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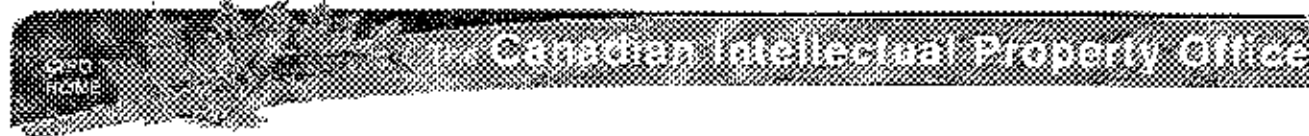
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(12) Patent:

(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

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CLAIMS: Show all claims

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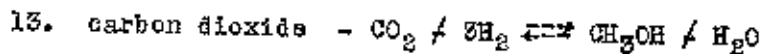
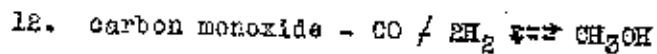
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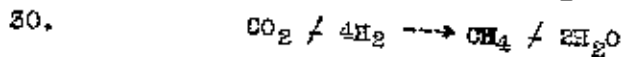
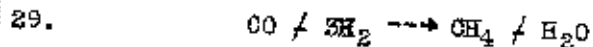
1. Our invention relates to the production of
 2. methanol by the high pressure catalytic combination of
 3. oxides of carbon with hydrogen, and pertains more
 4. directly to the preparation and employment of improved
 5. catalysts in the process.

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:



1. In addition to the methane ~~side~~^{main} reaction
2. there are other side-reactions which sometimes occur
3. in which there are produced esters, aldehydes, organic
4. acids, ketones, and hydrocarbons other than methane;
5. these reactions occurring as the result of the poly-
6. merization or condensation of methanol or its decompo-
7. sition products.

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

19. The substances formed by such a process
20. depend, both as to identity and as to amount, almost
21. entirely on the nature and activity of the catalytic
22. substance present. In general, finely divided metals
23. or mixtures of metallic oxides non-reducible to free
24. metal under the conditions of the methanol synthesis
25. are catalytic substances which cause the production of
26. more or less methanol. Iron and nickel and their
27. oxides, while useful hydrogenating and dehydrogenating
28. catalyze in many other instances, have in the past
29. been deemed unsuitable for employment as methanol
30. catalyze on account of their strong methanating action
31. which largely prevents methanol formation, the carbon
32. oxides being reduced to methane.

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

9. It is known that metal oxides, non-reducible
10. or difficultly reducible to metals under the conditions
11. of the methanol reaction serve as satisfactory base or
12. principal materials in the formulation of methanol
13. catalysts (U. S. Patent 1,568,539). For example the
14. oxides of metals of the second group in the Periodic
15. Table of Elements - such as zinc and magnesium - may be
16. alternatively employed as principal catalysts, but since
17. by themselves the oxides are not true catalysts they
18. are combined with smaller quantities of catalyst
19. "promoters" - which in turn may consist of other metallic
20. oxides of the Third to Seventh Periodic Table groups.

21. For example, zinc oxide - per se - is not a
22. suitable catalyst, but in admixture with a less basic
23. metal oxide, such as the oxides of chromium, manganese,
24. molybdenum, titanium, cerium, vanadium, tungsten, etc.,
25. the said additive oxides apparently acting as "pro-
26. moters", the mixture becomes a good catalyst for methanol
27. production.

28. Similarly magnesium may be used to replace
29. zinc in the production of such catalysts. In the prior
30. art the catalyst mixtures of this type uniformly contain-
31. ed a greater proportion of the more basic (zinc or

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1. magnesium) oxide, and a lesser proportion of the
2. additive oxide.

3. We have now discovered that methanol catalysts
4. comprising mixtures of non-reducible or difficultly
5. reducible metallic oxides may be greatly improved by the
6. addition of a metallic halide. The precise metal
7. employed in the halide may be either identical with or
8. different from the metal of the oxides.

9. The method by which the metallic halides
10. produce the improvement is not known to us. At least
11. three theories may be used to account for the
12. phenomena - namely:-

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

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

21. (3) The metallic halide may be reduced by the
22. high pressure contact with hydrogen and carbon
23. oxides during the commencement of its use as a
24. catalyst and the resultant finely divided metal may
25. increase the catalyst activity, or alternatively,
26. the metallic halide may first react with some other
27. metal producing the halide thereof, which may be
28. reduced in the same manner.

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

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1. To produce our improved catalysts it is not
 2. necessary that the amount of metallic halide added bear
 3. any exact weight relation to the remaining constituents
 4. of the catalyst, though the amount of halide added should
 5. preferably be less than one chemical equivalent of the
 6. amount of principal metallic oxide present in the
 7. catalyst.

8. Our invention is of widespread usefulness in
 9. the methanol art and to further disclose it but in no
 10. manner to limit it beyond the limitations derived from
 11. the whole specification we append the following examples:

12. Our improved catalysts consist of the follow-
 13. ing elements.

14. I. An oxide of a Second group (Mendeleeff's
 15. Periodic Table) metal;

16. II. An oxide of a metal of the Third to
 17. Seventh Group to serve as a promoter;

18. III. A metallic halide.

19. Below are appended illustrative examples of
 20. such catalyst mixtures:-

21. zinc oxide - chromium oxide - zinc chloride

22. zinc oxide - chromium oxide - vanadium chloride

23. zinc oxide - manganese oxide - magnesium chloride

24. magnesium oxide - vanadium oxide - magnesium fluoride

25. magnesium oxide - chromium oxide - chromium chloride

26. strontium oxide - chromium oxide - zinc chloride

27. zinc oxide - vanadium oxide - magnesium chloride

28. In general, catalysts of this type are most

29. effective if the oxide of the second group metal is

30. present in predominating quantity over the other,

31. promoting, oxide. However catalysts containing oxides

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1. in the reverse ratio produce methanol and are included
2. in our invention.

3. The addition of a solution of zinc chloride
4. to a mixture of zinc oxide and chromium oxide, followed
5. by a drying and recovery of the mass, produces a
6. catalyst giving results superior to those known in the
7. art. Similar improved catalysts are obtained when other
8. combinations of second group metal oxides and metallic
9. halides are combined - for example magnesium compounds.

10. As illustrative of our improved catalysts the
11. following results are appended.

12. EXAMPLE I

13. A catalyst base material is prepared by
14. dissolving 8 kilograms of chromic nitrate
15. $(Cr(NO_3)_3 \cdot 9H_2O)$ in 5 liters of water; adding with
16. stirring 5 kilograms of zinc oxide, evaporating the mass
17. to dryness, and heating until the chromic nitrate is
18. converted to chromic oxide. The mixture is then broken
19. up and sieved through a 65 mesh screen.

20. If a quantity of this material is mixed with
21. 10% of dextrin or a similar agglutinating agent
22. dissolved in 10 parts of water and the resultant mixture
23. dried and broken up into granules, a catalyst is obtained
24. such as is described in the prior art.

25. When a mixture of carbon oxides and hydrogen
26. comprising, say 10% of carbon dioxide and 90% of
27. hydrogen at a pressure of 2200 pounds is passed through
28. 1000 cubic centimeters of such a catalyst at a space
29. velocity of 75,000 and at a temperature of about 350 -
30. 400° C. there will be produced about 300 - 1000 cubic
31. centimeters of condensate per hour. On analysis this
32. condensate will show 40-46% methanol, the remainder

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1. being largely water. An analysis of the residual gas
2. will show a considerable methane formation.
3. If to the dextrin solution used to granulate
4. the sieved material there is added a zinc halide,
5. preferably zinc chloride in such amount that it
6. represents from 5-10% of the weight of zinc oxide and
7. chromic oxide, the mass being dried and broken up in the
8. same manner, an improved catalyst will result. Under
9. the same reaction conditions this catalyst will produce
10. from 1.7 - 2.0 liters of condensate per hour and this
11. condensate will show about 55% of methanol, the remain-
12. der being substantially pure water. Furthermore an
13. analysis of the residual gases will show a diminution in
14. methane formation.

15. EXAMPLE II

16. If the zinc halide mentioned in Example I
17. is replaced by an equivalent quantity of magnesium
18. chloride similar improved results will be obtained.
19. The yield of condensate may fall to about 1.6 liters
20. per hour, the methanol content being unchanged.

21. EXAMPLE III

22. 2200 grams of zinc oxide and 300 grams of
23. chromic oxide are mixed in a solution of about 200 grams
24. of zinc chloride and 250 grams of dextrin in 3 liters
25. of water. The mass is dried and broken up into granules.
26. When a gas mixture comprising 10% carbon dioxide, 2%
27. carbon monoxide, and 88% hydrogen is passed through
28. 1000 cubic centimeters of the catalyst, at a temperature
29. of about 380-420° C., at a space velocity of 75,000 -
30. 100,000 and at a pressure of 3000 pounds there will be

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1. produced, hourly, about 2 liters of condensate
2. analyzing about 67% methanol.

3. In the absence of the zinc chloride the total
4. volume of condensate will be reduced and the percentage
5. yield of methanol will be greatly reduced.

6. EXAMPLE IV

7. If in Example III, the zinc oxide is replaced
8. by magnesium oxide, the resultant catalyst under similar
9. operating conditions will produce about 1.5 liters of
10. condensate per hour, the methanol content remaining
11. about the same.

12. EXAMPLE V

13. 2600 grams of zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$
14. and 160 grams of tungstic oxide (WO_3) are mixed and
15. heated until the zinc nitrate is converted to zinc
16. oxide. The resultant yellow mass is powdered and mixed
17. with 400 grams of 50% zinc bromide solution. The re-
18. sultant mass is dried and broken up into granules. When
19. a gas mixture comprising 5% carbon dioxide, 5% carbon
20. monoxide, and 90% hydrogen is passed through 1000 cubic
21. centimeters of this catalyst at a space velocity of about
22. 100,000, a temperature of about 400° , and at a pressure
23. of 2500-3000 pounds, there will be produced, hourly,
24. about 1.5 liters of condensate analyzing about 50%
25. methanol.

26. EXAMPLE VI

27. 3900 grams zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and
28. 500 grams uranium nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) is dissolved
29. in 5 liters of warm water. To this mixture is added
30. sufficient potassium carbonate to precipitate all of the
31. zinc and uranium as carbonate and basic carbonate. The
32. resultant precipitate is recovered, washed, dried, and

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1. moistened with a solution containing 200 grams zinc
2. chloride. The mass is again dried, and is broken up
3. into granules, whereupon it is ready for use.
4. When a gas mixture comprising 10% carbon
5. dioxide and 90% hydrogen is passed at a space velocity
6. of 75,000 over 1 liter of catalyst granules at a
7. pressure of 2500 pounds and a temperature of 380 - 440°
8. C. there is obtained hourly about 3 liters of condensate
9. analyzing about 48% methanol. A similar catalyst to
10. which a metallic halide is not added gives a far
11. smaller yield and conversion to methanol.

12. -----
13. The specific examples we have related are
14. intended to display various phases of our invention and
15. not to limit it. While in the above specific examples
16. we have shown the use of metallic chlorides and metallic
17. bromides, it should be understood that similar results
18. are attained with other halides, though in general we
19. prefer to employ chlorides on account of their relative
20. non-volatility and ready accessibility. There exists,
21. of course, a possibility of almost infinite variety in
22. changes of percentage composition of our improved
23. catalysts. We have observed however, that while changes
24. in the proportionate amount of second group metal to
25. promoter produce changes in catalyst effectiveness, at
26. the same time the presence of a metal halide in the
27. catalyst invariably produces greatly improved results.

28. It is, of course, obvious that one may replace
29. a single second group oxide by a mixture of two such
30. oxides. For example zinc oxide may be replaced by a
31. mixture of zinc oxide and magnesium oxide. Likewise
instead of one promoter oxide such as chromium oxide,

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1. one may employ a mixture. Such changes are within the
2. spirit of our invention and the appended claims.
3. An increased space velocity produces an
4. increased hourly yield and an increase in operating
5. pressure has the same effect. Likewise the use of pure
6. carbon monoxide as distinguished from carbon dioxide
7. or a mixture of the two results in an increased
8. methanol percentage in the condensate, and, since
9. carbon monoxide seems to react more readily, an
10. increased condensate volume.

1. Now having described our invention, we claim
2. the following as new and novel:-
3. 1. A methanol catalyst comprising a plurality
4. of difficultly reducible second group metal oxides, a
5. plurality of difficultly reducible metal oxides from the
6. third to seventh groups, and a metallic halide.
7. 2. A methanol catalyst comprising a difficult-
8. ly reducible second group metal oxide, a difficultly re-
9. ducible oxide of the third to seventh groups, and a
10. metallic halide.
11. 3. A methanol catalyst initially comprising
12. a difficultly reducible second group metal oxide, a
13. difficultly reducible oxide of the third to seventh
14. groups, and a metallic halide.
15. 4. A methanol catalyst initially comprising a
16. difficultly reducible second group metal oxide, a lesser
17. quantity of a difficultly reducible oxide of the third
18. to seventh groups, and a metallic halide.
19. 5. A methanol catalyst initially comprising a
20. difficultly reducible second group metal oxide, a lesser
21. quantity of a difficultly reducible oxide of the third
22. to seventh groups, and a metallic chloride.
23. 6. A methanol catalyst initially comprising a
24. difficultly reducible second group metal oxide, a lesser
25. quantity of a difficultly reducible metal oxide of the
26. third to seventh groups, and a metallic halide in amount
27. not exceeding one chemical equivalent of the second
28. group oxide.
29. 7. A methanol catalyst initially comprising a
30. difficultly reducible second group metal oxide, a lesser
31. quantity of a difficultly reducible metal oxide of the

1. third to seventh groups, and a metallic chloride in
2. amount not exceeding one chemical equivalent of the
3. second group oxide.
4. 8. A methanol catalyst comprising zinc oxide,
5. chromium oxide, and a metallic halide.
6. 9. A methanol catalyst comprising zinc oxide,
7. chromium oxide and a metallic chloride.
8. 10. A process for the production of synthetic
9. methanol which comprises passing a mixture of hydrogen
10. and carbon oxides at a pressure in excess of 50
11. atmospheres and at an elevated temperature, over a
12. catalyst initially comprising a mixture of difficultly
13. reducible oxides and a metallic halide.
14. 11. A process for the production of synthetic
15. methanol which comprises passing a mixture of hydrogen
16. and carbon oxides at a pressure in excess of 50
17. atmospheres and at an elevated temperature, over a
18. catalyst initially comprising a mixture of difficultly
19. reducible oxides and a metallic chloride.
20. 12. A process for the production of synthetic
21. methanol which comprises passing a mixture of hydrogen
22. and carbon oxides, at a pressure in excess of 50 atmos-
23. pheres and at an elevated pressure, over a catalyst
24. initially comprising a mixture of zinc oxide, chromium
25. oxide, and zinc chloride.

1. Now having described our invention, we claim
2. the following as new and novel:-
3. 1. A methanol catalyst comprising a plurality
4. of difficultly reducible second group metal oxides, a
5. plurality of difficultly reducible metal oxides from the
6. third to seventh groups, and a metallic halide.
7. 2. A methanol catalyst comprising a difficult-
8. ly reducible second group metal oxide, a difficultly re-
9. ducible oxide of the third to seventh groups, and a
10. metallic halide.
11. 3. A methanol catalyst initially comprising
12. a difficultly reducible second group metal oxide, a
13. difficultly reducible oxide of the third to seventh
14. groups, and a metallic halide.
15. 4. A methanol catalyst initially comprising a
16. difficultly reducible second group metal oxide, a lesser
17. quantity of a difficultly reducible oxide of the third
18. to seventh groups, and a metallic halide.
19. 5. A methanol catalyst initially comprising a
20. difficultly reducible second group metal oxide, a lesser
21. quantity of a difficultly reducible oxide of the third
22. to seventh groups, and a metallic chloride.
23. 6. A methanol catalyst initially comprising a
24. difficultly reducible second group metal oxide, a lesser
25. quantity of a difficultly reducible metal oxide of the
26. third to seventh groups, and a metallic halide in amount
27. not exceeding one chemical equivalent of the second
28. group oxide.
29. 7. A methanol catalyst initially comprising a
30. difficultly reducible second group metal oxide, a lesser
31. quantity of a difficultly reducible metal oxide of the

1. third to seventh groups, and a metallic chloride in
2. amount not exceeding one chemical equivalent of the
3. second group oxide.
4. 8. A methanol catalyst comprising zinc oxide,
5. chromium oxide, and a metallic halide.
6. 9. A methanol catalyst comprising zinc oxide,
7. chromium oxide and a metallic chloride.
8. 10. A process for the production of synthetic
9. methanol which comprises passing a mixture of hydrogen
10. and carbon oxides at a pressure in excess of 50
11. atmospheres and at an elevated temperature, over a
12. catalyst initially comprising a mixture of difficultly
13. reducible oxides and a metallic halide.
14. 11. A process for the production of synthetic
15. methanol which comprises passing a mixture of hydrogen
16. and carbon oxides at a pressure in excess of 50
17. atmospheres and at an elevated temperature, over a
18. catalyst initially comprising a mixture of difficultly
19. reducible oxides and a metallic chloride.
20. 12. A process for the production of synthetic
21. methanol which comprises passing a mixture of hydrogen
22. and carbon oxides, at a pressure in excess of 50 atmos-
23. pheres and at an elevated pressure, over a catalyst
24. initially comprising a mixture of zinc oxide, chromium
25. oxide, and zinc chloride.