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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements relating to Catalytic Processes particularly for the Hydrogenation and Dehydrogenation of Organic Compounds.

We, E. I. Du Pont de Nemours and Co., a corporation organized 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, 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 a process of preparing valuable organic compounds by catalytic hydrogenation-dehydrogenation reactions. It relates particularly to syntheses of organic compounds by the catalytic hydrogenation under pressure of oxides of carbon, e.g., carbon monoxide.

It is well known that valuable organic compounds may be produced by the catalytic hydrogenation under pressure of oxides of carbon, particularly carbon monoxide. According to numerous descriptions, the composition of the liquid products so produced is largely a function of variable operating conditions among which are the composition of the gaseous mixture, the temperature and composition of the contact mass, and the rate of gas passage over the catalyst. If the gas contains besides hydrogen and the oxides of carbon, a large proportion of ethylenic hydrocarbons, or if the oxides of carbon are present in large excess over the hydrogen, the resulting product consists largely of liquid hydrocarbons. The substantial absence of olefins or a lower concentration of carbon monoxide relative to the hydrogen favors the formation of alcohols, particularly methanol and other oxygenated organic compounds such as acids, ketones, esters and aldehydes.

As catalytic bodies suitable for the formation of methanol and other oxygenated organic compounds, the hydrogenating metals other than those of the platinum group or those known to form methane readily from carbon monoxide and hydrogen, have previously been suggested. Such metals are copper, cadmium, silver, tin, lead and zinc, which may either be used alone or when promoted with non-reducible oxides or compounds of the alkali metals. Owing to their activity for methane formation, metals of the so-called iron group, i.e., iron, cobalt and nickel, are undesirable unless combined with some non-metallic elements such as arsenic, antimony, sulfur, phosphorus, or boron, or as solid solutions with non-methanating metals, or when combined with non-reducible oxides in such a way that no elementary metal is present under the conditions of operation. Among other catalysts which may be used are those oxides which are non-reducible to metals under the conditions of operation, especially when employed in intimate mixtures containing two or more oxides having different degrees of acidity or basicity.

It has been set forth in U.S. Patent 1,558,559 that the more basic oxide should preponderate. For example, a catalyst composed of zinc and chromium oxides should contain a proportion of zinc oxide greater than the amount necessary to form the neutral compound zinc chromate ($ZnCrO_4$), or in other words, over 2 mols ZnO against 1 mol chromic oxide. As the hexavalent form of chromium is not stable in the presence of a reducing gas, it readily passes over to the trivalent form, the corresponding oxide being chromium sesquioxide (Cr_2O_3), commonly called chromium oxide or chromic oxide. Therefore, in a catalyst containing a preponderating quantity of zinc oxide, the zinc oxide-chromium sesquioxide molecular ratio is greater than two. The basic zinc chromates of commerce, commonly prepared by precipitation, are compounds of this type, and are frequently referred to as especially suitable catalysts for the production of oxygenated organic compounds. These usually contain a large excess of zinc oxide, it being very difficult to prepare exactly neutral zinc chromate.

It has been proposed to synthesise oxygenated organic compounds such as methanol from oxides of carbon and hydrogen, by catalytic reaction at elevated temperatures, and pressures, in which chromite catalysts are used These catalysts may be prepared in a variety of ways such as by gently igniting basic zinc ammonium chromate for instance, by which treatment a loosely constructed compound of zinc oxide and chromium sesquioxide, known as zinc chromite, is formed, which may be leached with dilute acids, whereby uncombined zinc oxide is removed. This compound decrepitates when heated with loss of oxygen and ammonia.

When pure, basic zinc ammonium chromate, as well as its ignition product, obviously contains two molecular weights of zinc oxide for each molecular weight of chromium sesquioxide. However, whereas zinc chromate as generally prepared by precipitation always contains an excess of zinc oxide and hence is a basic zinc chromate, the double zinc and ammonium chromate always contains a slight excess of chromium oxide because of the unavoidable occlusion of ammonium bichromate in the product during its precipitation. Therefore, it is rarely possible by this method to obtain a product containing as much as two molecular weights of zinc oxide for each molecular weight of chromium sesquioxide. The ratio usually found in the commercial products is about 1.95. Good results are also obtained according to the process stated using catalysts in which zinc is replaced by manganese.

It is understood, of course, that other methods of preparing the chromite catalysts may be used. It is possible to prepare a suitable contact material by grinding in suitable mills a mixture of zinc oxide with ammonium bichromate in excess, the mass being wet with water. In this manner it is possible to obtain any desired ratio of zinc oxide to chromium oxide. However, the use of a definite compound as the parent substance of the catalyst results in a contact mass in which there is a more intimate relationship between the basic and acidic oxide. Furthermore, the use of a decrepitating compound results in the formation of a highly porous residue well adapted to granulation by pressure.

The zinc chromite catalysts just described, when free from alkali metals bring about the formation of practically pure methanol from reaction mixtures containing hydrogen and carbon monoxide.

In the manufacture of oxygen-containing organic compounds from organic compounds containing a carbonyl group, it has been proposed to suppress wholly or in part the normal dehydrating effect of a hydrogenating oxide catalyst, by incorporating in the catalyst a basic substance such as an oxide, hydroxide, carbonate or other salt of a weak acid of an alkali or alkaline-earth metal of groups 1 and 2 of the Periodic System.

According to the present invention the improved process of synthesising oxygenated organic compounds by catalytic hydrogenation or dehydrogenation at elevated temperatures and pressure is characterised by the use of a catalyst comprising difficultly reducible basic and acidic oxides together with from 0.25% to 5% of an alkali metal compound calculated as the element, the acidic oxide being in excess of that necessary to form a neutral compound with the basic oxide.

In order however to obtain substantial quantities of higher alcohols, particularly normal propanol, isobutanol, and amyl alcohols, as well as acids, ketones, esters and aldehyde, we have found that the addition of small amounts of alkali metal compounds, particularly sodium compounds, is necessary. Furthermore, contrary to prior practice, it has been found possible to operate at high space velocities with our catalysts even though they contain alkali metal compounds which are preferably used in small quantities. Potassium compounds, sodium compounds or mixtures of the two may be employed but it is generally more desirable to use the sodium compounds which are cheaper and more available.

The alkali metals may be introduced into the catalysts as sulphate, phosphate, chromate, hydroxide, or carbonate, or as the salt of any of the heavy metal oxygen acids or organic acids. Regardless of the form in which the alkali is introduced its ultimate effect in bringing about higher alcohol production is the same. Introduction of the alkali as the salt of a heavy metal oxygen acid, while temporarily postponing the attainment of maximum higher alcohol production, has the additional advantage of introducing a larger proportion of the acidic oxide. For example, the addition of sodium chromate or bichromate to the zinc oxide-chromium oxide catalyst already described has the twofold advantage of further increasing the preponderance of the chromium oxide over the zinc oxide and furnishing a support for the alkaline compounds generated during the course of the reaction.

The advantages which accrue from the use of low concentrations of alkali metal compounds with our hydrogenation catalysts are many. The product obtained from the hydrogenation is homogeneous and relatively free from water, often containing as much as 40% of compounds of a higher order than methanol. Furthermore, there is formed little or no tarry matter and but a small proportion of hydrocarbons is produced as compared with the product from a reaction in which the catalyst used contains higher concentrations of alkali. The contact mass retains its good structure whereas in the presence of a higher concentration of alkali metal compound, the catalyst tends to sinter into a solid mass thereby impeding or preventing gas flow through the catalyst chamber. Furthermore, with the catalyst low in alkali, carbon deposition is at a minimum, as contrasted with contact masses of greater alkali content.

In employing compounds of the alkali metals with our catalysts for the production of higher alcohols, it is preferred to use such an amount that the finished catalyst will contain from 0.25% to 5.0% of alkali metal calculated as the element, the amount varying within these limits depending upon the conditions of operation. For example, when operating at a temperature of 475° C. and 30,000 space velocity (30,000 liters of gas per hour, measured at 0° C. and 760 mm. of mercury, per liter of catalyst), a zinc oxide-chromium oxide catalyst containing about 2% of sodium gives especially good results.

The following is given as a specific example of carrying out the process:—

A contact mass is prepared by grinding together in the wet way the product resulting from the exothermic decomposition of a mixture of a precipitated basic zinc ammonium chromate with about 5% of its weight of anhydrous sodium chromate. The intimate mixture prepared is dried, granulated, and charged into a suitable pressure resistant catalyst chamber. Water-gas containing approximately 50% hydrogen and 35% carbon monoxide by volume with small percentages of carbon dioxide, methane, ethylene, and nitrogen is passed at a pressure of about 275 atmospheres over the contact mass at the rate of 40,000 liters per hour per liter of catalyst, the latter being heated to about 475° C. Under these conditions there is produced per hour a volume of condensable liquid organic compounds about equal to the volume of catalyst employed, containing about 40% each of methanol and higher boiling organic compounds, chiefly isobutanol.

As illustrating the improvement derived from the use of a catalyst containing but a small amount of alkali metal compound, as compared with a catalyst containing a large amount of such compound, a catalyst similar in every respect to that used in the specific process example given, except that it contains about 20% of potassium chromate (8% potassium) in place of 5% sodium chromate, when used in the process operated under the same conditions, produces per liter of catalyst per hour about 0.3 liters each of methanol and compounds having a higher molecular weight.

It has also been found that the catalysts which have been described as forming the subject matter of the present invention, in addition to their use as hydrogenation catalysts, may also be utilized for the reverse reaction, that is, dehydrogenation. For instance, a catalyst prepared as described from a mixture of basic zinc ammonium chromate with 5% sodium chromate may be used as a dehydrogenating catalyst and when isopropanol is passed over such a catalyst heated to 400° C., it is converted almost completely to acetone. The process, of course, is carried out under pressures above atmospheric.

It is to be understood that the present invention covers the field of catalysts, both as applied to hydrogenation as well as dehydrogenation. These catalytic processes are generally carried out at temperatures around 475° C. and at a pressure of around 275 atmospheres. However, in general, the processes may be carried out at temperatures of from 375° to 500° C. with the use of pressure ranging from 100 to 1,000 atmospheres.

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. An improved process of synthesising oxygenated organic compounds by catalytic hydrogenation or dehydrogenation at elevated temperatures and pressures characterised in this that the catalyst comprises difficultly reducible basic and acidic oxides together with from 0.25% to 5.0% of an alkali metal compound calculated as the element, the acidic oxide being in excess of that necessary to form a neutral compound with the basic oxide.

2. An improved process according to Claim 1 in which the catalyst comprises zinc oxide and chromium oxide, the ratio of zinc oxide to chromium oxide being preferably less than 2.

3. An improved process as claimed in Claim 2 in which the catalyst contains about 5% of its weight of anhydrous sodium chromate.

4. An improved process as claimed in any one of the preceding claims in which

the reaction is effected at a temperature of around 475° C. to 500° C. and under a pressure of from 100—1000 atmospheres, preferably of 275 atmospheres.

5. The improved processes substantially as hereinbefore described.

Dated this Sixth day of June, 1929.

MARKS & CLERK.

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