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CATALYTIC HYDROGENATION PROCESS

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This invention relates to catalytic processes and more particularly to processes for the liquid phase hydrogenation of carbon compounds by means of metallic hydrogenating catalysts.

This case is a continuation in part of my copending applications Serial No. 456,299 filed May 27, 1930 issued June 26, 1934 as U. S. Patent No. 1,964,000, Serial No. 559,487 filed August 26, 1931, and Serial No. 629,754 filed August 20, 1932.

Considerable work has been done in the field of catalytic chemistry with a view to developing efficient materials for the hydrogenation of such unsaturated compounds as the olefines unsaturated fats and fatty acids, benzene and its derivatives and a large number of other compounds containing unsaturated functions, such as aldehydes, nitriles, amides, and heterocyclic unsaturated rings. Most of this work has been based upon the classical discovery of Sebatier, that finely divided metallic nickel is capable of causing the union of hydrogen with these compounds. This method has been further expanded and supplemented by the work of Ipatiew on the application of high pressures to these reactions. Extensive research has been carried out heretofore with the result that several different methods for the preparation of hydrogenation catalysts have been developed, the most common of which involve the precipitation and reduction of nickel or copper hydroxides or carbonates, reduction of nickel or copper oxides prepared by ignition of the nitrates, anodic oxidation followed by reduction, heating to their decomposition temperatures of certain organic salts of hydrogenating metals and electrochemical deposition of the metals. Furthermore, various methods of reduction have been proposed ranging from the ordinary dry reduction with hydrogen to reduction in an inert liquid vehicle or in the presence of the oil or other substance undergoing hydrogenation.

As is well known, these catalysts have found extensive use in the commercial hydrogenation of fats, oils and similar readily hydrogenated substances. It has now been found, however, that in general catalysts prepared by the above methods, although ordinarily suitable for the hydrogenation of fats and oils, may be entirely inadequate for the more difficult hydrogenation of such compounds as aldehydes, ketones, sugars, phenols, furfural and its derivatives, or benzene and pyridine and their homologs. Although many types of nickel and copper catalysts have been used for various liquid or vapor phase hydrogenations, so far as I am aware, a catalyst prepared by heating a double chromate of a nitrogen base and copper to its decomposition temperature has not previously been employed for the hydrogenation or dehydrogenation of organic compounds.

This invention has as an object to carry out catalytic processes by the use of highly efficient

copper chromite catalysts. A further object is the provision of a process for the hydrogenation of carbon compounds in the liquid phase by the use of highly efficient hydrogenating metal catalysts, prepared by heating a multiple salt of copper and a nitrogen base to its spontaneous decomposition temperature with or without a subsequent reduction by means of hydrogen. It is a specific object to carry out the hydrogenation of organic compounds containing unsaturated oxygen to carbon linkages by the use of copper chromite catalysts derived from a double chromate of ammonium and copper. A still further object is to carry out the dehydrogenation of organic compounds capable of dehydrogenation employing this type of catalyst.

Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its general aspects, comprises the employment in hydrogenations and dehydrogenations of copper chromite catalysts such as those prepared by heating a double chromate of a nitrogen base and copper to its spontaneous decomposition temperature, thereby converting the chromate to a chromite. This conversion constitutes a species of reduction since the valence of the chromium atom has been changed from a higher to a lower value. This heating or ignition may be, but need not be, accompanied or followed respectively by the step of simultaneously or subsequently reducing the resulting chromite with hydrogen.

Methods for the preparation of catalysts of this type have been disclosed in my copending application, Serial No. 456,299 filed May 27, 1930 and the theory of their formation has been thoroughly discussed. The methods therein disclosed in detail for nickel chromite catalysts are equally applicable to the preparation of copper chromite catalysts which may be made from multiple chromates of copper with nitrogen bases such as pyridine, aniline, methylamine, toluidine, diethylamine, and the like. Thus, a very active copper chromite catalyst preparation is formed by the interaction of equimolecular proportions of copper nitrate and normal ammonium chromate solutions, followed by ignition of the precipitate. Basic copper ammonium chromate, as formed by the precipitation, yields a complex mixture of copper oxide and copper chromite on ignition which is directly applicable to the liquid phase hydrogenation of a large number of unsaturated organic compounds. It has been found that further improvements in the usefulness and efficiency of the copper chromite catalysts may be obtained if carrier materials such as kieselguhr, pumice, silica gel, charcoal, or other inert materials are mixed with the precipitate of copper ammonium chromate and the mixture ignited to form an

extended copper chromite catalyst supported on a substratum.

The proposed methods of catalyst preparation have several advantages. Not only is the catalyst extremely active in hydrogenation reactions, but it is also capable of withstanding catalyst poisons, such as oxygen and sulfur. This is presumably because of the potential supply of unreduced hydrogenating metal which may be continuously activated under the conditions of hydrogenation. When badly poisoned, the chromium oxide component of the catalyst facilitates regeneration which is brought about by gentle ignition followed by reduction. Another advantage is that the materials of this invention lend themselves very readily to compression into a form which may be used in a continuous operation wherein the liquid to be hydrogenated is permitted to flow over the contact mass in the presence of hydrogen under pressure. Copper chromite is readily briquetted with the ordinary types of pharmaceutical tablet machinery without injury to the porosity or activity of the catalyst.

Copper chromite catalysts prepared by methods other than ignition of the chromate, as for example by precipitation or fusion methods, such as by the precipitation and ignition of basic copper chromates or by coprecipitation of copper and chromium hydroxides followed by ignition, may be employed in the processes of the present invention but in general they are not as effective as the catalyst prepared by the methods given above.

It will be apparent that a continuous method of operation using the catalysts of this invention offers many advantages over the usual autoclave process.

Having outlined above the general purposes of the invention the following examples of the application of the catalytic materials herein described to particular reactions are included for purposes of illustration and not in limitation:

Example 1

Fifteen hundred grams of copper nitrate dissolved in 4 liters of water was mixed with a solution containing 1000 grams of ammonium chromate in an equal volume of water. Ammonium hydroxide was added to neutralize the acidity developed during precipitation of the copper ammonium chromate. The precipitate was washed by decantation, filtered, and dried, after which it was ignited at a temperature of 400° C. The resulting copper chromite powder was employed for the hydrogenation of esters without further treatment. One hundred fifty grams of ethyl azelate and 15 grams of copper chromite, prepared as described, were placed in a shaking autoclave. Hydrogen was introduced until the pressure reached 3000 pounds per square inch. The mixture was heated to 270° C. and agitated for four hours, after which the absorption of hydrogen had ceased. On recovery and separation of the products, it was found that the yield of nonamethylene glycol was approximately 50%.

In another experiment carried out under approximately the same conditions except that the temperature was raised to 325° C. ethyl sebacate was hydrogenated in good yields to ethanol and decamethylene glycol. Good results were also obtained by the use of butanol as a diluent for the esters in this process.

Example 2

Copper chromite prepared as described in Ex-

ample 1 was extracted with 10% acetic acid, washed and dried. One hundred fifty grams of ethyl oleate and 20 grams of the extracted copper chromite were agitated in a shaking autoclave at 250° C. and under a hydrogen pressure of 4900 lbs. After two hours treatment in this manner it was found that the ester had been converted in 83% yield to ethyl alcohol and a mixture of oleyl and stearyl alcohols.

Example 3

Twenty-six grams of barium nitrate and 218 grams of cupric nitrate are dissolved in 0.8 liter of water by heating to 70° C. A solution of 126 grams of ammonium bichromate and 0.15 liter of 28% ammonium hydroxide in 600 cc. of water is added with stirring. The precipitate is filtered, dried and ignited at 400° C. The ignition residue is then extracted twice with 10% acetic acid, washed and dried.

In an alloy steel tube having a capacity of about 0.4 liter is placed 252 grams (1.25 moles) of diethyl adipate (B. P. 144-145°/29 mm.) and 20 grams of copper chromite catalyst prepared as described above.

The tube is closed, made gas-tight, and secured in a suitable agitating device. Connection is made with the hydrogen supply and hydrogen is introduced until a pressure of about 2000 lbs. per square inch is reached. Agitation is started and the reaction system is heated as rapidly as possible to 255° C. Additional hydrogen is now admitted to a total pressure of 3000 lbs. per square inch. The temperature is maintained at 255° C. while hydrogen is introduced periodically to maintain the pressure between 2500 and 3000 lbs. After 2-2.5 hours, the rate of absorption of hydrogen becomes quite slow. At this point the temperature is decreased to 240° C. and the hydrogenation is continued until hydrogen absorption is complete. The agitation is stopped and the tube closed off, cooled, and the pressure released. The contents are transferred to a 600-cc. beaker with the aid of four 25-cc. portions of 95% alcohol. The catalyst is removed by filtering with suction and is washed on the filter with four more 25-cc. portions of alcohol. Fifty cc. of 40% sodium hydroxide is added and the alcoholic solution is boiled for 2 hours under a reflux condenser. The solvent is distilled off up to a temperature of 95° C. The residue is then transferred to an apparatus for the continuous extraction of liquids and is exhaustively extracted with ether. The ether is distilled and after the removal of water and alcohol the glycol is distilled under vacuum in a 250-cc. Claisen flask. The yield is 125 to 132 g., or 85 to 90% of the theoretical amount. Hexamethylene glycol boils at 143-144° C. (bath at 160° C.) under 4 mm. pressure and melts at 41 to 42° C.

Example 4

Eleven grams of copper chromite promoted with barium prepared as described in Example 3 above was mixed with 140 grams of ethyl phenylstearate and charged into a shaker autoclave. Hydrogen was admitted to a pressure of 3000 lbs. per square inch, and the mixture was heated to 260° C. and agitated for 3 hours, at the end of which time hydrogen absorption was complete. Recovery and separation of the product yielded about 90% of phenylstearyl alcohol.

Example 5

Four hundred twenty-eight grams of copper

nitrate and 176 grams of chromic acid were dissolved in 2760 cc. of water and 88 grams of anhydrous ammonia was added to the solution with agitation during a period of 15 to 30 minutes.

5 The precipitate was filtered, washed once on the filter and dried, after which it was ignited at 500° C. The resulting copper chromite powder was extracted twice by stirring it for 15 minutes each time with a solution of 200 grams of glacial acetic acid and 1800 cc. of water. After extraction it was washed free from acid, filtered, dried, and screened through a 20 mesh screen. Two hundred seventy-five grams of this catalyst and 4330 grams of ethyl hydroxystearate were placed in an autoclave and hydrogen was introduced to a pressure of 3000 lbs. per square inch. The mixture was then heated to 260° C. and agitated for 9 hours, after which hydrogen absorption had ceased. The decrease in saponification number of the ester during this treatment corresponded to 95% hydrogenation of the carboxyl group while recovery and separation of the product yielded 19% stearyl alcohol and 58% octadecanediol.

Example 6

25 Two hundred parts of copper sulfate and 84 parts of chromic acid were dissolved in 1668 parts of water and 34 parts of anhydrous ammonia was added with agitation during a period of 15 to 30 minutes. After washing the precipitate by decantation, 161 parts of chromic acid was added to redissolve the precipitate and the solution was made up to a volume equal to the original copper sulfate-chromic acid solution. Copper ammonium chromate was reprecipitated by the addition of 32 parts of anhydrous ammonia. This precipitate was washed, filtered and dried after which it was ignited at 400° C. The resulting chromite was then extracted twice by stirring for 15 minutes each time in a solution of 100 parts of glacial acetic acid and 900 parts of water. After extraction, the chromite was washed free from acid, filtered and dried at 150° C. and screened to 20 mesh size. Two hundred pounds of coconut oil having a saponification number of 260 and 10 lbs. of copper chromite prepared as described were charged into an autoclave and the gaseous mixture consisting of 70% hydrogen and 30% nitrogen was admitted to a pressure of 4500 lbs. per square inch. The charge was then heated to 240° C. and agitated for 5 hours while the temperature was slowly increased to 320° C. at which point it was held constant for 45 minutes. At the end of this time the saponification number of the oil had been reduced to 3, equivalent to 99% hydrogenation of the carboxyl group. A yield of 88% of crude coconut oil alcohols was obtained which was found to contain 65% of a mixture of alcohols varying between 6 and 18 carbon atoms.

Example 7

A catalyst consisting of copper chromite supported on kieselguhr was prepared exactly as described in Example 5 above, except that 205 grams of kieselguhr was added to the copper nitrate-chromic acid solution and kept in suspension by vigorous agitation during precipitation with ammonia. The catalyst thus prepared consisted of copper chromite supported on kieselguhr, the two components being present in equal weight proportions. Ten grams of the catalyst prepared as described and 200 grams of furfural were placed in a shaker autoclave and hydrogen was admitted to a pressure of 1500 to 2500 lbs. per square inch. The mixture was then heated

ed to 165 to 175° C. and vigorously agitated for 15 minutes after which hydrogen absorption was complete. Distillation of the product under reduced pressure yielded 90% of furfuryl alcohol.

Example 8

A copper chromite catalyst was prepared as follows: A two-molar solution of neutral ammonium chromate was added to an equal volume of a two-molar solution of copper nitrate with stirring at a temperature of 25° C. Ammonium hydroxide was added to neutrality to litmus and the precipitate allowed to settle. The liquor was decanted and the precipitate was washed 5 times by decantation with cold water, filtered, and dried at 110° C. The copper ammonium chromate thus obtained was ignited at 400° C. to drive off ammonia and oxygen, thereby converting the residue to a bluish black powder characterized as copper chromite.

A mixture consisting of 15 grams of copper chromite thus prepared and 200 grams of furfural was shaken with hydrogen at a pressure of 1800 lbs. per square inch and at a temperature of 175° C. Hydrogen absorption stopped after 2 hours. The liquid product was found by distillation to contain 67 grams of furfuryl alcohol, 75 grams of higher boiling material, and 13 grams of unchanged furfural.

The copper chromite catalyst prepared as described may, before use, be reduced with hydrogen at about 400° C. The resulting composition containing reduced copper, copper oxide, and copper chromite may then be used in the hydrogenation of furfural under the conditions given for the non-reduced copper chromite catalyst.

Example 9

A copper-chromium oxide catalyst was prepared by igniting basic copper ammonium chromate at 400° C. and reducing the resulting copper chromite in hydrogen at 300 to 350° C. for four hours. Five grams of the catalyst was shaken with 300 grams of nitrobenzene at 150° C. under a hydrogen pressure of 1800 pounds. Aniline was formed quantitatively, the reaction being completed after three hours.

Example 10

Fifteen grams of copper chromite catalyst prepared as described in Example 5 above, was mixed with 150 grams of para-nitrotoluene, and the mixture was placed in a shaking autoclave. After heating the mixture to 180° C. hydrogen was admitted to a pressure of about 2000 lbs. The mixture was then agitated while maintaining the hydrogen pressure between 1600 to 2600 lbs. At the end of 2.5 hours hydrogen absorption was complete and 87% of the para-nitrotoluene was found to be hydrogenated to para-toluidine.

In another experiment made exactly as described above, alpha-nitronaphthalene was hydrogenated in about 85% yield to alpha-naphthylamine in seven hours. Alternatively, nitrocompounds may be hydrogenated to the corresponding aromatic amines in a continuous liquid phase process in which the nitrocompound is allowed to flow over a granulated copper chromite catalyst in an atmosphere of flowing hydrogen ether at atmospheric or elevated pressures, and at temperatures in the same range as employed in the batch process.

Example 11

Fifteen grams of copper chromite prepared as

described in Example 5 above, was mixed with 159 grams of methyl isobutyl ketone and heated for one hour in a shaker-autoclave at 160 to 170° C., under a hydrogen pressure of 2000 lbs. per square inch. Quantitative hydrogenation of the ketone occurred, the product consisting of 95 to 97% methyl isobutyl carbinol distilling at 130 to 131° C.

Example 12

Twelve and seven tenths grams of copper-barium chromite prepared as described in Example 3, was mixed with 159 grams of benzaldehyde and agitated in a tube autoclave for 1.5 hours at 145° C. under 2000 lbs. hydrogen pressure. Recovery and separation of the product showed no benzaldehyde remaining, and a yield of 136 grams or 85.5% of benzyl alcohol, the remaining 14.5% consisting of high boiling oils the principal constituent of which was benzyl benzoate. No toluene was formed.

Example 13

Twenty grams of copper-barium chromite prepared as described in Example 3 was agitated with 240 grams of ethyl alpha hydroxyisobutyrate under a hydrogen pressure of 2500 lbs. per square inch. Hydrogen absorption was rapid at about 200° C. and the reaction was complete in about one hour. On distillation of the product there was obtained a 91% yield of 2-methylpropanediol-1,2.

Example 14

A charge consisting of 245 grams of salicyl aldehyde and 20 grams of copper chromite catalyst prepared as described in Example 5, was placed in a shaking autoclave and agitated at 145 to 155° C. and 1800 lbs. per square inch pressure for one hour. The products of reaction were taken up in ether and the catalyst removed by filtration. The ether was evaporated and 300 grams of benzene added. Upon chilling the solution 130 grams of salicyl alcohol crystals were obtained. A second crystallization after the addition of petroleum ether yielded an additional 33 grams of salicyl alcohol. The total yield of 163 grams corresponded to 85% of theory. Upon distillation of the residue there was obtained 45 grams of unreacted salicylaldehyde.

In a similar manner, anisaldehyde, vanillin, piperonal, and phenylacetaldehyde may be hydrogenated over copper chromite catalysts to give as the products anisyl alcohol, vanillyl alcohol, piperonyl alcohol and phenylethyl alcohol.

Although in the above examples certain definite conditions of temperature, pressure, amounts of material, durations of reactions, etc., have been indicated, it is to be understood that any and all of these may be varied widely within the scope of the invention since the particular conditions of operation are governed largely by the specific reaction catalyzed, the materials treated, and the catalyst selected for a given reaction. Thus, the temperature used for hydrogenation may vary from 50° C. to the decomposition temperature of the substance being treated under the conditions of the reaction. Thus temperatures as high as 400° C. may be employed for the more stable organic compounds. The reaction may be conducted at ordinary pressure or at increased pressure even up to 700 atmospheres or more. The hydrogenation reactions may be carried out either in batch or continuous processes.

It will be apparent from the examples given that the catalysts of this invention have many

valuable applications. Although their use in certain selected liquid phase hydrogenations have been described in illustration of particularly advantageous properties, they are capable of use broadly in many types of hydrogenations as well as in dehydrogenations in the liquid phase. Thus, copper chromite catalysts are particularly well suited to the hydrogenation of unsaturated organic compounds wherein the unsaturation represents a deficiency of hydrogen in a carbon-oxygen or nitrogen-oxygen bond. Hence, copper chromite catalysts are especially applicable to a type of unsaturation which may be termed oxygen-unsaturation, and the full advantages of the invention flow from the hydrogenation with copper chromite catalysts of organic compounds containing unsaturated oxygen atoms. Several types of organic compounds contain such oxygen-unsaturation. First, there are the nitro-compounds, which, as the examples show, are readily hydrogenated to the corresponding amines. The nitro-compounds may be of either aliphatic or aromatic type. The invention is applicable to the hydrogenation of nitrobenzenes, nitrotoluenes, nitronaphthalenes, methoxynitronaphthalenes, nitrophenols, nitroanilines, etc. The second large class of oxygen-unsaturated carbon compounds are the carbonyl compounds typified by the aldehydes and ketones. The process of the present invention is applicable to aliphatic and aromatic aldehydes and to aliphatic, aromatic and mixed ketones. Thus through hydrogenation with copper chromite, benzaldehyde is converted to benzyl alcohol, acetaldehyde to ethanol, butyraldehyde to butanol, acetone to isopropanol, methyl isobutyl ketone to methyl isobutyl carbinol, etc. Substituted aromatic aldehydes such as p-toluic aldehyde, vanillin, piperonal, salicyl aldehyde, etc. are converted smoothly into the corresponding substituted aromatic alcohols. Other types of oxygen-unsaturated organic compounds are represented by the large class of carboxylic acids, esters, amides, and salts, several cases of the hydrogenation of which are disclosed in the examples. In this connection it is to be noted that many organic hydrogenation reactions represent an equilibrium in which the product of hydrogenation, unless continuously removed from the reaction zone, undergoes dehydrogenation. In this type of reaction there are present three compounds, namely, a compound capable of hydrogenation, a compound capable of dehydrogenation and hydrogen. The catalysts of this invention are not only effective in causing the reaction to proceed in the direction of hydrogenation but also under the proper conditions to induce dehydrogenation.

As indicated by the examples, copper chromite may be prepared by a number of methods within the scope of the invention. Ordinarily it is preferable to start with copper nitrate and prepare the catalyst as described in Example 5, but for reasons of economy other copper salts such as copper sulfate may be used provided precautions are taken to eliminate poisonous impurities from the finished catalyst. Acid extraction of the copper chromite is advantageous in many cases but may be avoided in special cases, such as the hydrogenation of furfural, without sacrificing catalytic efficiency. Improved activity and physical properties, and economic utilization of the catalyst may be effected by supporting it upon a carrier such as kieselguhr, and it is sometimes advantageous particularly in the hydrogenation of esters and furfural to incorporate small amounts

of an alkaline buffer such as barium oxide or magnesia to counteract the effect of acidity which is sometimes detrimental both to the catalyst, and to the stability of the reactants.

5 Unlike nickel chromite, it is unnecessary that copper chromite be prerduced before use in a hydrogenation reaction although it may be done without detriment to the catalyst if desired.

10 Although the use of copper chromite has been described for the most part in certain liquid phase batch hydrogenations it is also capable of use in a continuous liquid phase hydrogenation as well as in dehydrogenation reactions in either vapor or liquid phase.

15 As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

20 I claim:

1. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound 25 in the liquid phase in contact with hydrogen in the presence of a catalyst prepared by heating a multiple chromate of a nitrogen base and copper to its spontaneous decomposition temperature.

30 2. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature of at least 50° C.

35 3. The process in accordance with claim 1 characterized in that the process is a continuous flow liquid phase process and the catalyst is in a granulated briquetted form.

40 4. The process in accordance with claim 1 characterized in that the nitrogen base is ammonia.

45 5. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst prepared by heating to its spontaneous decomposition temperature a multiple chromate of a nitrogen base and copper which is supported on a substratum.

50 6. The process in accordance with claim 5 characterized in that the nitrogen base is ammonia.

55 7. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst prepared by heating to its spontaneous decomposition temperature a multiple chromate of a nitrogen base and copper supported on kieselguhr.

60 8. The process in accordance with claim 7 characterized in that the reaction is carried out at a temperature of at least 50° C.

65 9. The process in accordance with claim 7 characterized in that the nitrogen base is ammonia.

70 10. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound

in the liquid phase in contact with hydrogen in the presence of a catalyst comprising essentially copper chromite prepared by igniting a double chromate of a nitrogen base and copper.

11. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst comprising essentially copper chromite prepared by precipitating copper chromate in the presence of ammonium hydroxide and heating the resulting precipitate to its spontaneous decomposition temperature.

12. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst prepared by heating a multiple chromate of a nitrogen base and copper to its spontaneous decomposition temperature and thereafter reducing the resulting composition in hydrogen.

13. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst formed by reacting in aqueous solution substantially equimolar proportions of a copper salt and ammonium chromate, adding ammonia to neutralize the acidity developed during the precipitation, washing, filtering, drying and igniting the precipitate by heating it to its spontaneous decomposition temperature and thereafter reducing the resulting composition in hydrogen.

14. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a catalyst formed by reacting in aqueous solution substantially equimolar proportions of a copper salt and ammonium chromate, adding ammonia to neutralize the acidity developed during the precipitation, washing, filtering, drying and igniting the precipitate by heating it to its spontaneous decomposition temperature, extracting the ignited precipitate with acetic acid, and thereafter reducing the resulting composition in hydrogen.

15. The process of hydrogenating an unsaturated oxygen-to-carbon linkage capable of hydrogenation of an organic compound containing same, which comprises bringing said compound in the liquid phase in contact with hydrogen in the presence of a copper chromite catalyst.

16. The process of claim 15 characterized in that the organic compound is a carbonyl compound.

17. The process of claim 15 characterized in that the catalyst is supported on a substratum.

18. The process of claim 15 characterized in that the catalyst is supported on kieselguhr.

19. The process of claim 15 characterized in that the process is a continuous-flow liquid phase process and the catalyst is in a granulated briquetted form.

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