[Second Edition.]

PATENT SPECIFICATION

Convention Date (United States): May 26, 1926.

271,840

Application Date (in United Kingdom): April 20, 1927. No. 10,647/27.

Complete Accepted: Sept. 20, 1928.

3978

COMPLETE SPECIFICATION

Improvement in Catalysts for Synthetic Methanol Production.

We, COMMERCIAL SOLVENTS CORPORATION, a corporation organised and existing under the laws of the State of Maryland, United States of America, located at Terre Haute, Vigo County, State of Indiana, United States of America (Assignees of JOHN CAULFIELD WOODRUFF, a citizen of the United States of America, of 1526, South Sixth Street, Terre Haute, Vigo County, State of Indiana, United States of America, and GROVER BLOOMFIELD, a citizen of the United States of America, of 1306, South Center Street, Terre Haute, Vigo County, State of Indiana, 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 the production of methanol by the high pressure catalytic combination of oxides of carbon with hydrogen, and pertains more directly to the preparation and employment of improved catalysts in the process.

Methanol may be produced by combining oxides of carbon with hydrogen in the presence of a suitable catalyst at elevated temperature and pressure. Carbon monoxide, carbon dioxide, and mixture of the two oxides may be employed, these substances reacting with hydrogen according to the following equations:—

Carbon monoxide—$CO + 2H_2 = CH_3OH$.
Carbon dioxide—$CO_2 + 3H_2 = CH_3OH + H_2O$.

It is observed that when carbon dioxide is the oxide employed, one molecule of water is formed for every molecule of methanol produced. On the other hand when pure carbon monoxide is used, theoretically there is nothing produced by the reaction but methanol. Actually in practice pure carbon monoxide and pure carbon dioxide are both difficult to obtain economically, so that the methanol synthesis is carried out by reacting a mixture of carbon monoxide and carbon dioxide with hydrogen.

In addition to the reactions producing methanol there are, in the methanol synthesis, undesirable side-reactions which cut down the yield of the desired product. The principal side-reaction which may occur is the formation of methane, which is illustrated below:

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

In addition to the methane side-reaction there are other side-reactions which sometimes occur in which there are produced esters, aldehydes, organic acids, ketones, and hydrocarbons other than methane; these reactions occuring as the result of the polymerization or condensation of methanol or its decomposition products.

When a gas mixture comprising carbon oxides mixed with an excess of hydrogen over the amount theoretically required to produce methanol is passed over a catalytic substance comprising metals or their oxides at a pressure above 50 atmospheres and at a temperature above 250° C., for example at 350° to 450° C., there is nearly always produced some reaction between the gaseous components. The extent of this reaction depends to some degree on space velocity, temperature, and pressure, but the fact remains that under the conditions outlined, carbon oxides and hydrogen react to some extent in all cases.

The substances formed by such a process depend, both as to identity and as to amount, almost entirely on the nature and activity of the catalytic substance present. The methanol catalysts proposed in the past have been of two principal types, i.e.:—

1. Mixtures of finely divided metals, or, what is equivalent, mixtures of easily reducible metal oxides;
2. Mixtures of oxides of metals non-reducible, or difficultly reducible under the conditions of the methanol synthesis.

In the past, also, one class of easily reducible metal oxides, that is the oxides of iron, nickel, and cobalt, have been described as absolutely worthless for the production of methanol catalysts since these metals under normal conditions prevent the formation of methanol, the reaction producing only methane.

We are aware that in the art of preparing hydrogen and carbon dioxide from carbon or carbon-containing substances it has been proposed to use as a catalyst a mixture comprising oxygen-containing salts of the alkali or alkaline earth metals or compounds from which such salts under the conditions of the process may be formed, together with inorganic oxides or hydroxides having the character of a non-volatile weak acid or acid anhydride or compounds, which may include aluminium or tin chloride, from which such oxides or hydroxides under the conditions of the process may be formed; in this manufacture oxides of iron, chromium or manganese or combinations of such oxides can be incorporated with a view to increasing the catalytic effect.

We have discovered a new type of methanol catalyst which produces a higher yield of methanol than those formerly employed in the art, and at the same time produces a very pure methanol, uncontaminated by by-products. An additional advantage accruing from the use of our catalysts is that the formation of methane in the process—with the consequent destruction of valuable hydrogen —is practically eliminated.

We have now discovered a new type of valuable methanol catalyst which initially comprises three main elements, i.e.:—

(1) One or more difficultly reducible metal oxides such as the oxides of zinc, magnesium, cadmium, chromium, vanadium, tungsten.

(2) One or more easily reducible metal oxides such as the oxides of copper, silver, iron, nickel, cobalt.

(3) A metallic halide.

The new catalyst forming a part of the subject matter of the present invention preferably has a predominating proportion of difficultly reducible oxide, while the oxides used are generally those of metals in the second, sixth and seventh groups of Mendeleef's Periodic Table of the Elements.

By the term "difficultly reducible metal oxide" is meant a metallic oxide which is substantially non-reducible by hydrogen or mixtures of hydrogen and carbon monoxide under the operating conditions of the methanol synthesis. Easily reducible metal oxides, on the other hand are reduced under those conditions.

It will be observed that in our improved catalyst we may employ substances normally deleterious to the methanol reaction —namely the oxides of "methanating metals"—iron, nickel or cobalt. In our improved catalyst compositions these normally deleterious substances serve advantageously, apparently exerting only a normal hydrogenating catalytic action productive of methanol. Or we may employ easily reducible oxides such as those of copper or silver which are already known in the art as advantageous components of certain methanol catalysts. In these cases, however, our improved catalysts containing halides produce far better results than those known in the art for otherwise identical catalyst mixtures.

The precise method by which the metallic halides produce the improvement is not known to us. At least three theories may be used to account for the phenomenon—namely:—

(1) The metallic halide acts as an ordinary "promoter" in increasing catalyst activity;

(2) The metallic halide interacts with other metallic oxides present in the catalyst to produce oxychloride compounds which, in turn, either serve as catalyst promoters, or may so modify the purely physical state of the mass as to produce a more active catalyst;

(3) The metallic halide may be reduced by the high pressure contact with hydrogen and carbon oxides during the commencement of its use as a catalyst and the resultant finely divided metal may increase the catalyst activity, or alternatively, the metallic halide may first react with one of the metals of the original oxides producing the halide thereof, which may be reduced in the same manner.

However, the precise explanation for the improved result attained by the addition of metallic halides to methanol catalysts is not known and forms no part of our invention.

To produce our improved catalysts it is not necessary that the amount of metallic halide added bear any exact weight relation to the remaining constituents of the catalyst, though the amount of halide added should preferably be less than that which is chemically equivalent to the amount of the metallic oxide present in the largest molecular proportion in the catalyst.

As illustrative of our invention we will cite a number of specific catalysts. In order to indicate the comparative efficacy of these catalysts in methanol production we have selected a standard set of conditions of use as follows. The reported yields of condensate from the methanol reaction by use of the following catalysts is based on the effect produced when a gas mixture comprising 8% carbon dioxide, 3% of carbon monoxide and 89% hydrogen is passed through 1 liter of catalyst granules at a space velocity of 75,000—100,000, at a pressure of 2000 pounds, and at a temperature of 340—450° C.

In selecting a standard set of conditions it is our intention only to thus display the catalyst efficacy and by no means to limit the scope of our invention. Modification of the conditions of the reaction will, of course, modify the results, but the results will always depend on the catalyst employed.

For example, an increased space velocity produces an increased hourly yield and an increase in operating pressure has the same effect. Likewise the use of pure carbon monoxide as distinguished from carbon dioxide or a mixture of the two results in an increased methanol percentage in the condensate, and, since carbon monoxide seems to react more readily, an increased condensate volume.

Example I.

8 kilograms of chromic nitrate ($Cr(NO_3)_3.9H_2O$) and 1.5 kilograms of nickel nitrate ($Ni(NO_3)_2.6H_2O$) are dissolved in 150 liters of water, and to this solution there is added the theoretical amount (5.4 liters of 12.75 normal) of ammonium hydroxide to precipitate chromium hydroxide and nickel hydrate. The solution is then centrifuged to recover the precipitated hydrates and the resultant precipitate is thoroughly washed with water, dried, and broken up into granules.

The resultant granules are moistened with an aqueous solution of 200 grams zinc chloride and again dried, whereupon they are ready for use.

The hourly yield of condensate is about 1 liter, which analyzes about 35% methanol.

Example II.

2250 grams of nickel nitrate ($Ni(NO_3)_2.6H_2O$) are dissolved in 250 liters of water and the solution is heated to 95° C. 7500 grams of zinc oxide is then added with stirring. To this solution there is added sufficient ammonium hydroxide to precipitate the nickel as nickel hydrate. The precipitated mass is recovered by decantation and filtration, is washed, dried, and broken up into granules.

To this mass is added a solution containing 740 grams of zinc chloride and the mass is again dried.

The hourly yield of condensate is about 1 liter and contains about 30% methanol.

If the amount of zinc chloride used is doubled, the hourly condensate will be increased to about 2.5 liters and the percentage of methanol will be increased to about 56%.

Substitution of chemically equivalent quantities of magnesium chloride or zinc bromide for the zinc chloride produces similar results.

Example III.

2250 grams of cobalt nitrate ($Co(NO_3)_2.6H_2O$) are dissolved in 250 liters of water and the solution is heated to 95° C. There is then added 7.5 kilograms of zinc oxide after which the solution is vigorously stirred and sufficient ammonium hydroxide is added to precipitate the cobalt as cobalt hydrate. The precipitated mass is recovered by decantation and filtration, is washed, dried, and broken up into granules. The granules are then moistened with a solution containing 1480 grams zinc chloride and dried once more.

The hourly yield of condensate is about 1.5 liters and contains about 58% of methanol.

Example IV.

If the zinc chloride in Example III is replaced by 1300 grams of magnesium bromide the hourly yield of condensate and percentage yield of methanol is not greatly modified.

Example V.

3500 grams of ferric nitrate is dissolved in 50 liters of water and sufficient ammonium hydroxide is added to precipitate all of the iron as ferric hydroxide. The flocculent mass is filtered and washed and to it is added 9 kilograms of zinc oxide and the mixture thoroughly stirred. The resultant pasty mass is allowed to dry and is then broken up into granules. To these granules is added a solution containing 1500 grams ferric chloride. The mass is again dried, whereupon it is ready for use.

The hourly yield of condensate is about 1.5 liters and contains about 55% methanol.

Example VI.

4 kilograms chromic nitrate ($Cr(NO_3)_3.9H_2O$) and 750 grams nickel nitrate ($Ni(NO_3)_2.6H_2O$) are dissolved in 5 liters of water. 2.5 kilograms of zinc oxide is added with stirring and the mass is heated to dryness and is then further heated till no more nitric oxide fumes are given off, whereby the mixture is transformed to chromic oxide, nickel oxide, and zinc oxide. The resultant mass is broken up into granules and is then moistened with a solution containing 450 grams of zinc chloride. The granules are again dried and are ready for use. If desired, 450 grams of dextrin or a similar agglutinating agent may be added with the zinc chloride, whereby firmer granules are obtained on drying.

The hourly yield of condensate is about 1 liter and contains about 30% of methanol.

Example VII.

In place of moistening the granules of the catalyst in Example VI with zinc chloride a chemically equivalent amount of chromic chloride may be employed.

The results will not be greatly varied.

EXAMPLE VIII.

2600 grams of zinc oxide in powdered form is mixed by thorough sifting with 500 grams of black copper oxide. The resultant mixture is moistened with an aqueous solution containing 150 grams cuprous chloride and 200 grams of dextrin. The resultant mass is dried and broken up into pieces whereupon it is ready for use.

The hourly yield of condensate is about 1.2 liters containing about 40% of methanol.

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 methanol catalyst initially comprising one or more difficultly reducible metal oxides, one or more easily reducible metal oxides, and a metal halide.

2. A methanol catalyst as claimed in Claim 1, characterised in this that a predominating proportion of difficultly reducible oxide is present.

3. A methanol catalyst as claimed in Claims 1 and 2, in which the metallic halide is present in amounts less than or proportional to that which is chemically equivalent to the amount of the difficultly reducible metal oxide or oxides.

4. A methanol catalyst as claimed in Claims 1 to 3, characterised in this that an oxide of a metal of the second, sixth or seventh periodic group is present.

5. A methanol catalyst as claimed in Claims 1 to 4, characterised in this that the difficultly reducible metal oxide or oxides comprise one or more of the following metals:—zinc, magnesium, cadmium, chromium, vanadium, tungsten.

6. A methanol catalyst as claimed in Claims 1 to 5, characterised in this that the easily reducible metal oxide or oxides comprise one or more of the following metals:—iron, nickel, cobalt, copper.

7. A methanol catalyst as claimed in any of the preceding claims in which a magnesium halide constitutes the halide.

8. A methanol catalyst as claimed in any of the preceding claims, in which a metallic chloride, such as zinc chloride or magnesium chloride or chromic chloride, is employed.

9. A methanol catalyst as claimed in Claims 1 to 7, in which a metallic bromide, such as magnesium bromide, or zinc bromide, is used.

10. The methanol catalyst substantially as hereinbefore described.

11. An improved process for the production of synthetic methanol which comprises passing a mixture of hydrogen and carbon oxides under pressure at an elevated temperature over the improved catalyst hereinbefore described and claimed.

12. An improved process for the production of synthetic methanol as claimed in Claim 11, in which the gases are subjected to a pressure in excess of 50 atmospheres at a temperature of 350° C. to 450° C.

13. The improved process for the production of synthetic methanol substantially as hereinbefore described.

Dated this 20th day of April, 1927.
MARKS & CLERK.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 56A.—125/2/1929.]

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