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**Canadian Patents Database**

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(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

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ABSTRACT:

CLAIMS: [Show all claims](#)

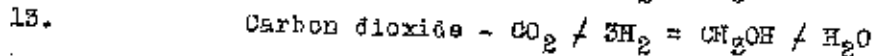
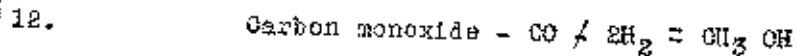
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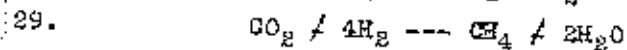
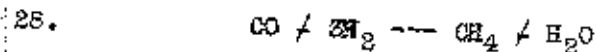
1. Our invention relates to the production of  
 2. methanol, by the high pressure catalytic combination of  
 3. oxides of carbon with hydrogen, and pertains more dir-  
 4. ectly to the preparation and employment of improved  
 5. catalysts in the process.

6. Methanol may be produced by combining oxides  
 7. of carbon with hydrogen in the presence of a suitable  
 8. catalyst at elevated temperature and pressure. Carbon  
 9. monoxide, carbon dioxide, and mixtures of the two oxides  
 10. may be employed, these substances reacting with hydrogen  
 11. according to the following reactions:-



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

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



30. In addition to the methane side-reaction there  
 31. are other side-reactions which sometimes occur in which

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1. there are produced esters, aldehydes, organic acids,
2. ketones, and hydrocarbons other than methane, these
3. reactions occurring as the result of the polymerization
4. or condensation of methanol or its decomposition products.

5. When a gas mixture comprising carbon oxides  
 6. mixed with an excess of hydrogen over the amount theo-  
 7. retically required to produce methanol is passed over a  
 8. catalytic substance comprising metals or their oxides  
 9. at a temperature above 250° C. there is nearly always  
 10. produced some reaction between the gaseous components.  
 11. The extent of this reaction depends to some degree on  
 12. space velocity, temperature, and pressure, but the fact  
 13. remains that under the conditions outlined, carbon oxides  
 14. and hydrogen react to some extent in all cases.

15. The substances formed by such a process depend,  
 16. both as to identity and as to amount, almost entirely on  
 17. the nature and activity of the catalytic substance pre-  
 18. sent. The methanol catalysts proposed in the past have  
 19. been of two principal types:- i.e. -

20. 1. Mixtures of finely divided metals, or,  
 21. what is equivalent, mixtures of easily reducible  
 22. metal oxides;

23. 2. Mixtures of oxides of metals non-reducible,  
 24. or difficultly reducible under the conditions of the  
 25. methanol synthesis.

26. In the past, also, one class of easily reducible metal  
 27. oxides, that is the oxides of iron, nickel, and cobalt  
 28. have been described as absolutely worthless for the pro-  
 29. duction of methanol catalysts since these metals under  
 30. normal conditions prevent the formation of methanol, the  
 31. reactions producing only methane.

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

9. We have now discovered a new type of valuable  
10. methanol catalyst which comprises three main elements -  
11. i.e.

12. (1) One or more difficultly reducible metal  
13. oxides such as zinc, magnesium, cadmium, chromium,  
14. vanadium, tungsten, uranium, zirconium, titanium,  
15. aluminium, manganese, molybdenum, thorium, cerium,  
16. etc.

17. (2) One or more easily reducible metal oxides  
18. such as copper, silver, iron, nickel, cobalt, etc.

19. (3) A metallic halide.

20. It will be observed that in our improved  
21. catalyst we may employ substances normally deleterious  
22. to the methanol reaction - namely the "methanating  
23. metals" - iron, nickel, or cobalt. In our improved com-  
24. positions these normally deleterious substances serve  
25. advantageously, apparently exerting only a normal hydro-  
26. genating catalytic action productive of methanol. Or  
27. we may employ easily reducible oxides such as those of  
28. copper or silver which are already known in the art as  
29. advantageous components of certain methanol catalysts.  
30. In these cases however, our improved catalysts contain-  
31. ing halides produce far better results than those known

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1. in the art for otherwise identical catalyst mixtures.

2. The precise method by which the metallic

3. halides produce the improvement is not known to us. At

4. least three theories may be used to account for the

5. phenomenon - namely:-

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

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

14. (3) The metallic halide may be reduced by the  
15. high pressure contact with hydrogen and carbon ox-  
16. ides during the commencement of its use as a catalyst  
17. and the resultant finely divided metal may increase  
18. the catalytic activity, or alternatively, the  
19. metallic halide may first react with some other  
20. metal producing the halide thereof, which may be  
21. reduced in the same manner.

22. However, the precise explanation for the im-  
23. proved result attained by the addition of metallic  
24. halides to methanol catalysts is not known and forms no  
25. part of our invention.

26. To produce our improved catalysts it is not  
27. necessary that the amount of metallic halide added bear  
28. any exact weight relation to the remaining constituents  
29. of the catalyst, though the amount of halide added should  
30. preferably be less than one chemical equivalent of the  
31. amount of principal metallic oxide present in the cata-

1. lyst.

2. As illustrative of our invention we will cite  
3. a number of examples which show the possible methods of  
4. preparing and employing the catalyst which we have dis-  
5. covered. In order to indicate the efficiency of our  
6. catalyst typical results obtained by its use are given  
7. below. In giving these specific examples it is our in-  
8. tention only to thus display the catalyst efficacy and  
9. by no means to limit the scope of our invention. Modif-  
10. ications of the conditions of the reaction will, of  
11. course modify the results.

12. For example, an increased space velocity pro-  
13. duces an increased hourly yield and an increase in oper-  
14. ating pressure has the same effect. A change in the tem-  
15. perature will also effect the rate of conversion of the  
16. gases to methanol. Likewise the use of pure carbon  
17. monoxide as distinguished from carbon dioxide or a mix-  
18. ture of the two results in an increased methanol  
19. percentage in the condensate.

20. EXAMPLE I

21. 160 grams chromium nitrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ )  
22. are dissolved, with heating in 60 c.c. water. After the  
23. solution has cooled 10 grams zinc chloride and 96 grams  
24. ferric nitrate are added. To the resulting cold solution  
25. 100 grams zinc oxide are then added with constant stirring  
26. The resulting wet mass is heated in a porcelain evapo-  
27. rating dish to dryness and then placed in a copper  
28. crucible in which it is heated over a Fletcher burner to  
29. drive off the nitrogen peroxide fumes.

30. The material thus obtained is crushed  
31. sufficiently to pass a 65 mesh screen and to it 8.2 grams

1. zinc chloride dissolved in 80 c.c. water are added. The
2. product thus obtained hardens spontaneously and is olive
3. green in color.

4. The yields of methanol condensate obtained

5. with this catalyst when a gas mixture comprising 16-17%
6. carbon monoxide and 84-88% hydrogen is passed thru 1
7. liter of catalyst granules at a space velocity of
8. 20,000-75,000, at a pressure of 2000 pounds per square
9. inch and at a temperature of 400-420° C. will be about
10. 400-950 c.c. of condensate per hour, which analyses
11. 87.6-95.4% by volume of methanol.

#### 12. EXAMPLE II

13. 7.2 kilograms chromium nitrate  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

14. and 4.8 kilograms ferric nitrate are dissolved in 5
15. liters of water by heating in a large porcelain evapor-
16. ating dish on a steam bath. 450 grams zinc chloride
17. (which may contain 0.0002% arsenic) are then dissolved
18. in this solution.

19. Separately there is made up a suspension of

20. 4.5 kilograms zinc oxide (which may contain traces of
21. chlorides and heavy metals slightly in excess of U.S.P.
22. limit) in 11 liters of water. By stirring this sus-
23. pension well and breaking up by hand any lumps that
24. form, a practically complete suspension is obtained. To
25. this suspension there is slowly added with vigorous
26. stirring the above solution of salts. A thick pasty
27. mass is formed which is spread out in a thin layer to
28. dry and harden. To accelerate this process, a current
29. of air from an electric fan may be allowed to play on
30. the surface of the mass. On the following day, the
31. hardened mass is broken up and placed in a furnace con-

1. sisting of an aluminum tube inside of which is placed a  
 2. sealed copper vessel which contains the catalyst and thru  
 3. which a current of gas composed of 15-25% carbon  
 4. monoxide and 85-75% hydrogen is passed. The mass is  
 5. heated until the temperature registered by a pyrometer  
 6. placed in the center of the copper vessel reaches  
 7. approximately 350° C. and the heating continued at this  
 8. temperature until nitrogen peroxide fumes are no longer  
 9. given off.

10. When a gas mixture comprising 10-60% carbon  
 11. monoxide and 90-40% hydrogen is passed over this  
 12. catalyst at a temperature of 400-420° C. at a space  
 13. velocity of 20,000-40,000, and at a pressure of 3200-  
 14. 3500 pounds per square inch, from 1.5 to 2.5 liters of  
 15. condensate per hour per liter of contact mass, analyzing  
 16. 95.0-97.2% by volume of methanol, are obtained.

#### 17. EXAMPLE III

18. When a gas mixture comprising 25% by volume  
 19. carbon dioxide and 75% by volume hydrogen is passed over  
 20. the catalytic mass prepared as described in Example II  
 21. above, at a temperature of 385-400° C. at a space  
 22. velocity of 20,000-40,000, and at a pressure of 3500  
 23. pounds per square inch, a yield of 2.0-4.0 liters of  
 24. condensate per hour per liter of catalyst, analyzing  
 25. 65% by volume of methanol, is obtained.

26. It will be noted that in both of the herein  
 27. described specific examples, the catalyst mass, as  
 28. finally prepared for use, comprises zinc oxide, chromium  
 29. oxide, iron oxide, and zinc chloride. In the case of  
 30. Example I, the nitrates of chromium and iron were de-  
 31. composed to the oxide by simple heating of the dry mass.  
 32. In the case of Example II, this reduction was accomplished



Case 11

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1. by means of a mixture of carbon monoxide and hydrogen.
2. The effect on the composition is the same in both
3. treatments.

4. Broad claims relating to the use of mixtures
5. of difficultly reducible oxides with oxides of iron
6. group metals and metallic halides as methanol catalysts
7. have been presented in our Serial Application
8. hence only specific claims are
9. presented herein.

10. Now having described our invention we claim  
11. the following as new and novel:-  
12. 1. A methanol catalyst initially comprising  
13. zinc oxide, chromium oxide, iron oxide and zinc  
14. chloride.  
15. 2. A methanol catalyst prepared by combining  
16. 4500 grams zinc oxide, 7200 grams chromium nitrate  
17.  $(Cr(NO_3)_3 \cdot 9H_2O)$ , 4300 grams ferric nitrate and 450-  
18. 320 grams zinc chloride in aqueous mixture, and convert-  
19. ing the nitrates to oxides.  
20. 3. A methanol catalyst prepared by combining  
21. 26.7-27.3% zinc oxide, 42.9-43.9% chromium nitrate  
22.  $(Cr(NO_3)_3 \cdot 9H_2O)$ , 25.6-26.1% ferric nitrate, and 4.8-2.7%  
23. zinc chloride in aqueous mixture, and converting the  
24. nitrates to oxides.  
25. 4. A process for the preparation of a methanol  
26. catalyst which comprises adding an aqueous solution con-  
27. sisting of chromium nitrate  $(Cr(NO_3)_3 \cdot 9H_2O)$ , ferric  
28. nitrate and zinc chloride to an aqueous suspension of  
29. zinc oxide, obtaining the resultant mixture in the form  
30. of a dry hardened mass, and heating the said mass to  
31. convert the nitrates to oxides.

1. 5. A process for the preparation of a methanol  
2. catalyst which comprises adding an aqueous solution  
3. consisting of 42.9-43.9% chromium nitrate ( $\text{Cr}(\text{NO}_3)_3$   
4.  $9\text{H}_2\text{O}$ ), 25.6-26.1% ferric nitrate and 4.8-2.7% zinc chlo-  
5. ride to an aqueous suspension containing 26.7-27.3%  
6. zinc oxide, obtaining the resultant mixture in the form  
7. of a hardened mass and heating the said mass in a  
8. current of hydrogen to a temperature of approximately  
9.  $350^\circ\text{C}$ . until nitrogen peroxide fumes are no longer  
10. given off.

11. 6. A process for the production of synthetic  
12. methanol which comprises passing a mixture of hydrogen  
13. and oxides of carbon at a pressure in excess of 2000  
14. pounds per square inch and at a temperature above  $250^\circ\text{C}$ .  
15. over a catalyst initially comprising zinc oxide, chromium  
16. oxide, iron oxide, and zinc chloride, cooling the  
17. reacted gases, and recovering the resultant methanol.

18. 7. A process for the production of synthetic  
19. methanol which comprises passing a mixture of hydrogen  
20. and oxides of carbon at a pressure in excess of 2000  
21. pounds per square inch and at a temperature to 385-  
22.  $420^\circ\text{C}$ . over a catalyst initially comprising zinc oxide,  
23. chromium oxide, iron oxide, and zinc chloride, cooling  
24. the reacted gases, and recovering the resultant methanol.