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DESULPHURIZATION PROCESS

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4 Claims. (Cl. 196—24)

This invention relates to catalysts for use in catalytic processes and it has particular relation to catalysts that contain chromium oxide in substantial amount and that have been prepared by the thermal decomposition of ammonium-containing salts of chromic acid. It further relates to the use of such catalysts for the treatment of hydrocarbons at elevated temperatures, particularly sulphur-containing hydrocarbon mixtures under conditions such as to effect desulphurization of such mixtures.

This application is a division of our copending application Serial No. 384,028, filed March 18, 1941, which is in turn a division of our copending application Serial No. 173,708, filed November 9, 1937, that has issued as Patent No. 2,294,414.

Catalysts consisting of or containing chromium oxide have been found useful in various catalytic processes. One method of preparing chromium oxide-containing catalysts has been the ignition of ammonium-containing salts of chromic acid. For example, Lazier in a number of United States patents (for example, Nos. 1,746,783; 1,964,000; 1,964,001; 2,019,419) has described the preparation of catalysts by the heating of a double chromate of a nitrogen base such as ammonia and a hydrogenating metal such as zinc, manganese, copper, nickel, and the like. Heretofore, however, the ignition conditions have not been considered to be of particular significance and therefore have not been subjected to definite control, with the consequence that the chromium oxide formed in this manner simultaneously underwent glowing or calorescence and thereby certain desirable properties were unwittingly destroyed in the catalyst. Thus, if a double chromate of ammonia and a hydrogenating metal is heated to a temperature at which a spontaneous exothermic decomposition takes place, in accordance with the teaching of the Lazier patents, generally at a temperature between about 200° and 400° C., there results an evolution of sufficient heat to leave a glowing residue. The resulting glowed or caloresced residue is noncoherent or finely divided and powdery in texture and therefore must generally be compressed or briquetted into suitable form for use. It consists substantially of the at least partially chemically combined oxides of chromium and of the hydrogenating metal of the original double salt in the form of a chromite, the chromium having been substantially completely reduced by the spontaneous decomposition from the hexavalent state present in chromates and dichromates to the trivalent state present in chromites. The spontaneous decomposition is generally very rapid and is always complete within a few minutes or at most within an hour or so and not infrequently it proceeds, as in the cases of ammonium chromate and ammonium dichromate, with explosive violence.

Chromium oxide catalysts prepared by ignition of ammonium dichromate have been described by Lazier and Vaughen in an article, "The catalytic properties of chromium oxide," published in the Journal of the American Chemical Society, vol. 54, August, 1932, pp. 3080–3095. The ignition resulted in the formation of a fluffy oxide having a tea-leaf appearance and exhibiting erratic catalytic behavior when tested for the hydrogenation of ethylene. It was non-homogeneous, as evidenced by the presence of particles of different colors, that is, dark colored particles which appeared to possess some catalytic activity and bright green particles which were apparently completely inactive. The green particles, whose formation appeared to be favored by ignition in deep layers, did not exhibit the glow phenomenon but the dark and active material glowed feebly when heated to 500° C. The best product obtained in this way by Lazier and Vaughen was prepared by warming one-gram portions of ammonium dichromate in a thin layer over a flame until ignition was initiated. The resulting oxide was granulated by briquetting. A 20-cc. portion of this best product, when tested at 400° C. with a 7-liter sample of an equimolar hydrogen-ethylene mixture passed over the catalyst in an hour, or at a space velocity of about 350, gave a conversion of 80 per cent of the ethylene into ethane. In preparing another sample of catalyst, Lazier and Vaughen heated ammonium dichromate in a vacuum at 200 to 250° C. for 4 or 5 hours. The product was a glistening black residue which contained no ammonia, was slightly paramagnetic and was stable at temperatures up to 400° C. but when further heated it suddenly glowed, leaving a light green residue without catalytic activity for ethyene-hydrogenation. A 20-cc. portion of the unglowed material, when tested at 400° C. with a 7-liter sample of an equimolar hydrogen-ethylene mixture passed over the catalyst in an hour, caused a conversion of 25 per cent of the ethylene into ethane. A similar portion, which had undergone glowing by being heated in a vacuum to 500° C., gave a conversion of only 3 per cent.

Such hitherto available catalysts prepared by ignition of ammonium-containing salts of chromic acid have found considerable application in reactions such as the synthesizing of methanol from oxides of carbon and hydrogen. They have

also found limited application in the hydrogenation of certain organic materials and in the dehydrogenation of alcohols to aldehydes. But although these hitherto available chromium oxide-containing catalysts have been more or less satisfactory for the conversion of oxygenated organic compounds such as alcohols and the oxides of carbon, they have been entirely inadequate for the conversion of certain organic compounds such as hydrocarbons. For this reason, they have been generally unsuited for the conversion of hydrocarbons by changing their carbon-to-hydrogen ratios and particularly so for the dehydrogenation of paraffin hydrocarbons into mono-olefins of the same number of carbon atoms. This inadequacy is well illustrated by the aforementioned conversion figures obtained by Lazier and Vaughen when they are compared with thermodynamic data. Thus, if equilibrium had been attained under the stated conditions of temperature and gaseous composition, a conversion of 99 per cent of the ethylene to ethane should have been obtained whereas a maximum of only 80 per cent was actually reached, in spite of the fact that the relatively low space velocity used was very favorable for the attainment of equilibrium.

It is an object of our invention to overcome the hereinbefore mentioned defects and difficulties of the prior art in preparing and using catalysts which contain substantial proportions of chromium oxide.

It is a further object to effect the controlled and nonspontaneous thermal decomposition of ammonium-containing salts of chromic acid.

Another object is to prepare catalytic materials in which the chromium oxide is substantially completely in the form of black and unglowed chromium oxide.

It is a further object to obtain chromium oxide-containing catalytic materials in a dense but porous, coherent and granular, and mechanically strong pseudocrystalline and crystallomorphous form directly suitable for use without compression or briquetting.

It is also an object to obtain catalysts containing black unglowed chromium oxide with a high resistance to the glow phenomenon, so that they can be heated to temperatures above 400° or 500° C. without loss of catalytic activity due to glowing.

Another object is to obtain such desirable catalysts uniformly and at will, without the formation of substantial amounts of green and inactive chromium oxide.

Another object is to carry out catalytic processes by the use of these catalysts derived through the nonspontaneous and controlled thermal decomposition of ammonium-containing salts of chromic acid.

Another object is to provide a process for the treatment of a hydrocarbon material which contains organic sulphur compounds to reduce the sulphur content thereof.

Further objects and advantages of our invention will be apparent to those skilled in the art from the following description.

We have found that it is possible to effect a slow thermal decomposition of ammonium-containing salts of chromic acid under controlled temperature conditions that do not cause spontaneous or explosive decomposition to take place, and that our procedure leads to the preparation of chromium oxide-containing catalysts that are definitely superior to the catalysts of the prior art in catalytic and mechanical properties. We have further found that the residue from such slow, controlled and nonspontaneous thermal decomposition, after being subjected to a controlled reduction retains its form and appearance at elevated temperatures, and is not readily subject to the glow phenomenon, which destroys the catalytic activity of such materials. For example, in the case of the nonspontaneous thermal decomposition of crystalline ammonium salts of chromic acid carried out in the light of our discoveries, the product is a porous but dense and coherent, and fairly hard pseudocrystalline or crystallomorphous granular residue retaining the apparent or gross crystalline shape of the original ammonium salt. The salt granules or crystals shrink appreciably during the nonspontaneous decomposition, and the product retains a small proportion of ammonia and of water derived from oxidation of a part of the ammonium in the original salt. The total chromium oxide of the residue has an approximate empirical formula of CrO_2, indicating that the chromium is, either actually or on the average, in a tetravalent state. The presence of chromium having a valence greater than three is readily observable by dissolving a portion of the catalyst in hot dilute sulphuric acid, cooling, and adding potassium iodide, whereupon iodine is liberated. Under the same conditions, trivalent chromium does not cause any liberation of iodine.

Before the residue from the nonspontaneous thermal decomposition is used as a catalyst in reactions such as changing the carbon-hydrogen ratios of hydrocarbons or for the desulphurization of sulphur-containing hydrocarbon distillates it is reduced and it is generally preferable to subject it to a controlled reduction in the presence of an atmosphere consisting of or containing a reducing gas or gases. After reduction, advantageous conditions for which are hereinafter described, the black, unglowed and crystallomorphous residue from the nonspontaneous thermal decomposition of ammonium salts of chromic acid possesses a high catalytic efficiency for reactions such as dehydrogenation, nondestructive hydrogenation, hydrocarbon desulphurization, and the like. It can be used as a catalyst at all temperatures at which the conversion is thermodynamically high enough to be desirable or profitable, such as temperatures within the range 200 to 600° C. Any carbonaceous deposit formed on it during use can be burned off with air under suitable temperature conditions without destruction of its catalytic activity and it can thereafter be used again. Furthermore, it can be repeatedly used and reactivated without undergoing the glow phenomenon or calorescence that may accompany or follow the spontaneous decomposition of ammonium salts of chromic acid or which may often be induced in other chromium oxide-containing preparations by heating to a temperature above about 400 or 500° C.

Whether or not the chromium oxide or the residue obtained by the nonspontaneous thermal decomposition of our process is truly tetravalent, as the empirical formula CrO_2 implies, is not definitely known by us. We prefer to consider that the residue has a composition that may be expressed by the formula $Cr_2O_3.CrO_3$, which has the same ratio of chromium to oxygen as CrO_2 and which implies that two-thirds of the chromium is trivalent and that one-third is hexavalent. Because of this preference and because of its convenience, we shall hereinafter refer, in the specification and claims, to the chromium of

higher valence than three which is present in the residue from the nonspontaneous thermal decomposition as being hexavalent, it being understood that we do not otherwise limit ourselves.

Advantage of the presence of this hexavalent chromium in the residue may be taken for the purpose of determining when the controlled and nonspontaneous thermal decomposition has reached a satisfactory end point. We have found that the nonspontaneous decomposition should be continued to a point at which the content of hexavalent chromium, as compared with the total chromium, lies within the range of 25 to 40 per cent, as determined by the method to be described directly. In our best preparations the hexavalent chromium content has generally been within the range of 27 to 35 per cent and we prefer that it be within the range of 30 to 33 per cent. Before the decomposition, generally all of the chromium is hexavalent, since a salt of chromic acid is the substance decomposed. Hence, the progress of the nonspontaneous decomposition may be readily followed by withdrawing samples from time to time and analyzing them for total chromium and for hexavalent chromium. The total chromium is determined by taking a weighed portion of the sample, suitably about one gram, gently heating it in an excess of a solution of mercurous nitrate, suitably in 5 cc. of a saturated solution of mercurous nitrate, whereby all of the hexavalent chromium is reduced to the trivalent condition, then evaporating the solution to dryness and igniting the residue strongly to constant weight, whereby all but chromic oxide is volatilized and removed, and finally weighing the residual chromic oxide, Cr_2O_3. The hexavalent chromium is determined by dissolving it out from a second weighed portion, suitably 0.1 to 0.2 gram, of the sample with hot dilute sulphuric acid, suitably with 500 cc. of 6 to 7 per cent sulphuric acid, which may require boiling for 20 to 30 minutes to effect dissolution, then cooling, adding an excess of potassium iodide, suitably 1 to 2 grams, and titrating the liberated iodine with sodium thiosulphate solution of known strength, suitably 0.1 normal, with starch as indicator. From the data thus obtained the percentage of the total chromium found as hexavalent chromium may be readily calculated. The controlled nonspontaneous thermal decomposition is preferably continued until the hexavalent chromium has decreased to approximately one-third of the total chromium, more or less.

In order that the decomposition may not become of the spontaneous character, which we have found to be undesirable and harmful to the catalytic and physical properties of the product, it is essential that the temperature during decomposition be not permitted to exceed about 225° or 230° C. We prefer to carry out the decomposition at temperatures not exceeding about 200° C., since thereby the danger of spontaneous or explosive decomposition is minimized. But it is not desirable to use temperatures much below 175° C., since such lower temperatures needlessly prolong the decomposition period. This is illustrated by the experimental facts that in the nonspontaneous decomposition of a sample of ammonium dichromate in air in an electric oven kept at 200° C. a minimum hexavalent chromium content of 32 per cent of the total chromium was reached in a period of about 15 hours, whereas when the oven was kept at 175° C. this period became about 11 days. For these reasons it is advantageous and preferable to carry out the decomposition at temperatures between about 175° and 200° C. It is possible, however, to decompose successfully ammonium salts of chromic acid at temperatures somewhat above this preferred range, up to about 225° or 230° C., if all conditions are favorable; but generally it is felt that the gain in shortening the period of nonspontaneous decomposition does not compensate for the increased danger of occurrence of the undesired spontaneous decomposition and its attendant destruction of mechanical strength and catalytic activity.

Another reason why it is preferable to use a maximum decomposition temperature not much in excess of 200° C. is that we have found that, if the heating of the nonspontaneously thermally decomposed material is continued in an oxidizing atmosphere such as air, the content of hexavalent chromium as defined herein becomes a minimum and then slowly increases again. For example, in the aforementioned case of the decomposition of ammonium dichromate in air at 200° C., in which a minimum hexavalent-chromium content of 32 per cent of the total chromium was reached in 15 hours, it was found that after a total of 45 hours the content of hexavalent chromium had increased to slightly over 40 per cent of the total chromium. Again, in the also aforementioned case of the decomposition of ammonium dichromate in air at 175° C., in which a minimum hexavalent-chromium content of 32 per cent of the total chromium was reached in 11 days, the hexavalent chromium became 35 per cent of the total chromium after a total period of 14 days. We have found that a content of hexavalent chromium in excess of approximately 35 per cent of the total chromium is undesirable and disadvantageous because there exists a pronounced tendency of the oxide or oxides of such hexavalent chromium, which appear to be formed on continuing the heating in an oxidizing atmosphere beyond the minimum content of hexavalent chromium, to undergo a spontaneous thermal decomposition which causes a destruction of mechanical strength and catalytic activity. For example, if a preparation containing such hexavalent chromium is heated to a sufficiently high temperature, such as a temperature of about 300° C. or more, the higher oxides decompose, sometimes with explosive violence, and the product, if it has not disintegrated into dust, is so fragile that it can be readily crushed or powdered between the fingers and it is practically worthless as a catalyst for dehydrogenation of paraffin hydrocarbons to the corresponding mono-olefins and likewise for hydrogenation reactions.

To avoid the reoxidation which has just been described it is generally advantageous to carry out the controlled and nonspontaneous thermal decomposition in a nonoxidizing or reducing atmosphere. We have found that we can successfully decompose ammonium dichromate and ammonium chromate in atmospheres of hydrogen, nitrogen, ammonia, and carbon dioxide. Hydrogen has the advantage that the reduction of the catalyst, which is necessary before it is ready to be used in a catalytic conversion process, can be carried on simultaneously with the non-spontaneous thermal decomposition. However, great care must be exercised that heat liberated by the reduction, which is highly exothermic, does not raise the temperature high enough to cause spontaneous thermal decomposition of the still unreduced oxides of hexavalent chromium. For this reason, we prefer to carry out the nonspontane-

ous thermal decomposition and the reduction as separate and consecutive steps. During the nonspontaneous decomposition we further prefer to use a flowing atmosphere of an inert nonoxidizing and nonreducing gas of high molar heat such as carbon dioxide because such gases efficiently absorb the heat liberated by any incipient spontaneous decomposition and thus minimize or inhibit the tendency for such undesirable spontaneous decomposition to occur or to continue.

The time required for the nonspontaneous thermal decomposition depends upon the temperature. We have hereinbefore given specific directions for determining when the decomposition is completed and have cited the lengths of representative periods at the two extremes of the preferred range of 175 to 200° C. Within this preferred range a generally suitable period of time for carrying out the controlled and nonspontaneous thermal decomposition may be found by adding to a period of 15 hours an additional period of 10 hours for every degree centigrade that the temperature used lies below 200° C. At lower temperatures, such as in the range of 150 to 175° C., the period would be of the order of two weeks or more and at higher temperatures (up to about 230° C.) it would be of the order of several hours or less, depending on the extent that the temperature used differed from the preferred range.

By similar controlled and nonspontaneous thermal decomposition of mixed or double ammonium-containing salts of chromic acid we may obtain homogeneously commingled catalysts containing chromium oxide that have as other constituents one or more metals or oxides of metals other than chromium. We have, for example, obtained catalytic preparations by slow controlled and nonspontaneous decomposition of the following compounds:

$(NH_4)_2CrO_4.(NH_4)_6.Mo_7O_{24}.4H_2O$
$2(NH_4)_2O.V_2O_5.2CrO_3.7H_2O$
$(NH_4)_2CrO_4.CuCrO_4.2NH_3$
$(NH_4)_2CrO_4.CdCrO_4.2NH_3$

and $(NH_4)_2CrO_4.2VO_2.CrO_4.6H_2O$. We have also used ammonium chromochromate,

$NH_4O.CrO_2.O.Cr.O.CrO_2.ONH_4$

which is an ammonium-containing salt of chromic acid containing also divalent chromium. Due, however, to greater difficulties of preparing these various ammonium-containing salts of chromic acid, their higher cost, and their tendency to form very small crystals or none at all, we do not consider such materials to be as advantageous for making catalysts by nonspontaneous decomposition as simple ammonium salts of chromic acid, such as ammonium chromate or ammonium dichromate. Of the advantageous materials we have found ammonium dichromate to be the more advantageous because of its relatively more desirable, because less elongated, crystalline shape.

With respect to the size of crystals, we prefer a size that passes through a 10-mesh and is retained by a 20-mesh screen; but we do not wish to have our invention limited to this particular size, as other sizes operate almost or equally as well. If the original material available is in the form of crystals larger than desired, they may be broken or crushed to granules of the desired size, preferably but not necessarily before the nonspontaneous thermal decomposition. If it is in the form of crystals smaller than desired, it may be recrystallized to yield larger crystals.

After the nonspontaneous thermal decomposition is complete, the chromium oxide-containing residue is reduced. This may be done with any reducing gas, such as hydrogen, carbon monoxide, butane, propane, and the like, or with an atmosphere containing such a reducing gas or gases. The reduction is preferably carried out as a separate step, but in many cases it may be incorporated as a part of the starting up of a run in which this material is to be used as a catalyst. For example, in a dehydrogenation procedure the material to be dehydrogenated may be passed over the chromium oxide-containing material while the catalyst chamber is in the warm-up period, the material to be dehydrogenated thus acting as the reducing gas. However, it is advantageous to use hydrogen or an atmosphere containing hydrogen as the reducing gas, as therewith the reduction can be carried out at the lowest possible temperature and the possibility of the simultaneous formation of a carbonaceous deposit on the catalyst is avoided. The temperature should not in any case be allowed to rise above about 300° C., and preferably not above about 250° C., before the reduction is complete, since above this temperature thermal decomposition of unreduced higher oxides of chromium is rapid and the catalyst particles may consequently disintegrate into dust and simultaneously lose much or all of their catalytic activity, and so limiting the temperature of reduction is a part of our invention.

Reduction can be carried out at as low a temperature as 175° C. or lower and we prefer to carry out the reduction with the temperature slowly and gradually increasing from below or about this value to one of about 250° C. If desired, room temperature may be the starting point. We further prefer to dilute the reducing gas with an inert diluent gas such as nitrogen or carbon dioxide, as the diluent gas advantageously tends to prevent or minimize any local rise in temperature caused by the reduction, which is highly exothermic in nature. Due to its higher molar heat and its greater tendency to be adsorbed on the catalyst, carbon dioxide is somewhat superior to nitrogen as a diluent gas, as it appears to be capable of absorbing more energy arising from the reduction than is a gas such as nitrogen, probably not only in the form of molecular and intramolecular energy but also in the form of latent heat of desorption. However, the lack of such dilution is not to be considered as going outside the scope of our invention. Completion of reduction can be readily determined by means that are well known to workers in the art, as by determining if water is being formed or by determining if any hydrogen is being consumed. Analyses of the oxide content may also be used for control purposes.

The following example will further illustrate the nature of this invention but the invention is not to be restricted thereby.

Example

As an example illustrating the practice of our invention, we cite the following: A quantity of ammonium dichromate crystals, screened to pass a 20-mesh sieve and to be retained by a 40-mesh sieve, was spread in a thin layer on a hot-plate and was then nonspontaneously decomposed by being heated to 200° C., and kept at this temperature for 16 hours. At the end of this time the

residue consisted of homogeneously black, porous but dense and coherent, and mechanically strong crystallomorphous granules that retained the apparent or gross crystalline shape of the original ammonium dichromate. It contained 33.8 per cent of the total chromium as hexavalent chromium, as previously discussed and defined and as determined by the analytical procedure hereinbefore described. The residue contained considerable ammonia and water which were evolved in the subsequent treatment now to be described. A 5-cc. sample was placed in a vertical catalyst chamber made from a piece of heat-resistant glass tube of about 8 mm. internal diameter and provided with a concentric internal thermocouple well. It was then slowly heated by an electric resistance furnace in the presence of a downwardly flowing atmosphere of hydrogen to a temperature of about 200° C. After reduction was complete at this temperature, the temperature was gradually increased to 450° C.

A mixture of hydrocarbons having a boiling range within the gasoline boiling range which contained 3 per cent of sulphur in the form of sulphur-containing organic compounds and that was prepared by the catalytic polymerization of cracking-still gas was treated with said catalyst in the following manner:

The hydrocarbon mixture was passed together with an excess of hydrogen over the catalyst at a temperature of 300° C. and a total pressure of 250 pounds per square inch.

The resultant gasoline, after being washed with an alkali solution, was sweet to the doctor test, showing efficient desulphurization, and was 98.5 per cent saturated, showing excellent hydrogenation.

We have found that our catalysts may be used for desulphurizing organic materials by converting the organic sulphur contained therein substantially completely into hydrogen sulphide, which can then be removed by well-known means, as by an alkali wash.

Mention has been made herein that the chromium oxide or oxides in the most desirable residue from the controlled and nonspontaneous thermal decomposition of ammonium-containing chromates or dichromates has an empirical formula which closely approximates CrO_2, and it has been shown that this may be further represented by a simple mixture or combination of chromium oxides such as $Cr_2O_3.CrO_3$. For this reason, and as a matter of convenience, the chromium with a valence higher than three has been spoken of as a certain amount of hexavalent chromium, and a method for determining this higher-valent chromium has been given. The true chemical formula of the residue has not been definitely established; but it is immaterial whether the higher-valent chromium is considered as being truly tetravalent, as in CrO_2, or as being partly truly hexavalent and partly truly trivalent, as in $Cr_2O_3.CrO_3$, since the chemical formula has no bearing on the invention other than as discussed herein. Therefore, any mention made herein or in the claims which follow of hexavalent chromium in chromium oxide or of chromium oxide of any particular content of hexavalent chromium, is to be considered in the light of this discussion and disclosure.

The terms "pseudocrystalline" and "crystallomorphous" used in this specification and in the accompanying claims are taken to mean that the granules of the product from the nonspontaneous thermal decomposition have the same apparent or gross shape or physical form as the original crystals or granules of ammonium-containing salt of chromic acid used as raw material. It is probable, but not definitely known, that the atoms in the product are definitely arranged and spaced and thus in this respect resemble the atoms in a true crystal; this may possibly contribute to the high catalytic efficiency of the product.

The term "coherent" as used herein is to be understood to imply that the residue from the nonspontaneous thermal decomposition persists in the form of the original granules or crystals instead of readily falling into powder; furthermore, it is not to be taken as implying a coalescence of granules into a larger mass or masses.

We do not wish to exclude from our invention certain modifications or alternatives which will be obvious to those skilled in the art. Furthermore, we do not wish to limit our invention to the details of materials, temperatures, pressures, times, and the like which we have cited in our illustrative example. Hence, we desire to have it understood that, within the scope of the appended claims, our invention is as extensive in scope and equivalents as the prior art allows.

We claim:

1. A process for the desulphurization of a hydrocarbon material which contains organic sulphur compounds to reduce the sulphur content thereof, which comprises contacting such a hydrocarbon material in admixture with hydrogen at a reaction temperature of approximately 300° C. and a pressure of approximately 250 pounds per square inch with an unglowed chromium oxide catalyst composed of coarse granules and prepared by subjecting a crystalline, granular and nonpowdery, ammonium-containing salt of chromic acid, the particles of which are sufficiently large to be retained on a 40-mesh sieve, to controlled heating in an oxidizing atmosphere containing free oxygen at an elevated temperature within a range of 75° C. below and adjacent to the spontaneous thermal decomposition temperature of said salt for a time sufficient to effect a substantially complete controlled decomposition of said salt homogeneously throughout said granules to an unglowed dark residue with a content of chromium having a valence higher than three within a range of approximately 25 to approximately 40 per cent of the total chromium and substantially at a minimum, said salt retaining its crystallic shape without substantial disruption of the granules thereof, and subsequently subjecting said decomposed salt to the action of a reducing atmosphere at a temperature within the range of approximately 175° to approximately 250° C. for a period of time sufficient to effect substantially complete reduction while substantially maintaining the unglowed and granular condition of said material.

2. The process for the desulphurization of a hydrocarbon material which contains organic sulphur compounds to reduce the sulphur content thereof, which comprises contacting such a hydrocarbon material in the presence of free hydrogen at a reaction temperature not in substantial excess of approximately 600° C. with a granular catalyst prepared by subjecting a granular, nonpowdery crystalline ammonium-containing salt of chromic acid, the particles of which are sufficiently large to be retained on a 40-mesh sieve, to controlled heating at an elevated temperature below the temperature at which said salt decomposes with incandescence, until the salt is substantially completely decomposed homogeneously throughout the individual granules while retaining its crystallic shape and without

substantial disruption of the granules, and subsequently subjecting the resultant material to the action of a reducing atmosphere at an elevated temperature below approximately 300° C., until reduction is substantially complete.

3. A process for the desulphurization of a hydrocarbon material which contains organic sulphur compounds to reduce the sulphur content thereof, which comprises contacting such a hydrocarbon material in admixture with free hydrogen at a reaction temperature of approximately 300° C. and a pressure of approximately 250 pounds per square inch with a granular catalyst prepared by subjecting a granular, nonpowdery crystalline ammonium-containing salt of chromic acid, the particles of which are sufficiently large to be retained on a 40-mesh sieve, to controlled heating at an elevated temperature below the temperature at which said salt decomposes with incandescence, until the salt is substantially completely decomposed homogeneously throughout the individual granules while retaining its crystallic shape and without substantial disruption of the granules, and subsequently subjecting the resultant material to the action of a reducing atmosphere at an elevated temperature below approximately 300° C., until reduction is substantially complete.

4. A process for the desulphurization of a hydrocarbon material which contains organic sulphur compounds to reduce the sulphur content thereof, which comprises contacting such a hydrocarbon material in admixture with free hydrogen at a reaction temperature of approximately 300° C. and a pressure of approximately 250 pounds per square inch with a granular unglowed chromium oxide catalyst prepared by subjecting crystals of ammonium dichromate, large enough to be retained on a 40-mesh sieve, to controlled heating at an elevated temperature in the range of approximately 150° to approximately 225° C., until said crystals are substantially completely transformed homogeneously throughout and without substantial disruption into granules of black chromium oxide having the same crystallic shape as the original crystals and having a content of chromium with a valence greater than three that is equivalent to a hexavalent chromium content in the range of approximately 25 to approximately 40 per cent of the total chromium, and subsequently subjecting said granules to the action of a reducing atmosphere at an elevated temperature in the range of approximately 175° to approximately 250° C. until reduction is substantially complete.

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