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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Decomposition of Metal Compounds Dissolved in Oxygen-containing Organic Products

We, N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, Holland, a Body Corporate organised under the Laws of The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for treating oxygen-containing organic compounds obtained by the action of carbon monoxide, with or without hydrogen, on various organic compounds in the presence of catalysts such as metal carbonyls, which are introduced as such or are formed during the treatment, and more particularly to the removal of dissolved metal from the products obtained in the said reactions.

It is known that in the presence of various metal carbonyls, such as the carbonyls of iron, nickel and cobalt, a great number of organic compounds react readily with CO to form compounds which contain the carbonyl group. The reaction is particularly applicable to organic compounds with a double bond. Thus it is possible to formylate various unsaturated hydrocarbons and their derivatives, such as hydrocarbons, with one or more double or triple bonds by means of a cobalt catalyst. When unsaturated compounds such as unsaturated aldehydes, ketones, alcohols, ethers, acids, halides, amides, sulphides, cyanides, sulphates, sulphonates and esters, such as vinyl esters, are used as initial materials, valuable and in many cases new aldehydes, ketones and acids are obtained. It is also possible to formylate various substances which do not contain unsaturated bonds, but a relatively feeble bond which may be broken under the reaction conditions. Examples of such substances are dialkyl formals, acetals, containing aromatic or cyclo-aliphatic groups, cyclic acetals, such as 1,3-dioxolane, and aliphatic cyclic ethers.

For carrying out the reactions referred to above, cobalt-hydrocarbonyl is a particularly suitable catalyst, or a reaction component yielding carbon monoxide and hydrogen. This hydro-carbonyl can, for example, be prepared as follows:

Cobalt nitrate, potassium hydroxide and potassium cyanate are dissolved in air-free water and carbon monoxide is then passed through the mixture until no more carbon monoxide is absorbed.

The suspension is subsequently acidified with phosphoric acid and a fresh flow of carbon monoxide is introduced. The discharged gas is dried and passed through a low-temperature condenser, in which cobalt hydrocarbonyl is collected by condensation.

According to another method gas consisting of or containing CO and H_2 is caused to act on cobalt-containing masses under a high pressure of, say, more than 100 atmospheres and at elevated temperature, particularly a temperature of 80—130° C. If desired, a liquid may also be passed over, such as a hydrocarbon mixture containing alkenes, to dissolve the hydrocarbonyls formed.

This cobalt-hydrocarbonyl can be used for converting alkenes for example alkenes with 5—8 carbon atoms in the molecule. For this purpose 20 parts of cobalt hydrocarbonyl and 30 parts of C_5—C_8 alkenes are introduced into an autoclave together with water gas under a pressure of 200 atmospheres, after which the mixture is gradually heated. The reaction is initiated at a temperature of between 130° C. and 140° C. and is completed in approximately 5 minutes. The product obtained contains, for example, 47% of aldehydes and approximately 0.74% of dissolved cobalt.

When oxygen-containing products are

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prepared with a metal carbonyl, the product obtained always contains a certain quantity of the metal in solution. Part of the metal is present in the form of dissolved metal carbonyl or hydrocarbonyl, but the greater part of the metal is present in the form of hardly definable CO-containing complex compounds with the organic reagent and/or an intermediate product and/or a final product of the reaction.

The metal carbonyls as well as the metal compounds referred to hereinafter are relatively unstable and under suitable conditions they can be decomposed to free the metal which can then be separated from the product. The dissolved metal compounds, however, tend to promote side reactions and when an attempt is made to free the reaction product from dissolved metal by subjecting it to conditions under which the metal carbonyls are no longer stable, a considerable part of the reaction product will be lost owing to reactions, such as the aldol condensation or other reactions.

It is possible to separate the metal by treating the reaction product with mineral acids, such as sulphuric acid and nitric acid; this treatment is, however, not only unsuitable and relatively costly, but, to a large extent, also gives rise to secondary reactions, thus reducing the yields.

When preparing oxygen-containing compounds by the so-called oxo process it is already known to separate the metal-containing compounds from the reaction product by a treatment with hydrogen at elevated pressure and temperature. The process known so far at the same time gave rise, however, to considerable hydrogenation of, for example, aldehydes to alcohols.

Consequently when it is desired to recover the aldehydes, the known process is unsuitable.

It has now been found that metal-containing reaction products obtained by treating organic compounds in the presence of catalysts which produce soluble metal compounds in the final product, such as complex compounds, metal carbonyls or hydro-carbonyls, which are introduced as such or are formed during the reaction, can be decomposed, without any noticeable side reactions, by treating them under a pressure of from 10 to 80 atmospheres with a gas containing, besides hydrogen, carbon monoxide in such quantity as to check reduction of the oxygen-containing compounds, by introducing a hydrogen-containing gas mixture containing from 0.1 to 50% of carbon monoxide.

Accordingly the present invention provides a process for treating oxygen-containing organic compounds obtained by the action of carbon monoxide, with or without hydrogen, on various organic compounds in the presence of catalysts which produce soluble metal compounds in the final product, such as complex compounds, metal carbonyls or hydrocarbonyls, which are introduced as such or are formed during the reaction, in order to decompose the metal compounds dissolved in the oxygen-containing organic compounds with a hydrogen-containing gas at elevated pressure and temperature, wherein the treatment is carried out at a pressure of from 10 to 80 atmospheres with a gas containing, besides hydrogen, carbon monoxide in such a quantity that reduction of the oxygen-containing compounds is checked, by introducing a gas mixture containing from 0.1—50% carbon monoxide.

The desired partial pressure of CO can be obtained by introducing CO-containing gas and by means of the CO which has been dissolved in the oxygen-containing compounds by keeping the latter under pressure or which has been liberated therefrom but is conveyed with the oxygen-containing compounds to the decomposition space.

The presence of the carbon monoxide in the hydrogen-containing gas mixture prevents the oxygen-containing compounds which are present from being hydrogenated, either entirely or partially, at the pressure applied.

Preferably a gas mixture is introduced which contains from 10 to 50% of carbon monoxide in addition to any admixtures present therein, such as methane, carbon dioxide and nitrogen. The introduction of gas is needed to give the desired agitation and to produce a gas phase which is sufficiently large for the decomposition of the metal compounds. A hydrogen-containing gas mixture with 0.1 or more % of CO contains more CO than the gas hitherto used for the decomposition of the metal compounds, which gas had been freed from CO by a methanating process and only contained some hundredths of a per cent. of carbon monoxide.

The metal separated in this treatment can, for example, be applied to a carrier material, such as pumice stone, which has been arranged to be stationary in the decomposition space in the form of lumps or which has been distributed in fine particles in the material to be treated. If so desired, the product obtained can be freed from separated metal and/or carrier material by filtration. It is also possible to use the metal which has been separated on carrier material as catalyst in the subsequent treatment of the product, for example when reducing the resultant aldehydes to alcohols.

The temperature to be applied may be as high as 250° C. and is preferably above 100° C. ranging, for example, from 150° C. to 220° C.

The total pressure used in the treatment is, preferably, 25—50 atmospheres. The pressure will be dependent on the volatility of the product to be treated and the temperature must be so high that the decomposition pressure of the carbonyl compounds is well above the partial pressure of the CO.

To decompose metal compounds, in particular cobalt compounds in formylation products which have been formed by the addition of CO and H_2 to organic compounds with at least one olefinic double bond at a pressure above 100 atmospheres, the formylation product obtained can be cooled and its pressure released to the pressure required for the decomposition of the cobalt compounds, after which it can be passed, together with the gas liberated during the release of pressure or after separating part or all of the gas liberated in the decompression, to the decobaltizing space.

The above treatment of the oxygen-containing compounds can be carried out batchwise in an autoclave or continuously, while the gas mixture can be recycled, if so desired.

The following examples show how the process of the invention may be carried into effect.

EXAMPLE I.

A reaction product mainly consisting of C_8-C_9 aldehyde and obtained by treating at elevated temperature and at a pressure of 200 atmospheres a fraction of C_7-C_8 alkenes with CO and H_2 in the presence of cobalt hydrocarbonyl, contained approximately 0.25% of dissolved cobalt. Less than 10% thereof was in the form of cobalt hydrocarbonyl and the rest in the form of complex compounds. This reaction product was heated to 200° C. and passed continuously through a high-pressure vessel filled with pieces of pumice stone, together with a gas mixture containing 41.1% of carbon monoxide and 54% of hydrogen, in addition to small quantities of impurities, while the pressure was maintained at 25 atmospheres. The liquid flowing through the vessel in countercurrent to the gas was recovered at the bottom of the vessel, almost completely freed from dissolved cobalt, while hardly any aldehydes had been reduced to alcohols.

EXAMPLE II.

A reaction product obtained by the formylation of a fraction of C_6-C_8 alkenes in the presence of a suspended cobalt catalyst on kieselguhr contained 60% of aldehydes.

When this product was decomposed with CO-free hydrogen at 180—200° C. under a pressure of 25 atmospheres, the decobaltized product contained 40% of aldehydes.

When using a gas with 22% of CO, the aldehyde content of the decobaltized product was 55%.

What we claim is:—

1. A process for treating oxygen-containing organic compounds obtained by the action of carbon monoxide, with or without hydrogen, on various organic compounds in the presence of catalysts which produce soluble metal compounds in the final product, such as complex compounds, metal carbonyls or hydrocarbonyls, which are introduced as such or are formed during the reaction, in order to decompose the metal compounds dissolved in the oxygen-containing organic compounds with a hydrogen-containing gas at elevated pressure and temperature, wherein the treatment is carried out at a pressure of from 10 to 80 atmospheres with a gas containing, besides hydrogen, carbon monoxide in such a quantity that reduction of the oxygen-containing compounds is checked, by introducing a gas mixture containing from 0.1—50% carbon monoxide.

2. A process as claimed in claim 1 for decomposing cobalt compounds which are present in oxygen-containing organic products obtained by the formylation of alkenes at a pressure above 100 atmospheres and at elevated temperature, wherein the formylation product, after cooling, is decompressed to 10—80 atmospheres and the liquid with catalyst suspended therein together with the gas liberated in the decompression or part thereof is passed into a decobaltizing zone, in which a temperature above 100° C. prevails, preferably between 150 and 220° C., and into which there is passed a gas containing, besides hydrogen, from 0.1 to 50% of carbon monoxide.

3. A process as claimed in claims 1 and 2, wherein the hydrogen-containing gas used contains from 10 to 50% of carbon monoxide.

4. A process for treating oxygen-containing organic compounds substantially as described with reference to the foregoing Examples.

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