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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvement in the Catalytic Preparation of Oxygenated Carbon Compounds.

We, E. I. Du Pont de Nemours and Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, New Castle County, State of Delaware, United States of America (Assignees of Wilbur Arthur Lazier, citizen of the United States of America, of 1001, Gilpin Avenue, Wilmington, Delaware, United States of America) do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement.

This invention relates to catalytic processes for the preparation of oxygenated carbon compounds and it comprises, more particularly, the application of highly efficient chromite catalysts in such processes, these catalysts being prepared by the high temperature treatment of mixtures or compounds containing hexavalent chromium to form chromites containing trivalent chromium.

Numerous mixtures and combinations containing oxides of chromium and other metals have been made and used as catalysts in various catalytic syntheses including the synthesis of oxygenated organic compounds. Such mixtures have been prepared in many different ways, such as by the co-precipitation of the hydroxides or carbonates of chromium and the other metals, by treating a metallic oxide with chromium trioxide in the wet way or by preparing fused masses consisting of alkali bichromates and the metallic oxides optionally with after reduction. In some cases metallic chromates have been used directly as catalysts.

Chromium containing catalysts of this type and which have found application in the synthesis of a variety of substances including ammonia, hydrogen, methyl alcohol and the like, have usually been employed at temperatures between about 200° and 600° C. since it was thought that high temperature treatment would destroy the activity of such catalysts. It has been proposed, however, to use a catalyst in the synthesis of ammonia in which a relatively small proportion of chromium is present in the catalyst which also contains a mixture of iron and magnesium oxides, this mixture being prepared by precipitating a mixture of iron nitrate and potassium bichromate with an excess of magnesium carbonate, subsequently heating the precipitate to 200 to 300° C. and finally to 700° C.

The invention consists in the process for the catalytic preparation of oxygenated carbon compounds which comprises passing a carbon compound in the form of a gas or vapour at suitable temperature and pressure over a catalyst containing chromium in the tervalent form, characterised in that the catalyst employed is prepared by subjecting mixtures or compounds containing hexavalent chromium and one or more of the "catalytic group" of metals i.e. zinc, copper, cadmium, magnesium, manganese, silver and iron, to treatment at a temperature above 600° C. Preferably a temperature of from 650° C. to 1000° C. is employed to form chromites containing trivalent chromium. For example by calcining suitable chromates or bichromates at temperatures of from 650° C. to 1000° C., the chromates are reduced to chromites with the liberation of oxygen. The chromite catalytic bodies thus derived show great superiority in catalytic cativity as compared with that of similar catalysts prepared, for example, by the reduction of the chromates by heating in hydrogen at temperatures below 600°. These improved results were entirely unexpected since prior knowledge has indicated that the activity of a catalyst is generally destroyed by heating to high temperatures.

In addition, it has been found that the activity of the chromite catalysts may be improved still further if the calcined product is treated to remove the less active substances present in such product, which substances are not combined in the form of chromite and are of low catalytic activity. The undesirable substances may be removed in any suitable way, such as by leaching the calcined product with a weak acid, e.g., acetic acid in concentrations of about 5—10%. The chromites made as described are stable and are substantially insoluble in water and in weak acids. The preparation of the catalysts, according to the present process, results in the formation of catalytic bodies of great porosity, which, after drying, consist of nearly pure, highly stable chromites substantially free from acid soluble oxides or other substances of low catalytic activity. These chromite catalysts are highly stable and do not lose their activity after use. For instance, zinc chromite, which has been prepared as just described and was leached with acid prior to its use as a catalyst, is found to contain no additional acid soluble zinc after use. The present catalysts have the further advantage that they are not affected by use at high temperature.

As has been pointed out, the active catalysts forming the subject of the present invention are chromite compounds containing chromium in the trivalent form. However, the term chromite, as here used, does not necessarily refer to a compound of definite chemical composition since the chromite may contain widely differing proportions of its components. Zinc chromites, for example, are known to contain a varying proportion of zinc oxide, and this proportion is dependent on the ratio of zinc to chromium in the compound or mixture of compounds calcined and upon the temperature and duration of the calcination. In any event, the chromites contain the chromium in trivalent form.

The chromite catalysts may be prepared by many varied methods in which a compound or mixture in which the chromium present is in the hexavalent form is reduced at temperatures of from 650° C. to 1000° C. to a compound containing the chromium in trivalent form. The following are some of the general methods of preparing a catalyst according to the present invention: (1) prolonged heating at a bright red heat of mixtures of chlorides or other salts of the metals hereinbefore mentioned with alkali chromates or bichromates, the resulting product being leached with water and dilute acids; (2) using in place of the salts described in (1) the oxides of the metals; (3) igniting a chromate of one of the metals hereinbefore mentioned and treating the ignited product with acid to remove the excess of metallic oxide not combined with the chromium oxide. Other suitable methods which involve the high temperature reduction of chromates to chromites may be used.

The present catalysts contain chromium sesqui-oxide combined with the oxides of the other elements specified, i.e., as the chromites, and are suitable for general use in the manufacture of oxygenated carbon compounds. For instance, the chromite catalysts are suitable for use in the high pressure synthesis of oxygenated organic compounds such as methanol and alcohols of higher molecular weight from mixtures of hydrogen and oxides of carbon. The chromite catalysts may also be used for the water gas reactions wherein carbon monoxide and water vapor are converted catalytically to carbon dioxide and hydrogen; or the catalysts may be used for dehydrogenations such as the catalytic conversion of an alcohol to an aldehyde.

Zinc combined with chromium oxide to form zinc chromite, is an extremely valuable catalyst when used for the methanol synthesis.

In the various embodiments of the present invention, any one of the "catalytic group" of metals may be used as the more basic element to form the chromite; or, if desired, several of these metals may be used to form mixtures of the desired chromites.

In order to describe the invention more fully the following specific example is given, it being understood that the present invention is not limited to this specific illustration.

EXAMPLE.

A contact mass is prepared by heating basic zinc chromate containing 42.5 per cent. by weight zinc and 25 per cent. chromium for four hours in air at a temperature of 800—900° C., after which the product is cooled and extracted with 10% acetic acid until no more zinc may be removed. This product is then washed and dried. The resulting product contains about 35% zinc and 39% chromium which, when calculated as ZnO and Cr_2O_3, equals 100%. One litre of such a catalyst when placed in a pressure resisting copper lined tube yields 950 cc. of crude condensate containing about 80% of methanol per hour at about 400° C. and about 300 atm. pressure from a gas consisting of about 30% carbon monoxide and about 60% hydrogen, when the gas mixture is passed through the catalyst at the rate of about 10,000 litres per hour as measured at normal temperature and pressure. As illustrating the improvement resulting from application of the above process, the basic zinc chromate before heating and extracting with acid produces only 750 cc. of crude condensate per hour under the same conditions.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. The process for the catalytic preparation of oxygenated carbon compounds, which comprises passing a carbon compound in the form of a gas or vapour at a suitable temperature and pressure, over a catalyst containing tervalent chromium, characterised in this that the catalyst employed is prepared by subjecting mixtures or compounds containing sexivalent chromium and one or more of the "catalytic group" of metals, that is zinc, copper, cadmium, magnesium, manganese, silver and iron to treatment at a temperature above 600° C.

2. An improved process as claimed in Claim 1, wherein mixtures or compounds are subject to treatment at from 650°—1000° C.

3. An improved process for the catalytic preparation of oxygenated carbon compounds as claimed in Claim 2, in which the mixtures or compounds containing sexivalent chromium comprise a chromate or a bichromate.

4. An improved process for the catalytic preparation of oxygenated carbon compounds as claimed in any of the preceding claims, characterised in this that the chromite is leached with dilute acid such as acetic acid.

5. The improved process for the catalytic preparation of oxygenated carbon compounds substantially as hereinbefore described.

6. The process of preparing methanol substantially as described in the foregoing example.

Dated this 13th day of June, 1927.

MARKS & CLERK.

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