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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 Company, 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, State of 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.

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.

It has been proposed to prepare a catalyst for use in manufacturing oxygenated organic compounds from ammonium bichromate, zinc oxide and potassium carbonate, the contact mass being preferably heated from about 450° to 500° Centigrade.

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 a mixture or compound containing a double chromate of one of the catalytic group of metals i.e. zinc, copper, cadmium, magnesium, manganese, silver and iron, to heat treatment at a temperature adequate to decompose the double chromate and to cause simultaneous reduction thereof.

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 to 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 temperatures.

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.

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, double chromates of each of several of these metals with a nitrogenous base may be used to form mixtures of the desired chromites. The chromite catalysts are prepared by gently heating the double chromate of a metal of the "catalytic group" and a nitrogenous base, until the decomposition sets in. The reaction will then proceed, without further application of heat, to leave a chromite of the metal.

Taking the preparation of zinc chromite as a typical example, a contact mass of excellent activity for methanol synthesis may be prepared by precipitating basic zinc ammonium chromate from solutions of soluble zinc salts and ammonium chromate. This precipitated compound is washed and dried, and when heated slightly to start the reaction, decomposes spontaneously with the evolution of sufficient heat to leave a glowing residue consisting of combined zinc oxide and chromium sesquioxide. That the greater part of the zinc oxide is combined with the chromium oxide is evidenced by the fact that only about one-third of the zinc oxide may be extracted by 5% acetic acid. Compounds of organic bases may be utilised in place of ammonium salts; for example, zinc bichromate tetrapyridine and zinc bichromate tri-aniline are crystalline salts which, when heated, behave in an analogous manner and yield zinc chromites useful as catalysts.

The present catalysts contain chromium sesquioxide combined with oxides of other elements, i.e. as the chromites, and are suitable for 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 reaction wherein carbon monoxide and water vapour 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.

In order to describe the invention more fully the following specific examples are given, it being understood that the present invention is not limited to these specific illustrations.

EXAMPLE 1.

Basic zinc ammonium chromate is prepared by cold precipitation as the result of mixing solutions containing molecular equivalents of zinc nitrate and ammonium chromate. When heated slightly to start the reaction, this basic salt decomposes spontaneously with the evolution of sufficient heat to leave a glowing residue. When used as a contact mass in the preparation of methanol without extraction with acids, this product yields per litre of catalysts, 1300 cc. of crude condensate containing about 90% methanol, if a mixture of 30% carbon monoxide and about 60% hydrogen is passed through the catalyst at the rate of about 10,000 litres per hour (measured at normal temperature and pressure), at about 400° C. and about 300 atmospheres pressure.

EXAMPLE 2.

Zinc bichromate tetrapyridine is prepared by the addition of pyridine in excess to a boiling solution of zinc bichromate, when the pyridine salt crystallizes out. When heated slightly to start the reaction, the pyridine salt decomposes spontaneously with the evolution of heat leaving zinc chromite as a glowing mass. Without extraction this product yields 900 cc. per hour of crude condensate containing about 90% pure methanol per litre of catalyst when used as in Example 1.

EXAMPLE 3.

Manganese ammonium chromate is prepared by precipitation as the result of mixing solutions containing molecular equivalents of manganese nitrate and ammonium chromate. This double salt is heated to its decomposition point and a residue is obtained which when used in the manner described in Example 1 produces 800 cc. of crude condensate per hour, containing about 50% methanol and 25% of alcohols of higher molecular weight.

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 suitable temperature and pressure over a

catalyst containing chromium in the tervalent form, characterised in this that the catalyst is prepared by subjecting a mixture or compound containing a double chromate of a nitrogen base and one of the catalytic group of metals that is zinc, copper, cadmium, magnesium, manganese, silver and iron, to heat treatment at a temperature adequate to decompose the double chromate and to cause simultaneous reduction thereof.

2. An improved process for the catalytic synthesis of oxygenated carbon compounds as claimed in Claim 1, in which a double chromate of zinc and ammonium is employed.

3. An improved process for the catalytic synthesis of oxygenated carbon compounds as claimed in Claim 2, in which the ammonium is substituted by an organic base.

4. An improved process as claimed in Claim 3, wherein the organic base comprises aniline or pyridine.

3. The improved process for the catalytic synthesis of oxygenated carbon compounds substantially as hereinbefore described.

6. The process of preparing methanol or other alcohols of higher molecular weight substantially as described in each of the foregoing examples.

Dated this 4th day of December, 1928.
MARKS & CLERK.

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