[Second Edition.]

PATENT SPECIFICATION

313,061

2398

Application Date : Feb. 28, 1928. No. 6182 / 28.

Complete Left : Nov. 28, 1928.

Complete Accepted : May 28, 1929.

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture of Aldehydes and Alcohols.

We, GILBERT THOMAS MORGAN and RAYMOND TAYLOR, Research Chemists, both of the Chemical Research Laboratory, Teddington, Middlesex, and both British Subjects, do hereby declare the nature of this invention to be as follows :—

Gaseous mixtures containing carbon monoxide and hydrogen when passed at elevated temperatures and pressures over cataylsts made from combinations of zinc and chromium oxides or zinc and manganese oxides in proportions which may be varied within wide limits give rise substantially to methanol or methyl alcohol.

We have now found that the addition of cobalt oxide to combinations of zinc and chromium oxides or zinc and manganese oxides or to combinations of these three oxides as a catalytic medium leads under high pressures and at high temperatures to a definite and regulated type of condensation resulting in the production from carbon monoxide and hydrogen of the homologous series of aliphatic aldehydes $C_nH_{2n+1}.CHO$ and the corresponding primary alcohols.

The process when carried out as in the following example is a controlled reaction inasmuch as a close examination of the resulting products has so far failed to reveal the presence of organic acids, esters, ketones or secondary alcohols, although as might be expected interaction between the alcohols and aldehydes produces ortho-ethers of the methylal and acetal series.

EXAMPLE.

Ten parts by weight of cobalt chromate, $CoCrO_4$, are added to 90 parts of basic zinc chromate, $3ZnO, CrO_3$, and the mixture is kneaded with water into a stiff paste which is extruded through dies into a vermiform mass. This material is dried at 130° C. and cut up into short lengths. These cylindrical granules, reduced by heating at 300—350° C. in a stream of hydrogen, are charged into a steel cylinder with an internal copper lining and heated at 400° C. in a current of carbon monoxide and hydrogen (1 vol. to 2 vols.) under a pressure of 200 atmospheres. The issuing gases are thoroughly cooled in order to condense the volatile mixture containing the aldehydes and alcohols. The aldehydes are separated from the alcohols by the use of suitable reagents such as sodium bisulphite, alcoholic ammonia, semicarbazide or phenylhydrazine and its nitro-derivatives. The final isolation of the individual aldehydes and alcohols is effected by fractional distillation.

In this controlled condensation the proportions of carbon monoxide and hydrogen in the gaseous mixture may be varied within wide limits and the proportion by weight of the catalytic oxides may also be varied considerably with consequent regulation in the relative amounts of lower and higher aldehydes and primary alcohols in the organic products of catalysis.

One characteristic of this controlled condensation is the high proportion of ethyl alcohol to methyl alcohol in the products of catalysis.

Dated the 23rd day of February, 1928.
GILBERT THOMAS MORGAN.
RAYMOND TAYLOR.

COMPLETE SPECIFICATION.

Improvements in the Manufacture of Aldehydes and Alcohols.

We, GILBERT THOMAS MORGAN, and RAYMOND TAYLOR, both British Subjects, and both of the Chemical Research Laboratory, Teddington, Middlesex, 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 :—

It is known that, in general, the presence of iron, nickel, or cobalt in catalysts used for the synthesis of methanol from carbon monoxide and hydrogen, has a deleterious effect upon the desired course of the reaction. It has been stated, however, that when any of these elements is present in the catalyst in a chemical combination or in the form of an alloy or a

[*Price*

solid solution, not allowing the formation of free iron, nickel or cobalt metal either by reduction or by decomposition under the conditions of working, and in the absence of free iron, nickel or cobalt on the surface of the apparatus exposed to the gases, the desired reaction is considerably improved, particularly in the direction of the production of alcohols higher in the series than methanol.

It is further known that catalysts made from zinc oxide and chromium oxide or zinc oxide and manganese oxide are good catalysts for producing methanol from a mixture of carbon monoxide and hydrogen.

The present invention is based on the observation that by introduction of cobalt into mixtures of zinc and chromium oxides or zinc and manganese oxides or zinc, chromium and manganese oxides, the cobalt being in a form reducible as a preliminary operation or during the condensation, a catalyst is obtained which has an influence on the course of reaction between carbon monoxide and hydrogen under high pressures and at high temperatures, which leads to a definite and regulated type of condensation producing the homologous series of aliphatic aldehydes

$$C_nH_{2n+1}.CHO$$

and the corresponding primary alcohols.

The invention consists in synthesising aliphatic aldehydes and primary alcohols from carbon monoxide and hydrogen at high temperature and pressure with aid of a catalyst containing cobalt as explained in the last preceding paragraph, with the outstanding advantage that the yield of ethyl alcohol is much larger than in known processes.

The reaction is conducted in a copper-lined vessel in known manner as this has a favourable influence on the rate of the reaction at a given temperature or alternatively allows the temperature to be reduced for a given rate of reaction. This effect may be enhanced by introduction of copper into the catalyst.

It may be said that the invention provides a controlled reaction, inasmuch as examination of the products shows the virtual absence of organic acids, esters, ketones or secondary alcohols, although as might be expected interaction between the alcohols and aldehydes produces ortho-ethers of the methylal and acetal series.

The following Examples illustrate the invention:—

EXAMPLE 1.

20 parts by weight of cobalt chromate $CoCrO_4$, are added to 100 parts of basic zinc chromate, $3ZnO, CrO_3$ and the mixture is kneaded with water to form a stiff paste which is extruded through dies into a vermiform mass. This material is dried at 130° C., and cut into short lengths. These cylindrical granules, reduced by heating at 300—350° C., in a stream of hydrogen, are charged into a steel cylinder with an internal copper lining and immersed in a molten lead bath heated to 400° C. A current of carbon monoxide and hydrogen is passed over the catalyst at a pressure of 200 atmospheres. The composition of the gases may be hydrogen two parts by volume, carbon monoxide one part by volume, but the proportions may vary within wide limits.

The issuing gases are thoroughly cooled in order to condense the volatile mixture containing the aldehydes and alcohols. The aldehydes are separated from the alcohols by the use of suitable reagents such as sodium bisulphite, alcoholic ammonia, semi-carbazide or phenylhydrazine and its nitro-derivatives. The final isolation of the individual aldehydes and alcohols is effected by fractional distillation.

EXAMPLE 2.

Cobalt chromate 1 part by weight and zinc chromate 1 part, are mixed together with a binding material, such as asbestos or clay, and made as previously described into granules which are charged into a copper-lined steel cylinder heated to 250—350° C. The passage of a mixture of carbon monoxide and hydrogen at 200 atmospheres gives a product containing methyl, ethyl and higher alcohols.

EXAMPLE 3.

Cobalt nitrate 2 parts by weight and zinc permanganate 1 part are dissolved in water and the solution is boiled to dryness. The mixture, together with a binding material, such as asbestos or clay, is made into granules as described in Example 1 and reduced by heating in hydrogen at 300—400° C.; the granules are charged into a copper-lined steel cylinder and heated to 200—300° C. The product obtained by the passage of a mixture of hydrogen and carbon monoxide at 200 atmospheres pressure over the heated catalyst contains aldehydes (acetaldehyde and higher aldehydes) also alcohols (methyl, ethyl and higher alcohols).

EXAMPLE 4.

2 parts by weight of cobalt nitrate, 1 part of zinc permanganate and 0.7 part of copper carbonate are made into granules in a manner as described in Example 1, and reduced by heating with hydrogen at 300—350° C.; the granules are charged into the copper-lined steel cylinder immersed in a molten metal bath heated to 350° C. The product obtained by the passage of a mixture of hydrogen and

carbon monoxide at 200 atmospheres over the heated catalyst contains aldehydes (acetaldehyde, propaldehyde, butaldehyde and higher aldehydes) and alcohols (methyl, ethyl, propyl and higher alcohols).

EXAMPLE 5.

Cobalt nitrate 60 parts by weight, zinc oxide 10 parts, chromic acid 20 parts and copper carbonate 10 parts are mixed together and made, as described in Example 1, into granules which are charged into the copper lined steel cylinder, immersed in a lead bath heated to 250—350° C. The passage of a mixture of carbon monoxide and hydrogen at 200 atmospheres pressure over the catalyst produces a mixture containing aldehydes and methyl, ethyl and higher alcohols.

In this controlled condensation according to this invention the proportions of carbon monoxide and hydrogen in the gaseous mixture may be varied within wide limits and the proportion by weight of the catalytic oxides may also be varied considerably with consequent regulation in the relative amounts of lower and higher aldehydes and primary alcohols in the organic products of catalysis, for example, an increase in the proportion by weight of cobalt tends to increase the ratio of ethyl and higher alcohols to the methyl alcohol also produced.

It will be understood that the particular combination of materials constituting the catalyst used in this invention has been selected as being one which leads to the production of a liquid mixture the organic constituents of which are practically all, if not entirely, primary alcohols and aldehydes and their condensation products, the mixture being characterised by a high percentage of ethyl alcohol. Typical yields of methyl, ethyl and higher primary alcohols are in the ratio 50 : 30 : 20 respectively with a catalyst containing zinc, manganese and cobalt. A survey of patent literature covering catalysts for influencing the reaction between carbon monoxide and hydrogen shows that nearly all the metals have been claimed, if not separately at least in combination in groups according to the periodic classification. There will be found in various prior publications (such as Specifications Nos. 279,378, 271,840, 229,715 and 20,488/13) references to catalysts containing named materials from which might be selected those essential to this invention, but we believe we are the first to make this selection and we have done so for the purpose of obtaining the mixture of organic compounds described above characterised by a high percentage of ethyl alcohol.

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. A manufacture of a mixture of organic liquids consisting practically entirely of primary alcohols and aliphatic aldeyhdes and their condensation products characterised by ethyl alcohol forming a relatively large percentage of the alcoholic constituents, by the catalytic condensation of carbon monoxide and hydrogen at a high temperature and pressure, wherein the catalyst contains cobalt in addition to zinc oxide and chromium oxide or zinc oxide and manganese oxide or all these oxides, the cobalt being in the form reducible as a preliminary operation or during the condensation.

2. A modification of the manufacture referred to in Claim 1, wherein copper is also present in the catalyst.

3. A process of synthesising aliphatic aldehydes and primary alcohols and their condensation products substantially as described in any of the Examples herein.

Dated this 28th day of November, 1928.

ABEL & IMRAY,
30, Southampton Buildings, London,
W.C. 2,
Agents for the Applicants.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 51A —125/9/1929.]