion took place with substantially no formation of carbon. About 40% by weight of the propylene was converted to a tar consisting for the most part of aromatic hydrocarbons.

Example IV

A clean, new steel tube of the same material as that described in Example III was pretreated as follows prior to its use for the cracking of propylene.

The steel tube was heated to a temperature of 800° C. while hydrogen sulphide was passed slowly through it for about 15 minutes. Propylene was then passed through the pretreated tube heated to a temperature of about 800° C. Conversion took place with practically no carbon formation. A tar of aromatic nature was formed in the amount of about 62 pounds per 1000 cu. ft. of propylene passed through the pretreated tube. The beneficial effect of the pretreatment of the tube lasted for more than 16 hours of continuous operation. The effluent non-condensed gases comprised about 15.0% ethylene, 9.9% hydrogen and 74.4% methane.

Example V

A stove oil was subjected to a vapor phase cracking treatment by passing it through a heated steel alloy tube the material of which contained about 4% to 6% chromium and about 0.5% molybdenum. The process was executed at a temperature of about 800° C. At first cracking was effected and a naphthalene tar was obtained while but little carbon was formed. After the tube had been in use for a short time, its interior surface suddenly became very active and the treated oil was decomposed to carbon, hydrogen and methane with the formation of only traces of naphthalene.

When the same reaction tube was originally used under the same conditions to crack the same stock of stove oil to which about 1.0% of hydrogen sulphide had been added, the process could be conducted indefinitely to obtain good yields of naphthalene tar with substantially no formation of carbon. At a temperature of 800° C., each barrel of oil treated yielded about 42% by weight of an aromatic tar and about 2800 cu. ft. of a gas having an olefine content of about 43%.

Substantially the same results were obtained when a substantially sulphur-free oil was treated in the same reaction tube which had been previously treated with sulphur vapor. The pretreatment of the tube was effected by heating it at a temperature of about 800° C. for about 10 minutes with its interior surface in contact with sulphur vapor diluted with nitrogen. The beneficial effect of the pretreatment lasted for about 20 hours after which time the tube was taken out of service and again pretreated and this cycle repeated about every 20 hours.

The same beneficial results were obtained when the tube was pretreated as described with dimethyl sulphide instead of sulphur vapor.

Example VI

Metal reaction tubes were pretreated as described in Example IV with the vapors of phosphorus, hydrogen selenide and hydrogen telluride, respectively. These pretreated metal tubes were used for propylene cracking under the conditions described in Example IV. The tube pretreated with phosphorus was used without carbon for-

mation for about 26 hours. The tubes treated with hydrogen selenide and hydrogen telluride were inactive for correspondingly long periods of time.

Example VII

A brass catalyst was packed in a steel catalyst tube having an inside diameter of about $\frac{5}{8}$ ". The tube was heated to a temperature of from about 425° C. to about 495° C. over a length of about 17" while pure isopropyl alcohol was passed through it at a rate of about 600 c. c. per hour. For the first few hours, the conversion of isopropyl alcohol to acetone was about 80%; it then began to drop off rapidly indicating a decrease in activity of the catalyst. It was found that considerable carbon had been formed and that the loss of activity of the catalyst was due to deposition of carbon on the surface thereof, said carbon formation being catalyzed by the material of the reaction tube.

A clean reaction tube of the same material and size and packed with the same catalyst as above-described was used under the same conditions of temperature, and isopropyl alcohol to which about 0.0025% of sulphur in the form of hydrogen sulphide had been added was passed through the heated tube at a velocity of about 600 c. c./hr. The process was operated continuously for about 56 hours during which time the conversion of isopropyl alcohol to acetone was about 80%. At the end of this time, examination of the catalyst showed that substantially no carbon had been formed.

Example VIII

Isopropyl alcohol containing about 0.005% sulphur was passed over a new brass catalyst packed in a steel tube of the same material and size as described in Example VII. The tube was heated to a temperature of from about 450° C. to 500° C. while the isopropyl alcohol was passed through it at a rate of 600 c. c./hr. The conversion of isopropyl alcohol to acetone was about 80% throughout the first 18 hours of operation, but it gradually decreased until it was only about 50% at the end of 24 hours, thus indicating a progressive decrease in catalytic activity. The operation was terminated and the catalyst examined. Substantially no carbon formation had occurred. The loss of activity of the catalyst was due to the use of an amount of the carbon formation-inhibiting sulphur greater than could be tolerated by the catalyst without loss of activity.

The catalyst was reactivated by passing substantially sulphur-free isopropyl alcohol through the tube under reaction conditions for about 5 hours, during which time the conversion rose to about 80%. The cycle was repeated as necessary to maintain the activity of the catalyst. Throughout the operation, carbon formation was substantially avoided.

Example IX

Isobutane was dehydrogenated to isobutylene by passing it in the vapor phase through a heated steel reaction tube packed with granules of an activated alumina catalyst. The temperature of the catalyst tube was maintained at about 600° C. and the space velocity of the isobutane through it was about 198. The dehydrogenation occurred to form isobutylene but after a short time the walls of the reaction vessel became so active that the treated isobutane was decomposed to carbon, hydrogen and methane exclusively.

When the same reaction tube and catalyst was used under the same conditions as above-described to dehydrogenate isobutane to which about 0.5% of hydrogen sulphide had been added, a 35% to 40% conversion of the isobutane to isobutylene was maintained over a period of 24 hours or longer without substantial carbon formation or loss of activity of the catalyst.

Example X

A steel reaction tube was packed with granules of an activated alumina and pretreated with hydrogen sulphide in the following manner:

The packed tube was heated to a temperature of about 600° C. while hydrogen sulphide was passed through it slowly for a period of about 30 minutes.

The pretreated reaction tube was used to effect the dehydrogenation of normal butane. The butane was passed, at a space velocity of about 198, through the tube maintained at a temperature of about 600° C. An average conversion of about 30% of the butane to butylene was maintained over a long period of time while substantially no carbon was formed.

The term "space velocity" as used in the above examples may be defined as the number of units of volume of gaseous material, measured at 0° C. and 76 cm. of mercury, contacted with a unit volume of catalyst per hour.

While I have described my invention in a detailed manner and provided specific examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

I claim as my invention:

1. In a process for the catalytic dehydrogenation of organic compounds in the vapor phase to valuable organic products containing fewer hydrogen atoms in metal reaction vessels at elevated temperatures, at least equal to about 400° C., the method of inhibiting the formation of non-asphaltic type carbon catalyzed by the reaction tube material which comprises pretreating the interior surface of the reaction tube with hydrogen sulphide at an elevated temperature greater than about 200° C. for a time adequate to poison the metallic surface and render it substantially inactive to catalyze carbon formation under the conditions at which the dehydrogenation is effected and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.

2. In a process for the catalytic dehydrogenation of organic compounds in the vapor phase to valuable organic products containing fewer hydrogen atoms in metal reaction tubes, at least equal to about 400° C., the method of inhibiting the formation of non-asphaltic type carbon which comprises effecting the dehydrogenation in the presence of a dehydrogenation catalyst which is substantially active to catalyze dehydrogenation in the presence of an amount of hydrogen sulphide, adequate to render the reaction tube material in contact with the reaction mixture substantially inactive to catalyze carbon formation under the conditions of the dehydrogenation, and maintaining in the reaction mixture during the dehydrogenation a minimum amount of such a carbon formation-inhibiting agent effective to keep the interior metallic surface of the reaction tube poisoned and substantially inactive to cata-

lyze carbon formation and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.

3. In a process for the dehydrogenation of a non-tertiary alcohol to the corresponding carbonylic compound in the presence of a brass catalyst contained in a steel reaction tube and heated to a temperature of about 500° C., the method of inhibiting the formation of non-asphaltic type carbon catalyzed by the interior surface of the reaction tube which comprises maintaining in the treated alcohol a minimum concentration of hydrogen sulphide effective to inhibit carbon formation by poisoning the interior surface of the metal reaction tube but ineffective to cause any substantial decrease in activity of the catalyst and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.

4. In a process for the catalytic dehydrogenation of a paraffin hydrocarbon to the corresponding hydrocarbon containing fewer hydrogen atoms in the presence of an activated alumina catalyst contained in a steel reaction vessel heated to a temperature of from about 400° C. to about 900° C., the method of inhibiting the formation of non-asphaltic type carbon catalyzed by the interior surface of the reaction vessel which comprises maintaining in the reaction vessel during the dehydrogenation a concentration of hydrogen sulphide effective to inhibit carbon formation by poisoning the interior surface of the metal reaction vessel but not sufficiently high to cause any substantial decrease in activity of the catalyst and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.

5. In a process for the catalytic dehydrogenation of isobutane to isobutylene in the presence of an activated alumina catalyst contained in a steel alloy reaction tube and heated to a temperature of from about 500° C. to about 800° C., the method of inhibiting the formation of non-asphaltic type carbon catalyzed by the interior surface of the reaction tube which comprises adding hydrogen sulphide to the treated isobutane in an amount sufficient to maintain a concentration of about 0.5% hydrogen sulphide in the reaction mixture in the reaction tube during the dehydrogenation and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.

6. In a process for the catalytic dehydrogenation of a butane to butylene in the presence of an activated alumina catalyst contained in a steel alloy reaction tube and heated to a temperature of from about 500° C. to about 800° C., the method of inhibiting the formation of non-asphaltic type carbon catalyzed by the interior of the reaction tube which comprises pretreating the reaction tube packed with the catalyst by heating it to a temperature of about 500° C. to about 800° C. and passing hydrogen sulphide through it for a time adequate to poison the interior surface of the reaction tube and render it substantially inactive to catalyze carbon formation during the execution of the dehydrogenation reaction and executing said catalytic dehydrogenation reaction wherein dehydrogenation predominates and cracking is substantially obviated.