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(12) **Patent:**

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(54) METANOL CATALYST

(54) CATALYSEUR DE METHANOL

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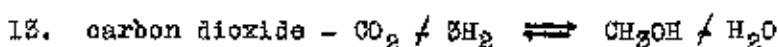
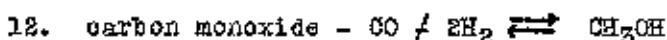
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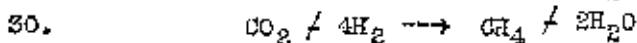
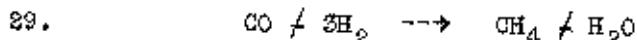
1. Our invention relates to the production of
2. methanol by the high pressure catalytic combination of
3. oxides of carbon with hydrogen, and pertains more
4. directly to the preparation and employment of improved
5. catalysts in the process.

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 mixture 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
16. every molecule of methanol produced. On the other
17. hand when pure carbon monoxide is used, theoretically
18. there is nothing produced by the reaction but methanol.
19. Actually in practice pure carbon monoxide and pure
20. carbon dioxide are both difficult to obtain economically,
21. so that the methanol synthesis is carried out by
22. reacting a mixture of carbon monoxide and carbon dioxide
23. with hydrogen.

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



31. In addition to the methane side-reaction
32. there are other side-reactions which sometimes occur
33. in which there are produced esters, aldehydes, organic

1. acids, ketones, and hydrocarbons other than methane;
2. these reactions occurring as the result of the polymerization or condensation of methanol or its decomposition products.

3. 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.

4. 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. -

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

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

7. 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

1. methanol, the reaction producing only methane.
2. 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.
3. We have now discovered a new type of valuable methanol catalyst which comprises three main elements - i.e.
4. (1) One or more non-reducible metal oxides such as zinc, magnesium, cadmium, chromium, vanadium, tungsten, etc.;
5. (2) One or more easily reducible metal oxides such as copper, silver, iron, nickel, cobalt, etc.;
6. (3) A metallic halide.
7. 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 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

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1. results than those known in the art for otherwise
2. identical catalyst mixtures.
3. The precise method by which the metallic
4. halides produce the improvement is not known to us. At
5. least three theories may be used to account for the
6. phenomenon - namely:-
 7. (1) The metallic halide acts as an ordinary
 8. "promoter" in increasing catalyst activity;
 9. (2) The metallic halide interacts with other
 10. metallic oxides present in the catalyst to produce
 11. oxychloride compounds which, in turn, either serve
 12. as catalyst promoters, or may so modify the purely
 13. physical state of the mass as to produce a more
 14. active catalyst;
 15. (3) The metallic halide may be reduced by the
 16. high pressure contact with hydrogen and carbon
 17. oxides during the commencement of its use as a
 18. catalyst and the resultant finely divided metal
 19. may increase the catalyst activity, or alternatively,
 20. the metallic halide may first react with some
 21. other metal producing the halide thereof, which may
 22. be reduced in the same manner.
23. However, the precise explanation for the
24. improved result attained by the addition of metallic
25. halides to methanol catalysts is not known and forms no
26. part of our invention.
27. To produce our improved catalysts it is not
28. necessary that the amount of metallic halide added bear
29. any exact weight relation to the remaining constituents
30. of the catalyst, though the amount of halide added
31. should preferably be less than one chemical equivalent
32. of the amount of principal metallic oxide present in the
33. catalyst.

274015

1. As illustrative of our invention we will cite
2. a number of specific catalysts. In order to indicate
3. the comparative efficacy of these catalysts in methanol
4. production we have selected a standard set of conditions
5. of use as follows. The reported yields of condensate
6. from the methanol reaction by use of the following
7. catalysts is based on the effect produced when a gas
8. mixture comprising 3% carbon dioxide, 3% of carbon
9. monoxide and 99% hydrogen is passed through 1 liter of
10. catalyst granules at a space velocity of 75,000 -
11. 100,000, at a pressure of 2000 pounds, and at a temper-
12. ature of 340 - 400° C.

13. In selecting a standard set of conditions it
14. is our intention only to thus display the catalyst
15. efficacy and by no means to limit the scope of our
16. invention. Modification of the conditions of the
17. reaction will, of course, modify the results, but the
18. results will always be proportionate to the catalyst
19. employed.

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

28. Example I

29. 8 kilograms of chromic nitrate
30. ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 1.5 kilograms of nickel nitrate;
31. ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in 150 liters of water,
32. and to this solution there is added the theoretical

1. amount (5.4 liters of 12.75 Normal) of ammonium hydroxide.
2. to precipitate chromium hydroxide and nickel hydrate.
3. The solution is then centrifuged to recover the
4. precipitated hydrates and the resultant precipitate is
5. thoroughly washed with water, dried, and broken up into
6. granules.

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

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

12. Example II

13. 2250 grams of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
14. are dissolved in 250 liters of water and the solution
15. is heated to 95° C. 7500 grams of zinc oxide is then
16. added with stirring. To this solution there is added
17. sufficient ammonium hydroxide to precipitate the
18. nickel as nickel hydrate. The precipitated mass is
19. recovered by decantation and filtration, is washed,
20. dried, and broken up into granules.

21. To this mass is added a solution containing
22. 740 grams of zinc chloride and the mass is again dried.

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

25. If the amount of zinc chloride used is doubled,
26. the hourly condensate will be increased to about 2.5
27. liters and the percentage of methanol will be increased
28. to about 50%.

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

274014

1. Example III
2. 2250 grams of cobalt nitrate
3. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are dissolved in 250 liters of water
4. and the solution is heated to 95° C. There is then
5. added 7.5 kilograms of zinc oxide after which the
6. solution is vigorously stirred and sufficient ammonium
7. hydroxide is added to precipitate the cobalt as cobalt
8. hydrate. The precipitated mass is recovered by
9. decantation and filtration, is washed, dried, and
10. broken up into granules. The granules are then
11. moistened with a solution containing 1460 grams zinc
12. chloride and dried once more.
13. The hourly yield of condensate is about 1.5
14. liters and contains about 58% of methanol.

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

20. Example V
21. 5500 grams of ferric nitrate is dissolved in
22. 50 liters of water and sufficient ammonium hydroxide is
23. added to precipitate all of the iron as ferric
24. hydroxide. The flocculent mass is filtered and washed
25. and to it is added 9 kilograms of zinc oxide and the
26. mixture thoroughly stirred. The resultant pasty mass
27. is allowed to dry and is then broken up into granules.
28. To these granules is added a solution containing 1500
29. grams ferric chloride. The mass is again dried,
30. whereupon it is ready for use.

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

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1.

Example VI

2. 4 kilograms chromic nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
3. and 750 grams nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are
4. dissolved in 6 liters of water. 2.5 kilograms of zinc
5. oxide is added with stirring and the mass is heated to
6. dryness and is then further heated till no more nitric
7. oxide fumes are given off, whereby the mixture is
8. transformed to chromic oxide, nickel oxide, and zinc
9. oxide. The resultant mass is broken up into granules
10. and is then moistened with a solution containing 450
11. grams of zinc chloride. The granules are again dried
12. and are ready for use. If desired, 450 grams of
13. dextrin or a similar agglutinating agent may be added
14. with the zinc chloride, whereby firmer granules are
15. obtained on drying.

16. The hourly yield of condensate is about 2.5
17. liters containing about 68% methanol.

18.

Example VII

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

23.

Example VIII

24. 2600 grams of zinc oxide in powdered form is
25. mixed by thorough sifting with 500 grams of black
26. copper oxide. The resultant mixture is moistened with
27. an aqueous solution containing 150 grams cuprous
28. chloride and 200 grams of dextrin. The resultant mass
29. is dried and broken up into pieces whereupon it is
30. ready for use.

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

271015

1. Now having described our invention, we claim
2. the following as new and novel.
3. 1. A methanol catalyst initially comprising:
 4. a plurality of difficultly reducible metal oxides, a
 5. plurality of easily reducible metal oxides, and a
 6. metallic halide.
7. 2. A methanol catalyst initially comprising:
 8. a plurality of difficultly reducible metal oxides, an
 9. easily reducible metal oxide, and a metallic halide.
10. 3. A methanol catalyst initially comprising:
 11. a difficultly reducible metal oxide, an easily reducible
 12. metal oxide, and a metallic halide.
13. 4. A methanol catalyst initially comprising:
 14. a difficultly reducible metal oxide, an easily reducible
 15. metal oxide, and a halide of one of the metals.
16. 5. A methanol catalyst initially comprising:
 17. a difficultly reducible metal oxide, an easily reducible
 18. metal oxide, and a metallic chloride.
19. 6. A methanol catalyst initially comprising:
 20. a difficultly reducible metal oxide, an easily reducible
 21. metal oxide, and a metallic halide in amount equal to
 22. one chemical equivalent or less of the difficultly
 23. reducible metal oxide.
24. 7. A methanol catalyst initially comprising:
 25. a predominating quantity of a difficultly reducible
 26. metal oxide, a lesser quantity of an easily reducible
 27. metal oxide, and an amount of a metallic halide equal
 28. to or less than one chemical equivalent of the
 29. difficultly reducible oxide.
30. 8. A methanol catalyst initially comprising:
 31. an oxide of a second group metal, an easily reducible

274014

1. metal oxide of the eighth group, and a metallic halide.
2. 9. A process for the production of synthetic
3. methanol which comprises passing a mixture of hydrogen
4. and carbon oxides, at a pressure in excess of 50
5. atmospheres and at a temperature of 350-450° C. over a
6. catalyst initially comprising a plurality of difficultly
7. reducible metal oxides, a plurality of easily reducible
8. metal oxides, and a metallic halide.
9. 10. A process for the production of synthetic
10. methanol which comprises passing a mixture of hydrogen
11. and carbon oxides at a pressure in excess of 50 at-
12. mospheres and at a temperature of 350-450° C. over a
13. catalyst initially comprising a difficultly reducible
14. metal oxide, an easily reducible metal oxide, and a
15. metallic chloride.
16. 11. A methanol catalyst initially comprising
17. a plurality of difficultly reducible metal oxides, an
18. oxide of an iron group metal, and a metallic halide.
19. 12. A methanol catalyst initially comprising
20. a difficultly reducible metal oxide, iron oxide, and a
21. metallic halide.
22. 13. A methanol catalyst initially comprising
23. zinc oxide, chromium oxide, an oxide of an iron group
24. metal, and a metallic halide.
25. 14. A methanol catalyst initially comprising
26. zinc oxide, iron oxide, and zinc chloride.
27. 15. A methanol catalyst initially comprising
28. zinc oxide, chromium oxide, an oxide of an iron group
29. metal, and zinc chloride.
30. 16. A process for the production of synthetic
31. methanol which comprises passing a mixture of hydrogen

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1. 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, an oxide of an iron group metal, and zinc chloride.
6. 17. 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, iron oxide, and zinc chloride.