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(12) Patent:

(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

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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:-

12. carbon monoxide -  $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

13. carbon dioxide -  $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$

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:

29.  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$

30.  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

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 poly-
3. merization or condensation of methanol or its decompo-
4. sition products.

5.               When a gas mixture comprising carbon oxides  
6. mixed with an excess of hydrogen over the amount  
7. theoretically required to produce methanol is passed  
8. over a catalytic substance comprising metals or their  
9. oxides at a pressure above 50 atmospheres and at a  
10. temperature above 250° C. there is nearly always produced  
11. some reaction between the gaseous components. The ex-  
12. tent of this reaction depends to some degree on space  
13. velocity, temperature, and pressure, but the fact  
14. remains that under the conditions outlined, carbon oxides  
15. and hydrogen react to some extent in all cases.

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

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

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

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1. methanol, the reaction producing only methane.
2. We have discovered a new type of methanol
3. catalyst which produces a higher yield of methanol than
4. those formerly employed in the art, and at the same time
5. produces a very pure methanol, uncontaminated by by-
6. products. An additional advantage accruing from the
7. use of our catalysts is that the formation of methane in
8. the process - with the consequent destruction of
9. valuable hydrogen - is practically eliminated.
10. We have now discovered a new type of valuable
11. methanol catalyst which comprises three main elements -
12. i.e.
13. (1) One or more non-reducible metal oxides
14. such as zinc, magnesium, cadmium, chromium,
15. vanadium, tungsten, etc.;
16. (2) One or more easily reducible metal oxides
17. such as copper, silver, iron, nickel, cobalt, etc.;
18. (3) A metallic halide.
19. It will be observed that in our improved
20. catalyst we may employ substances normally deleterious
21. to the methanol reaction - namely the "methanating
22. metals" - iron, nickel, or cobalt. In our improved
23. catalyst compositions these normally deleterious
24. substances serve advantageously, apparently exerting
25. only a normal hydrogenating catalytic action productive
26. of methanol. Or we may employ easily reducible oxides
27. such as those of copper or silver which are already
28. known in the art as advantageous components of certain
29. methanol catalysts. In these cases however, our
30. 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;

16.           (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 alternative-
20. ly, 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.

274814

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 89% hydrogen is passed through 1 liter of  
 10. catalyst granules at a space velocity of 75,000 -  
 11. 100,00, 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

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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 56%.

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

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Example III

- 1.
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  $95^\circ \text{C}$ . 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 1480 grams zinc
12. chloride and dried once more.

13. The hourly yield of condensate is about 1.5
14. liters and contains about 50% of methanol.

Example IV

- 15.
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.

Example V

- 20.
21. 3500 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 ( $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ )  
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. 2500 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.

271011

1. How 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

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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
2. atmospheres, and at a temperature of 350-450° C. over
3. a catalyst initially comprising zinc oxide, chromium
4. oxide, an oxide of an iron group metal, and zinc
5. chloride.
6.           17. A process for the production of synthetic
7. methanol which comprises passing a mixture of hydrogen
8. and carbon oxides at a pressure in excess of 50
9. atmospheres and at a temperature of 350-450° C. over a
10. catalyst initially comprising zinc oxide, iron oxide,
11. and zinc chloride.