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(12) **Patent:**

(54) METHYL ALCOHOL PRODUCTION

(54) PRODUCTION D'ALCOOL METHYLIQUE

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ABSTRACT:

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Our invention relates to the production of methyl alcohol by catalytic, synthetic means from hydrogen and carbon monoxide or carbon dioxide. It is well known that methyl alcohol may be catalytically prepared by reacting the above gases at elevated temperatures and pressures in the presence of a proper catalyst. The two chemical reactions which are illustrative of the reaction follow:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

Both of these reactions are reversible and take place only at elevated temperatures and pressures.

A very wide variety of substances and mixtures of substances has been proposed as catalysts for the reaction. Some of these catalysts are so easily poisoned and destroyed that they are uneconomical in use. Others are extremely expensive and still others do not produce pure methyl alcohol, but rather a variety of substances including acids and gaseous hydrocarbons such as methane.

It is the purpose of our invention and application to provide a workable economical process for the production of methyl alcohol from hydrogen and oxides of carbon and this purpose has been accomplished by the preparation of a novel and efficient catalyst and by the discovery of proper working conditions for the use of this catalyst whereby methyl alcohol may be produced in good yield.

As a catalyst we employ a metallic alloy of zinc and copper in which the copper is present in larger proportion than the zinc. The copper-zinc alloy may also contain a small percentage of another metal such as tin or manganese. The following substances are typical alloys, such as are contemplated for use in our process.

brass - zinc, 1 part; copper, 2-5 parts

bronze - zinc, 1-2 parts; copper, 7-9 parts; and tin, 1-2 parts

manganese bronze - which is an ordinary bronze containing about .3% of manganese.

Before use as catalysts these alloys must be preliminarily activated. This may be accomplished by reducing the alloy to small particles suitable to serve as contact catalysts, for example - filings or turnings, and then subjecting the surface to an oxidizing action. This oxidation attacks the surface of the catalyst and makes it irregular and porous. On exposure to a reducing atmosphere, such as hydrogen gas, the oxidized surface is partially reduced to metal and the complex mixture of copper alloy and derived oxides constitutes an active methanol catalyst.

While our invention is directed generally to the use of activated alloys of the above type in the production of methyl alochol, we prefer to activate the catalysts by means of a process described as "anodic oxidation". For example, the brass or bronze filings are made to serve as the anode in an electrolytic cell. Nickel or carbon may serve as the cathode, and a suitable electrolyte is a 2% solution of sodium carbonate. For example, 30 pounds of brass filings contained in a cylindrical column 30 inches high and 4-5 inches in diameter and located 2-4 inches from a cathode of about equal size, when exposed to a current of 10 volts and 30-50 amperes for about 30 hours will result in the anodic oxidation of the entire catalyst surface to a sufficient depth to form an active catalyst.

This anodic oxidation results in a surface change on the metal and the formation of a penetrable film of oxides. If this catalyst mass is now partially reduced to metallic state by heating it in a current of hydrogen, a very active methyl alcohol catalyst will result. We prefer to reduce the mass immediately prior to methanol production by passing hydrogen over it at a temperature, of about 200°C.

While we have described in detail an anodic oxidation method of activating a copper alloy to serve as a catalyst for methyl alcohol production it should be understood that these catalysts may be oxidized by other means, such as exposure to an atmosphere of oxygen at an elevated temperature. The anodic oxidation method produces a better product, but our invention is not so limited, and refers broadly to the use of copper alloys as methyl alcohol catalysts.

When carbon monoxide gas in the presence of a molecular excess of hydrogen is passed over one of our copper-alloy catalysts at elevated temperature and pressure, methyl alcohol is produced in substantially pure form. Pressures in excess of 100 atmospheres and temperatures in excess of 200°C. should be employed. The reaction temperature - i.e. of the catalyst mass - should not exceed 600°C. There is no definite upper limit of pressure except the practical limit which can be attained by apparatus available.

At pressures and temperatures within the range described, methanol will be produced in every case by the use of our copper alloy catalysts. The yield will vary with the pressure, temperature, and rate of gas flow over the catalyst. In general we prefer to use pressures between 100-200 atmospheres and a temperature of 250-300° C.

Where pure carbon monoxide gas is used we prefer to use an excess of hydrogen in the relation of one molecule of carbon monoxide to five molecules of hydrogen. A gaseous mixture of carbon monoxide with carbon dioxide or pure carbon dioxide gas may be also employed, but in this case more hydrogen must be used as some is consumed in producing water according to the reaction

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$$

In the case where a substantial quantity of the oxide of carbon employed is carbon dioxide, we prefer to use a much larger excess of hydrogen - for example twenty molecules of hydrogen per molecule of carbon dioxide.

When a mixture of carbon monoxide and hydrogen in the proportion of one volume of the former to five of the latter is passed over our copper-alloy catalyst at a pressure of 200 atmospheres and a temperature of 280°C. at a speed of about 10 cubic meters of gas per kilogram of catalyst, about 15% of the carbon monoxide present is converted to methyl alcohol, which, on cooling the gaseous mixture, is condensed to liquid form and thus removed from the process. The residual gas mixture is continually recirculated over the catalyst and from time to time carbon monoxide and hydrogen is added to maintain approximately the original percentage composition of gases.

Carbonyl forming metals such as iron, nickel, and cobalt must not be present in the catalyst or used in constructing the catalyst chamber as the presence of these metals results in the formation of methane in accordance with the following equation:-

$$CO + 3H_2 = CH_4 + H_2O$$

The apparatus for conducting the reaction may well be made of steel internally lined with copper.

While we have described the use of pure carbon oxides and hydrogen as the raw materials for methyl alcohol production, it should be understood that small percentages of gaseous hydrocarbons such as methane and inert gases such as nitrogen may be present in the gaseous mixture without bad results.

Now having fully described our invention, we claim the following as new and novel.

1. A process for the production of methyl alcohol which comprises passing a gaseous mixture of oxides of carbon and hydrogen over a copper alloy catalyst at an elevated temperature and pressure.

2. A process for the production of methyl alcohol which comprises passing a gaseous mixture of oxides of carbon with a molecular excess of hydrogen over a copper-zinc alloy catalyst containing some oxides, at an elevated temperature and pressure.

3. A process for the production of methyl alcohol which comprises passing a gaseous mixture of oxides of carbon with a molecular excess of hydrogen over a copper alloy catalyst containing some oxides, at 250-300° C. and at a pressure in excess of 100 atmospheres.

4. A process for the production of methyl alcohol which comprises passing a gaseous mixture consisting of 1 volume of oxide of carbon and 5-20 volumes

of hydrogen over a copper-zinc alloy catalyst containing some oxides, at 250-300° C. and at a pressure in excess of 100 atmospheres.

5. A process for the production of methyl alcohol which comprises passing a gaseous mixture consisting of 1 volume of carbon monoxide and 5-20 volumes of hydrogen over a copper-zinc alloy catalyst containing some oxides, at a temperature of 250-300° C. and at a pressure in excess of 100 atmospheres.

6. A process for the production of methyl alcohol which comprises passing a gaseous mixture consisting of 1 volume of carbon monoxide and 5 volumes of hydrogen over a copper-zinc alloy catalyst containing some oxides, at 280° C. and at a pressure of about 200 atmospheres.

7. In a process for the production of methyl alcohol, the step which comprises leading a gaseous mixture of carbon monoxide and hydrogen at elevated temperature and pressure over a catalyst consisting of an alloy containing copper and zinc, partially oxidized.

8. In a process for the production of methyl alcohol, the step which comprises leading a gaseous mixture of carbon monoxide and hydrogen at elevated temperature and pressure over a catalyst consisting of an alloy containing copper and zinc which has been activated by anodic oxidation and subsequent partial reduction.

9. In a process for the production of methyl alcohol, the step which comprises preparing a suitable catalyst by anodically oxidizing the surface of a copper-zinc alloy and partially reducing the surface by contact with hydrogen.