

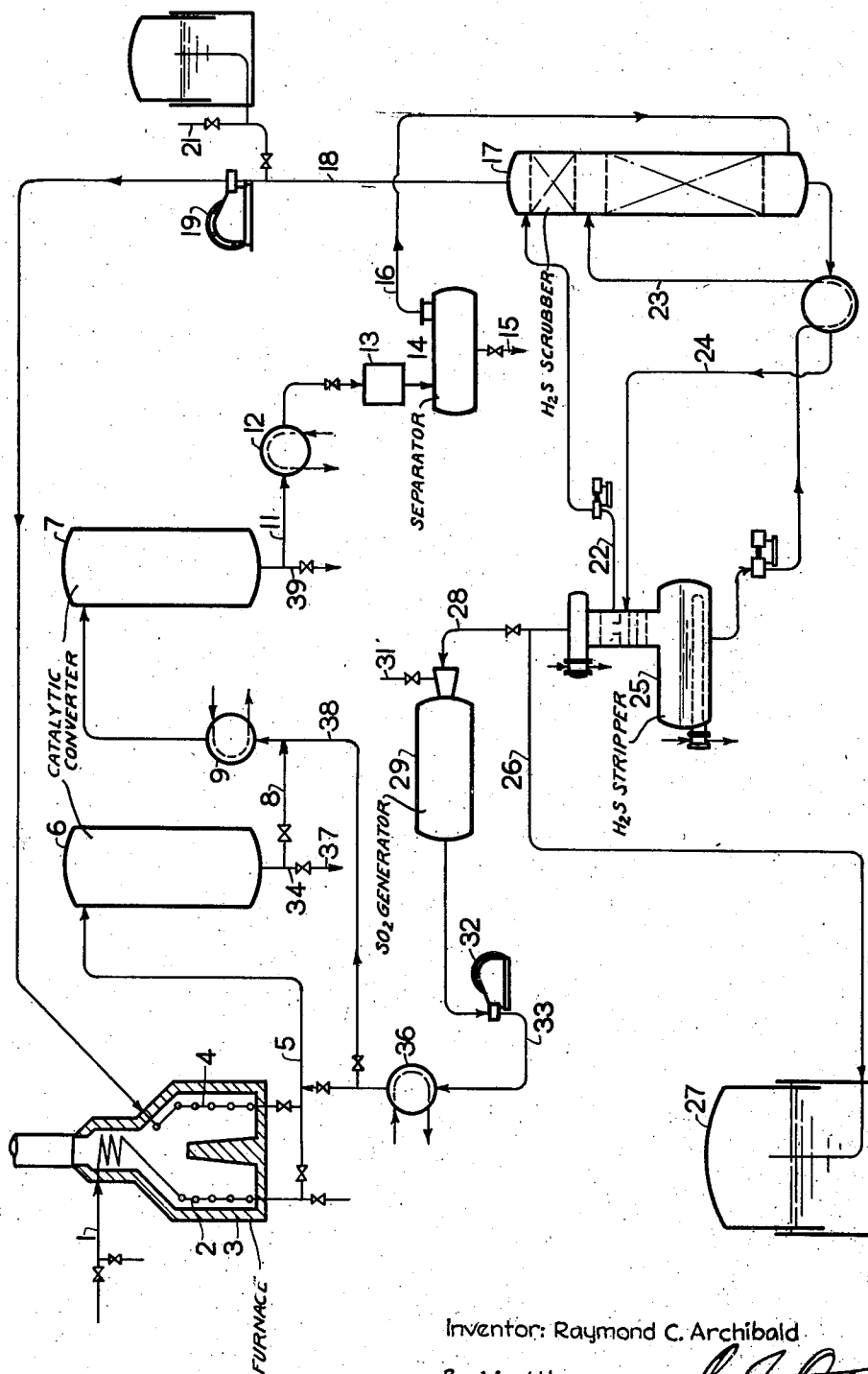
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to an improvement in the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with sulf-active catalysts consisting essentially of piled dehydrogenating metal sulfides. More particularly, the invention relates to a method for increasing the effective life of the catalyst in said processes by a periodic treatment of the catalyst *in situ*.

As is known, there is a great demand for an economical and practical process for the catalytic dehydrogenation of the lighter hydrocarbons such as hydrocarbons boiling within the gasoline boiling range. Most of the hydrocarbon materials which it is desired to treat by catalytic dehydrogenation are derived from petroleum and/or coal tar distillates and contain from traces to appreciable amounts of sulfur compounds. A practical catalytic process suitable for use with these hydrocarbon materials therefore requires the use of a sulf-active catalyst. Many processes have been developed wherein these various hydrocarbon materials are treated using dehydrogenating metal oxide catalysts. In general, the dehydrogenating metal oxides are very active dehydrogenating catalysts at elevated temperatures and are employed in relatively small amounts supported upon major amounts of suitable adsorptive carriers such, in particular, as active alumina. Some of these proposed processes are suitable for certain applications. All of them, however, have the great disadvantage that they require so-called "short cycle" operation. When using these metal oxide type catalysts, it is invariably necessary when effecting catalytic dehydrogenation to stop the process every few hours and burn off the deposited carbonaceous materials with oxygen or an oxygen-containing gas. This periodic regeneration of the catalyst is not only time-consuming and costly but materially decreases the production capacity per catalytic converter. Furthermore, the periodic regeneration by burning carbonaceous deposits with air subjects the apparatus to frequent temperature change and alternate oxidizing and reducing conditions. This requires that these processes be effected in apparatus constructed of special steels or alloys. The rate of deposition of carbonaceous materials upon the catalyst in certain processes can be repressed to a certain extent by the use of hydrogen pressure. This, however, is generally considered impractical inasmuch as under high hydrogen pressures the dehydrogenation reaction is usually considerably repressed. On the other hand, very excellent sulf-active catalysts which may be applied under very high hydrogen pressures have been developed particularly for use in destructive hydrogenation of higher boiling hydrocarbons. One type of such catalysts consists essentially of a mixture of metal sulfides. Under the

conditions for which these catalysts were intended, that is, for destructive hydrogenation, considerable hydrogen pressures prevail and there is little deposition of carbonaceous material. Consequently, under these conditions these catalysts have a very long active life. Furthermore, in the destructive hydrogenation when the catalyst is finally spent, the valuable components are recovered and regenerated. The regeneration in this case is, however, not similar to that employed in the above-mentioned oxide type catalyst but consists in an entire remaking of the catalyst.

It is found that the above-described sulf-active catalysts are very suitable for the catalytic dehydrogenation of lighter hydrocarbons, for example, dehydrogenatable hydrocarbons boiling in the gasoline boiling range. In the use of these catalysts for this purpose, dehydrogenation rather than hydrogenation conditions prevail, carbonaceous materials gradually deposit upon the catalyst, and in time the dehydrogenation activity of the catalyst declines. Since, however, in the dehydrogenation of such hydrocarbons with catalysts of this type certain quantities of hydrogen, for instance 1 to 50 atmospheres, are suitably employed, the deterioration of the catalyst by carbonaceous deposits is very slow. These catalysts may therefore be employed for the dehydrogenation of these hydrocarbons over relatively long periods, for instance 400 hours, before regeneration of the catalyst is necessary. This, it will be seen, is a distinct advantage over the use of the above-described oxide type catalyst.

These sulf-active metal sulfide catalysts can be applied to carrier materials, as described, for the oxide type catalysts and, in such cases, can be regenerated by conventional means, that is, by burning off the carbonaceous deposits with air. During such regeneration, however, the metal sulfides are converted to the corresponding oxides and after the carbonaceous deposits have been removed, it is necessary to subject the catalyst to a thorough sulfurization. This latter step is often difficult and costly. These sulf-active metal sulfide catalysts, however, are not as active as the corresponding oxide catalysts for dehydrogenation and therefore it is preferred to use them in a much more concentrated form, such, for instance, as in the form of pellets consisting largely of the active metal sulfides. However, no method has hitherto been known whereby such pellets which have been deactivated in the catalytic dehydrogenation could be readily reactivated. The usual methods involving burning off of the carbonaceous deposits with oxygen or oxygen-bearing gases cause the pellets to lose strength and crumble. Oxygen-containing gases such as air, steam, etc. are furthermore unsuit-

able for the reason that they convert the metal sulfides to the corresponding metal oxides.

In copending application Serial No. 434,893, filed March 16, 1942, of which the present application is a continuation-in-part, there is described and claimed a method whereby these pelleted metal sulfide catalysts may be advantageously reactivated. According to the method more fully described in said copending application, catalysts consisting essentially of the above-described dehydrogenating metal sulfides, when deactivated in the catalytic dehydrogenation of hydrocarbons, are advantageously reactivated in situ by treatment with sulfur dioxide. Whereas regeneration by oxygen causes the catalyst pellets to immediately crumble, repeated reactivation of the catalyst with sulfur dioxide leaves the pellets substantially unaffected in physical shape and strength. Furthermore, the use of sulfur dioxide to reactivate the above-described sulfide catalysts does not cause substantial oxidation of the metal sulfides and does not require a subsequent re-sulfurization of the catalyst. Furthermore, the reactivation of these catalysts with sulfur dioxide is very effective, may be effected in a very short time, and does not require substantial change in the temperature conditions in the reactor.

It is now found that a gas mixture comprising sulfur dioxide and hydrogen sulfide is particularly excellent for effecting the reactivation. In the use of such gas mixtures all danger of oxidation of the catalyst or the reactor walls is eliminated. Also, due largely to the large heat capacity of hydrogen sulfide, the reactivation may be effected at a more rapid rate without causing deterioration of the catalyst by local overheating. Furthermore, as will be described in more detail below, mixtures comprising these gases which are particularly suitable may be easily obtained as a by-product from the conversion process.

The present activation treatment is applicable to any of the pelleted dehydrogenating metal sulfide catalyst of the above-described type. It is especially suitable for the treatment of dehydrogenating metal sulfide catalysts consisting essentially of a sulfide of a metal selected from Group VI of the Periodic System and a sulfide of a metal selected from Group VIII of the Periodic System. For example, it is especially suitable for use with catalysts consisting essentially of a pelleted mixture of tungsten sulfide and nickel sulfide. These metal sulfides when pelleted in the pure form often yield hard strong pellets having a metallic luster. In certain cases, however, the use of a small amount of one of the many known binders is advantageous. Also, the dehydrogenating metal sulfide or mixture of such sulfides may be pelleted in admixture with a minor amount of a relatively inert material such as a powder of alumina, kieselguhr, clay or the like. In the appended claims when referring to these catalysts the expression "consisting essentially of" is not meant to exclude minor amounts of such extenders in the catalyst pellets.

These catalysts are especially suitable and may be employed for the dehydrogenation of dehydrogenatable liquid hydrocarbons boiling in the gasoline boiling range such, in particular, as naphthenic hydrocarbons and naphthenic gasoline fractions. Suitable conditions applicable for the catalytic treatment of these various hydrocarbons and/or hydrocarbon mixtures with catalysts

of this type are, for example, approximately as follows:

Temperature	-----°C	425-525
Total pressure	-----atm	10-50
Ratio of hydrogen to hydrocarbon		
feed	-----mols/mol	2-20
Liquid hourly space velocity	-----	0.5-5

After the catalyst has been used on-stream for some time the activity gradually declines to a point where it is desirable to subject it to a regeneration or reactivation treatment. The hydrocarbon feed is discontinued and excess hydrocarbons purged from the catalyst, preferably with hydrogen or with an inert gas. The catalyst activity is then restored by a treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide. The ratio of sulfur dioxide to hydrogen sulfide in the gas mixture may vary widely. Even a small amount of hydrogen sulfide in the sulfur dioxide is sufficient to prevent oxidation of the catalyst by any contaminating air or oxygen. Larger amounts allow the gas mixture to be passed through the catalyst bed at high rates without danger of overheating the catalyst. Also, the gas mixture may contain one or more inert gases such as nitrogen, carbon dioxide or the like. Very suitable gas mixtures may, if desired, be prepared by burning hydrogen sulfide with an insufficient amount of air. The concentration of hydrogen sulfide and sulfur dioxide in the gas may be adjusted and controlled by adjusting and controlling the concentration of oxygen in the oxygen-containing gas, for instance, by adding a diluent to air, and by adjusting and controlling the ratio of hydrogen sulfide to oxygen-containing gas. Also, if desired, the concentrations of sulfur dioxide and hydrogen sulfide in the combustion gases may be reduced to any desired low concentration by adding a diluent gas, such as recycled spent regeneration gas, flue gas, or the like. This can also be effected, if desired, by burning a suitable quantity of a hydrocarbon such as natural gas with the hydrogen sulfide.

The time required for the reactivation treatment depends upon several factors such, in particular, as the amount of catalyst, the length of the catalyst bed, the concentration of sulfur dioxide in the gas mixture, the rate of addition of the gas mixture, and the temperature. One of the advantages of the present process, however, is that the activation may be effected in a very short time. Thus, the reactivation requires, in general, only a fraction of the time required to regenerate oxide catalysts with oxygen-containing gases. For example, converters of conventional size and design may usually be reactivated in one-half to four hours. Longer periods of reactivation such as five to ten hours are, however, in no way detrimental. During reactivation treatment very little sulfur dioxide is usually found in the exit gas. When the sulfur dioxide passes through the catalyst mass and appears in the exit gas the reactivation is usually substantially complete.

The reactivation of the above-described pelleted catalysts according to the present process is exothermic. When applying the process to large masses of the catalyst the rate of passage of the gas mixture through the catalyst bed is therefore controlled to avoid deactivation of the catalyst by local overheating.

A great advantage of the present process is that the reactivation may be effected in situ over

a wide range of temperatures. The reactivation according to the present process may therefore be conveniently effected at the temperature at which the catalyst is employed in the dehydrogenation. Thus, for example, when effecting the dehydrogenation process in the above-mentioned temperature range of 425° C.-525° C., the reactivation may be effected at the reaction temperature. Thus, the delays in bringing the reactor from the reaction temperature to a different reactivation temperature, and vice versa, are avoided. Also, the cost of heating and cooling and the detrimental effect of substantial temperature changes on the reactor and the catalyst are avoided. The temperature of the reactivation may, however, if desired, be above or below the reaction temperature. The maximum reactivation temperature depends upon the thermal stability of the catalyst. With most catalysts of the type in question, temperatures up to about 750° C. may be applied. In general, however, no advantage is gained in applying temperatures above about 600° C. The minimum applicable temperature also depends somewhat upon the catalyst. In the reactivation of the spent catalyst with the sulfur dioxide-hydrogen sulfide mixture, a pronounced heat effect is observed. The minimum applicable temperature is the lowest temperature above 400° C. at which this heat effect is observed. In case it is desired to effect the reactivation at the lowest possible temperature, the gas mixture may be passed through the catalyst mass at a low temperature and the temperature gradually raised until the heat effect is observed. The reactivation is, in general, preferably effected at temperatures above 400° C. where the reactivation is considerably faster.

The reactivation may be effected at any desired pressure. Ordinary pressures are, however, quite suitable and little advantage is gained in applying higher pressures.

As mentioned above, very suitable gas mixtures comprising sulfur dioxide and hydrogen sulfide may be advantageously obtained as by-products of the process. As pointed out, most of the hydrocarbonaceous materials which it is desired to treat with the above-described catalysts contain from small to appreciable amounts of sulfur compounds. Under the reaction conditions employed a considerable proportion of the sulfur is converted to hydrogen sulfide. This hydrogen sulfide which forms in the reaction accumulates in the recycled hydrogen. A small amount of hydrogen sulfide in the recycled hydrogen is usually not detrimental and may in some instances be beneficial. Any appreciable concentration of hydrogen sulfide in the recycled hydrogen, however, is detrimental since it causes lowered conversions. This hydrogen sulfide may be advantageously recovered from the recycled hydrogen, thereby maintaining the conversion at an optimum level. Furthermore, the recovered hydrogen sulfide may be burned with an insufficient amount of oxygen to produce a gas mixture comprising sulfur dioxide and hydrogen sulfide, which gas mixture is particularly excellent for effecting the reactivation of the catalyst.

One application of this modification of the process of the invention is illustrated in the attached drawing wherein there is shown by means of conventional figures not drawn to scale one assembly of apparatus wherein the process may be advantageously applied. The drawing will be

described in connection with the description of an operation within the scope of the invention. Referring to the drawing, the hydrocarbon feed to be treated, for instance a mixture of a straight run naphthenic gasoline fraction and an olfinic reformed gasoline fraction, said mixture containing about 0.1%-0.5% sulfur, is passed via line 1 to a coil 2 in furnace 3 wherein it is vaporized and heated to a suitable temperature. Recycle hydrogen is preheated in coil 4 in the furnace and then mixed with the hydrocarbon vapors in a ratio of, for instance, about 3:1 to 7:1. The temperatures of the hydrocarbon vapors and recycled hydrogen are adjusted such that the mixture is at about the desired reaction temperature, for instance 430° C.-500° C. The mixture of hydrogen and hydrocarbon vapors under a pressure of, for instance, 600-700 p. s. i. passes via line 5 to a series of catalytic converters 6 and 7, the liquid hourly space velocity of the hydrocarbon being, for instance, between about 1 and 4. (Liquid hourly space velocity, for the purpose of the present description, is defined as the volumes of hydrocarbon feed, measured as a liquid, passed through a given volume of catalyst per hour.) The converters 6 and 7 are filled with suitably supported beds of a sulf-active metal sulfide catalyst, for instance, consisting essentially of an intimate mixture of 2 mol parts of nickel sulfide and 1 mol part of tungsten sulfide, preferably in the form of pellets. The reaction mixture of hydrocarbon vapors and recycled hydrogen, after passing through the first bed of catalyst, are withdrawn via line 8, passed through heat exchanger 9, and then passed through converter 7. The reaction mixture is withdrawn from converter 7 via line 11, passed through heat exchanger 12, condenser 13, and then passed to a separator 14, wherein the liquid hydrocarbon product is separated from the gaseous fraction consisting mostly of hydrogen. The liquid hydrocarbon fraction is withdrawn via line 15. The gaseous fraction contains hydrogen sulfide produced by desulfurization of the hydrocarbon charge. This fraction is withdrawn via line 16 and treated to separate the hydrogen sulfide. This may be effected in a number of known manners. One excellent method is, for example, by means of the Shell Phosphate Process (see Refiner and Natural Gasoline Manufacturer, September 1941). Thus, the gaseous fraction is scrubbed with a potassium phosphate solution in a scrubber 17. The gas consisting mainly of hydrogen from which hydrogen sulfide has been substantially removed is recycled via line 18 and compressor 19 to the heating coil 4 and back to the process. Line 21 is provided for adding hydrogen to the system and/or for withdrawing hydrogen in excess of that desired for recycling. The potassium phosphate solution enters scrubber 17 via lines 22 and 23 and is withdrawn via line 24 to stripping apparatus 25 wherein the hydrogen sulfide is released and separated. The hydrogen sulfide is withdrawn via line 26 to an accumulator 27. The potassium phosphate solution is recycled in a known manner.

When it is desired to reactivate the catalyst in the converters, the hydrocarbon flow is stopped or directed to a unit not shown. Hydrogen sulfide gas from the stripper 25 and/or from the accumulator 27 is passed via line 28 to a sulfur dioxide generator 29 wherein it is burned with air or oxygen introduced via line 31. The ratio of hydrogen sulfide to air or other oxygen-containing gas

applied is adjusted such that after combustion there is an excess of hydrogen sulfide. The gas mixture comprising, for example, 5% sulfur dioxide and 4% hydrogen sulfide is passed via compressor 32, line 33, and heat exchanger 36 to line 5 leading to converter 6. The exit vapors from converter 6 may be withdrawn via line 37 or may, if desired, be passed through converter 7. A separate portion of the gas mixture is passed via line 38, line 8 and heat exchanger 9 to converter 7. The effluent gas may be withdrawn via line 39.

The assembly of apparatus illustrated in the drawing and described above may be modified in many ways. Thus, for example, three or more converters may be applied either in series or in parallel, or two or more separate banks of converters may be used. Also, converters of various designs may be employed and the exchanger 9 may sometimes be eliminated. If desired, the combustion of the hydrogen sulfide may be effected under pressure. Also, it may be effected continuously, if desired, and the gas mixture stored in an accumulator during the processing. Other variations and modifications will be apparent to those skilled in the art.

I claim as my invention:

1. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of dehydrogenating metal sulfide, the improvement which comprises periodically restoring the activity of the catalyst by treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

2. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of a sulfide of a metal of Group VI of the Periodic System and a sulfide of a metal of Group VIII of the Periodic System, the improvement which comprises periodically restoring the activity of the catalyst by treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

3. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of tungsten sulfide and a sulfide of a metal of Group VIII of the Periodic System, the improvement which comprises periodically restoring the activity of the catalyst by treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

4. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of tungsten sulfide and nickel sulfide, the improvement which comprises periodically restoring the activity of the catalyst by treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

5. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of

sulfides of tungsten and nickel containing the tungsten and nickel in a mol proportion of about 1:2, the improvement which comprises periodically restoring the activity of the catalyst by treatment with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

6. In a process for the catalytic treatment of hydrocarbons boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of dehydrogenating metal sulfide, the improvement which comprises periodically restoring the activity of the catalyst by treatment at a temperature between about 400° C. and 600° C. with a gas mixture comprising sulfur dioxide and hydrogen sulfide produced by burning hydrogen sulfide with an insufficient amount of oxygen for complete combustion.

7. In a process for the catalytic treatment of a sulfur-bearing hydrocarbon fraction boiling in the gasoline boiling range with the aid of a sulf-active catalyst consisting essentially of pellets of dehydrogenating metal sulfide wherein hydrogen is recycled through the reaction zone, the improvement which comprises continuously separating hydrogen sulfide from the recycled hydrogen and periodically restoring the activity of the catalyst by treatment at a temperature between about 400° C. and 600° C. with a gas mixture comprising sulfur dioxide and hydrogen sulfide produced by burning said separated hydrogen sulfide with an insufficient amount of oxygen for complete combustion.

8. The process for restoring the dehydrogenating activity of a sulf-active catalyst consisting essentially of pellets of dehydrogenating metal sulfide which has been deteriorated by non-halogen containing deposits, which comprises treating said catalyst with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

9. The process for restoring the dehydrogenating activity of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of a sulfide of a metal of Group VI of the Periodic System and a sulfide of a metal of Group VIII of the Periodic System which has been deteriorated by non-halogen containing deposits, which comprises treating said catalyst with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

10. The process for restoring the dehydrogenating activity of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of tungsten sulfide and a sulfide of a metal of Group VIII of the Periodic System which has been deteriorated by non-halogen containing deposits, which comprises treating said catalyst with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

11. The process for restoring the dehydrogenating activity of a sulf-active catalyst consisting essentially of pellets of an intimate mixture of tungsten sulfide and nickel sulfide which has been deteriorated by non-halogen containing deposits, which comprises treating said catalyst with a gas mixture comprising sulfur dioxide and hydrogen sulfide at a temperature between about 400° C. and 600° C.

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