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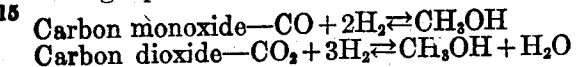
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CATALYST FOR SYNTHETIC-METHANOL PRODUCTION.

No Drawing. Original application filed May 26, 1926, Serial No. 111,884. Divided and this application filed September 25, 1926. Serial No. 137,810.

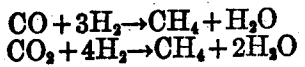
Our invention relates to the production of methanol by the high pressure catalytic combination of oxides of carbon with hydrogen, and pertains more directly to the preparation and employment of improved catalysts in the process.

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 mixtures of the two oxides may be employed, these substances reacting with hydrogen according to the following equations:—



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:



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 occurring as the result of the polymerization of 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. 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 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 comprises three main elements—i. e.

- (1) One or more non-reducible metal oxides such as zinc, magnesium, cadmium, chromium, vanadium, tungsten, etc.;
- (2) One or more easily reducible metal oxides such as copper, silver, iron, nickel, cobalt, etc.;
- (3) A metallic halide.

It will be observed that in our improved catalyst we may employ substances normally deleterious to the methanol reaction—namely the “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
5 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
10 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
15 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
20 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,
25 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
30 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 some other
35 metal 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
40 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
45 to the remaining constituents of the catalyst, though the amount of halide added should preferably be less than one chemical equivalent of the amount of principal metallic oxide present 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
50 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
55 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 340-400° C.

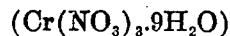
65 In selecting a standard set of conditions

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
70 will always be proportionate to the catalyst employed.

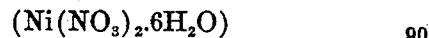
For example, an increased space velocity produces an increased hourly yield and an increase in operating pressure has the same
75 effect. Likewise the use of pure carbon monoxide as distinguished from carbon dioxide or a mixture of the two results in an increased methanol percentage in the condensate,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

Example I.

8 kilograms of chromic nitrate 85



and 1.5 kilograms of nickel nitrate



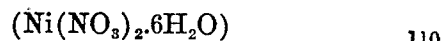
are dissolved in 150 liters of water, and to this solution there is added the theoretical amount (5.4 liters of 12.75 normal) of ammonium hydroxide to precipitate chromium hydroxide and nickel hydrate. The solution is then centrifuged to recover the precipitated hydrates and the resultant precipitate is thoroughly washed with water,
95 dried, and broken up into granules.

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

The hourly yield of condensate is about
105 1 liter, which analyzes about 35% methanol.

Example II.

2250 grams of nickel nitrate



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
115 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
120 740 grams of zinc chloride and the mass is again dried.

The hourly yield of condensate is about
125 1 liter and contains about 30% of 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 130

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

Example III.

4 kilograms chromic nitrate
($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)

and 750 grams nickel nitrate
($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

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 2.5 liters containing about 58% methanol.

Example IV.

In place of moistening the granules of the catalyst in Example III with zinc chloride a chemically equivalent amount of chromic chloride may be employed. The results will not be greatly varied.

This application is a division of our co-pending application Serial No. 111,884, filed May 26th, 1926. In the said application we have claimed, generically, methanol catalysts comprising difficultly reducible metal oxides, easily reducible metal oxides, and metallic halides and therefore such generic claims are not made herein.

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

1. A methanol catalyst initially compris-

ing a plurality of difficultly reducible metal oxides, nickel oxide, and a metallic halide.

2. A methanol catalyst initially comprising a difficultly reducible metal oxide, nickel oxide, and a metallic halide.

3. A methanol catalyst initially comprising zinc oxide, chromium oxide, nickel oxide, and a metallic halide.

4. A methanol catalyst initially comprising zinc oxide, nickel oxide, and a metallic halide.

5. A methanol catalyst initially comprising zinc oxide, chromium oxide, nickel oxide, and zinc chloride.

6. A methanol catalyst initially comprising zinc oxide, nickel oxide, and zinc chloride.

7. A process for the production of synthetic methanol which comprises passing a mixture of hydrogen and carbon oxides at a pressure in excess of 50 atmospheres and at a temperature of 350-450° C. over a catalyst initially comprising a plurality of difficultly reducible metal oxides, nickel oxide, and a metallic halide.

8. A process for the production of synthetic methanol which comprises passing a mixture of hydrogen and carbon oxides at a pressure in excess of 50 atmospheres, and at a temperature of 350-450° C. over a catalyst initially comprising a difficultly reducible metal oxide, nickel oxide and a metal halide.

9. A process for the production of synthetic methanol which comprises passing a mixture of hydrogen and carbon oxides at a pressure in excess of 50 atmospheres, and at a temperature of 350-450° C. over a catalyst initially comprising zinc oxide, chromium oxide, nickel oxide, and zinc chloride.

In testimony whereof we affix our signatures.

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