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EXECUTION OF CATALYTIC CONVERSIONS
IN THE PRESENCE OF FERROUS METALS

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The present invention relates to the catalytic conversion of organic materials in the vapor phase at elevated temperatures in the presence of ferrous metals. A particular aspect of the invention relates to the treatment of hydrocarbon vapors at elevated temperatures, i. e. from about 500° 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 conversions of organic materials 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 carbonaceous reactant therethrough under appropriate conditions of temperature, pressure, etc. In most cases when treating carbonaceous materials at temperatures of the order of 500° 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 catalysts for these various conversions are susceptible to poisoning by iron. These various catalysts, when used for the vapor phase conversion 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 these various conversions are often executed under pressure and since, furthermore, they generally require the introduction or with-

drawal of considerable quantities of heat, usually through the confining walls of the reaction zone, 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 proven 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.

We have now found a simple, practical and effective method whereby the contamination of these catalysts with iron, when used in such processes in contact with ferrous metals, may be substantially obviated. By the use of our method these processes may be executed in apparatus constructed of the more common, less expensive

steels and ferrous alloys such as the common KA2, KA2S, KA2MoT, KA2Cb, KA2Mo, and KA2ST steels, while at the same time avoiding all substantial contamination of the catalyst by iron. According to the method of our invention, this is effected by maintaining certain specific concentrations of sulfur compounds in the reaction zone.

It is generally known that when treating organic vapors at these elevated temperatures 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 takes 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 a 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. During only about 18 (and 38) process cycles the catalyst became contaminated with 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 0.35%) 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 containing 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 following iron contents of the catalyst after 200 process cycles were found:

Sulfur in feed	Iron in catalyst
Percent	Percent
0.0006	0.17
0.014	0.04
0.063	0.38

A similar series of experiments were made by adding various amounts of carbon disulfide, thiophene, sulfur trioxide, sulfur dioxide, ethyl mercaptan, and hydrogen sulfide. 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:

COS	0.0006-0.015
R-S-R	0.005-0.015
R-S-H	0.0005-0.003
SO ₃	0.002-0.015
SO ₂	0.002-0.015
CS ₂	0.002-0.008
H ₂ S	0.002-0.006
Thiophene	0.002-0.015

While the contamination of the catalyst by iron may be avoided by the presence of appropriate concentrations of sulfur compounds generally, we have found that all types of sulfur compounds are not equally effective. The most preferred sulfur compound is carbonyl sulfide. This compound is considerably more effective than any of the others tested. Slightly less preferred but still very effective are sulfur trioxide, thiophenic sulfur compounds, and dialkyl sulfides. Considerably less effective than these are the mercaptans, sulfur dioxide, carbon disulfide, and hydrogen sulfide. Surprisingly enough, hydrogen sulfide was the least effective of all sulfur compounds tested. Thus, when treating propane containing hydrogen sulfide under the above-described conditions with the optimum concentration of hydrogen sulfide (corresponding to 0.003% sulfur) the iron content of the catalyst after 200 process cycles was 0.11%. Comparing this figure with that shown in Example I, it is seen that hydrogen sulfide is effective. Comparing it with Example III, however, it is seen that it is not

nearly as effective as carbonyl sulfide. According to a preferred embodiment of the invention, therefore, a reducible sulfur compound, i. e. a compound other than hydrogen sulfide, is employed. Other metalloid compounds, such as the corresponding selenium and tellurium compounds, arsine, phosphine and the like, function in the same manner as the sulfur compounds, although usually to a lesser extent. Since the sulfur compounds are the most efficient and most practical compounds to use these other metalloid compounds are of much less practical interest.

The process of the present invention is generally applicable in the conversion of organic or carbonaceous materials in the vapor phase at elevated temperatures at least equal to 500° F. wherein the conversion is executed in ferrous metal equipment with the aid of catalysts which are affected by contamination with iron. It is particularly advantageous in all such processes where the catalyst is periodically regenerated in situ by burning off deposited tarry materials since in these processes the tendency for iron contamination is more pronounced. The present process is also most advantageous for such of these processes as are endothermic since in these processes the metal confining walls are usually heated, and this likewise increases the tendency for the catalyst to become contaminated by iron. Particular processes for which the present process is exceptionally well suited are, for example, the dehydrogenation of hydrocarbons such, for instance, as the catalytic dehydrogenation of propane, butane, pentane, cyclohexane, etc., to the corresponding olefines and/or diolefines, the catalytic cyclization of normally liquid paraffin hydrocarbons, the reforming of gasolines and light petroleum fractions, and the like.

The process of the invention is applicable with all solid catalysts which are employed at temperatures above about 500° F. with organic vapors and are affected by contamination by iron. As examples of such catalysts there may be mentioned by way of illustration the many catalysts comprising one or more of the metals, Ti, Zr, Ce, Th, V, Nb, Ta, Cr, Mo, W, U, and Mn, or the oxides thereof. These catalysts often contain minor percentages of these metals or compounds thereof such, for example, as the molybdates, tungstates, chromates, chromites, manganates, etc., in combination with major amounts of relatively inert materials such, for example, as alumina, magnesia, zirconia, fuller's earth, zeolites, permutites, active carbon, etc. They are usually substantially free of iron, cobalt and nickel. A preferred group of catalysts is, for example, the dehydrogenation catalysts such, for instance, as those comprising chromium oxide, and/or molybdenum oxide, and/or tungsten oxide, and alumina. These catalysts are exceptionally suitable for the dehydrogenation of hydrocarbons, the reforming of gasolines and the cyclization of aliphatic hydrocarbons, but suffer considerably from iron contamination when employed in ferrous metal equipment. Certain of the above-mentioned catalysts, it is known, are susceptible to poisoning by sulfur. It is found, however, that these catalysts are usually substantially unaffected by the small concentrations of sulfur compounds employed in the process of the invention. This is especially true when the sulfur compound, according to the present invention, is employed in the form of car-

bonyl sulfide. This compound and, to a lesser extent, dialkyl sulfides and sulfur trioxides are much less prone to cause sulfur poisoning than are, for example, sulfur dioxide, mercaptans, carbon disulfide, etc., and are infinitely less toxic than hydrogen sulfide. In fact, the reason why carbonyl sulfide, dialkyl sulfides and sulfur trioxide are less toxic is believed to be due to the fact that they are not converted in the process to any substantial extent to hydrogen sulfide, whereas mercaptans, carbon disulfide, etc., are often converted largely to hydrogen sulfide.

The contamination of the catalyst by iron in the execution of these various reactions 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 inability to withstand the more or less severe reaction conditions. Particularly suitable materials which may be used to considerable advantage, according to the present invention, 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 very expensive and difficult workable high-chrome steels such as 27 Cr, etc. These latter materials, although definitely superior to most low-chrome steels, are nevertheless far from satisfactory and cause iron contamination after a relatively short period of time. When these materials are used, according to the process of the present invention, any of these steels may be employed indefinitely without any appreciable tendency to cause iron contamination.

Many of the organic materials serving as reactants in the processes in which the present invention may be employed normally contain small to appreciable amounts of sulfur. It will be appreciated in view of the above, therefore, that in order to secure the advantages of the present method the sulfur content of these materials must be adjusted prior to treatment to within the narrow limits specified above. In such cases where the sulfur content of the feed is normally too low, it is merely necessary to add the required amount of sulfur to bring it within the specified limits. In such cases where the sulfur content is too high, as is often the case when treating petroleum fractions, 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 preferable to take into consideration the type of sulfur compounds present. Most sulfur-bearing petroleum distillates contain appreciable quantities of hydrogen sulfide and mercaptans. According to a preferred embodiment of the invention, less desirable sulfur compounds are substantially removed and the correct amount of a preferred sulfur compound, such as carbonyl sulfide, is added.

Although the sulfur or sulfur compound may be added to the reaction zone separately from the feed or by any other convenient method, the most convenient and practical method for introducing the desired sulfur or sulfur compound is as a vapor mixed with the reactant vapors. Thus, for instance, a normally gaseous sulfur compound may be mixed with the preheated reactant vapors entering the reaction zone or the sulfur com-

pound may be dissolved in a suitable concentration in the liquid feed prior to vaporization thereof. In certain cases a convenient means for dosing the desired concentration of sulfur into the feed is to vaporize the feed and pass the vapors through a bath or solution of the sulfur compound whereupon the sulfur is taken up in proportion to its vapor pressure.

Example V

This example illustrates the exceptional effectiveness of carbonyl sulfide sulfur in preventing iron poisoning of the catalyst and the vast superiority of carbonyl sulfide sulfur over mercaptan sulfur.

A commercial propane fraction containing about 0.007% sulfur, of which 0.0005% was mercaptan sulfur and the remainder was carbonyl sulfide, was treated under the conditions described above for about 1000 process cycles. During this time the conversion to propylene declined from 32% to 26%. The catalyst at the end of the 1000 process cycles analyzed 0.047 iron (initial iron content 0.02(5)%). If the 0.0005 mercaptan sulfur is replaced by carbonyl sulfide sulfur, no increase in the iron contamination of the catalyst takes place and the conversions are increased about 7% of the above value.

Example VI

A commercial propane fraction containing about 0.007% sulfur as carbonyl sulfide was treated with a 10% KOH solution in alcohol to reduce the sulfur concentration to about 0.002%. This material was treated under the conditions described above for about 1000 process cycles. During this time the conversion to propylene declined from 33-34% to 27.5%. The catalyst at the end of the 1000 process cycles analyzed 0.04% iron (initial iron content 0.02(5)%). It is seen from this example that the presence of about 0.002% sulfur as carbonyl sulfide is sufficient to substantially eliminate poisoning of the catalyst with iron.

The foregoing examples are submitted solely to illustrate the process of the invention and the advantageous results obtainable thereby, and are not to be construed as limiting the invention.

We claim as our invention:

1. In a process for the conversion of carbonaceous materials in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

2. In a process for the conversion of carbonaceous materials in the vapor phase in a chrome steel reactor at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

3. In a process for the conversion of carbonaceous materials in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with supported chromium oxide catalyst in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

4. In a process for dehydrogenating carbonaceous material in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a dehydrogenation catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

5. In a process for the dehydrogenation of butane in the vapor phase at an elevated temperature at least equal to 750° F. wherein butane vapors are contacted with a dehydrogenation catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

6. In a process for the dehydrogenation of propane in the vapor phase at an elevated temperature at least equal to 750° F. wherein propane vapors are contacted with a dehydrogenation catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

7. In a process for the catalytic reforming of a petroleum distillate wherein distillate vapors are contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone from 0.0006% to 0.015% sulfur in the form of a volatile oxygenated sulfur compound.

8. In a process for the conversion of carbonaceous materials in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone a quantity of carbonyl sulfide equivalent to from 0.0006% to 0.015% sulfur.

9. In a process for the conversion of carbon-

ceous materials in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone a quantity of sulfur trioxide equivalent to from 0.0006% to 0.015% sulfur.

10. In a process for the catalytic treatment of a petroleum hydrocarbon at an elevated temperature at least equal to 750° F. wherein the hydrocarbon vapor is contacted with a catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which

comprises pretreating the hydrocarbon feed to remove any hydrogen sulfide present and then adjusting the sulfur content of the feed to from 0.0006% to 0.015% by the addition of a volatile oxygenated sulfur compound.

11. In a process for the dehydrogenation of butane in the vapor phase at an elevated temperature at least equal to 750° F. wherein the reactant vapors are contacted with a dehydrogenation catalyst susceptible to contamination by iron in the presence of a ferrous metal and the catalyst is periodically regenerated in situ by the oxidation of combustible deposits therefrom, the step of inhibiting the contamination of the catalyst by iron which comprises maintaining in the feed to the reaction zone a quantity of carbonyl sulfide equivalent to from 0.0006% to 0.015% sulfur.

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