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01/09/2002 - 08:25:02
(1) CA 274912

(12) Patent:

(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

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(45) <u>Issued on</u> :	Oct. 25, 1927
(22) <u>Filed on</u> :	
(43) <u>Laid open on</u> :	
(52) <u>Canadian Class (CPC)</u> :	252/61
(51) <u>International Class (IPC)</u> :	N/A

Patent Cooperation Treaty (PCT): No

(30) Application priority data: None

Availability of licence: N/A
Language of filing: Unknown

ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

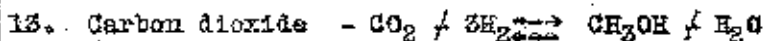
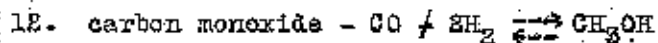
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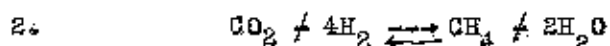
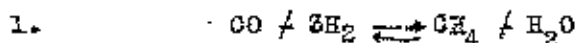
1. Our invention relates to the production of
 2. methanol by the high pressure catalytic combination of
 3. oxides of carbon with hydrogen, and pertains more
 4. directly to the preparation and employment of improved
 5. catalysts in the process.

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 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
 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 by 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 react-
 22. ing 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:



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

10. When a gas mixture comprising carbon oxides
 11. mixed with an excess of hydrogen over the amount
 12. theoretically required to produce methanol is passed
 13. over a catalytic substance consisting of metallic oxides
 14. at a pressure above 100 atmospheres and at a temperature
 15. above 250° C. there is nearly always produced some
 16. reaction between the gaseous components. The extent of
 17. this reaction depends to some degree on space velocity,
 18. temperature, and pressure, but the fact remains that
 19. under the conditions outlined, carbon oxides and hydrogen
 20. react to some extent in all cases.

21. The substances formed by such a process depend,
 22. both as to identity and as to amount, almost entirely
 23. on the nature and activity of the catalytic substance
 24. present. The methanol catalysts mentioned in prior
 25. patents and literature are combinations of metals or
 26. their oxides which substances normally exert a hydrogen-
 27. ating catalytic effect on gas reactions.

28. Without exception the literature on the high

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1. pressure catalytic process for synthesizing methanol
2. definitely states that the presence of iron or any of
3. its compounds in a catalyst destroys or poisons the
4. catalyst and inhibits methanol formation. While iron is
5. an excellent hydrogenating catalyst for many reactions,
6. in some forms it reacts with carbon monoxide, and with
7. mixtures of hydrogen and the carbon oxides (i.e. carbon
8. monoxide and (or carbon dioxide) used in the methanol
9. reaction, forming a volatile carbonyl compound and
10. inhibiting the methanol reaction. The normal effect of
11. the presence of iron in a methanol catalyst is to cause
12. the reaction of hydrogen and carbon oxides to produce
13. only methane.

14. We have now discovered a method of employing
15. iron in a methanol catalyst whereby the desirable
16. hydrogenating catalytic effect of the iron is obtained
17. and the tendency to methane formation is inhibited.
18. In preparing our improved catalyst we employ a mixture
19. of zinc oxide and ferric hydroxide. Zinc oxide - per
20. se - has no catalytic effect on the methanol reaction,
21. while ferric hydroxide - per se - has a positive
22. inhibiting effect. Nevertheless, when these two
23. ingredients are properly compounded a desirable methanol
24. catalyst is produced.

25. We have discovered that when ferric hydroxide
26. obtained by precipitation of iron from a ferric salt in
27. aqueous solution is incorporated with zinc oxide and the
28. mass is dried and broken up into granules the resultant

1. material produces an active catalyst for the synthetic
2. methanol reaction. While we are certain that in the
3. presence of the hydrogen and carbon oxide gas mixtures
4. used for synthesizing methanol the ferric hydroxide is
5. subsequently reduced to iron oxide and possibly in part
6. to iron - per se - the exact structure of the resultant
7. catalyst is not known to us.

8. The amount of ferric hydroxide may vary from
9. 3% to 25% of the weight of zinc oxide, though we prefer
10. to use about 10%. The zinc oxide may be incorporated
11. with ferric hydroxide in any convenient manner as is
12. indicated in the appended examples.

13. Example I

14. 313 grams of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
15. is dissolved in 25 liters of water which is then heated
16. to 95° C. To the hot solution is added 750 grams of
17. zinc oxide with stirring 190 cubic centimeters of 12.38
18. Normal Ammonium hydroxide is added to precipitate the
19. iron to the hydroxide form. The mixture is allowed to
20. stand, the supernatant liquid siphoned off, and the mass
21. is filtered and washed until there is no test for
22. nitrate in the filtrate.

23. The mass is then completely dried and broken
24. up into granules, whereupon it is ready for use.

25. It will be observed that the final composition
26. of this catalyst after precipitating the iron and drying
27. the mass is approximately 750 grams zinc oxide and 82
28. grams of ferric hydroxide.

1. Example II

2. 350 grams of ferric nitrate is dissolved in
3. 5 liters of water and sufficient ammonium hydroxide is
4. added to precipitate all of the iron as ferric hydroxide.
5. The resultant flocculent mass is thoroughly washed with
6. water and after decanting the excess water, 850 grams of
7. zinc oxide is thoroughly mixed therewith. The mixture
8. is then dried and broken up into granules.

9. Example III

10. In place of the ferric nitrate mentioned in
11. Examples I and II an equivalent quantity of another
12. soluble ferric salt may be employed.

13. When a mixture of 90% hydrogen gas with 10%
14. oxides of carbon, comprising about 7% carbon dioxide and
15. 3% carbon monoxide is passed over 1000 cubic centimeters
16. of catalyst granules thus prepared at a pressure of
17. 2000 pounds at a temperature of about 350°-450° C., and
18. at a space velocity of about 75,000 there will be
19. produced, hourly, about 1.2 liters of condensate contain-
20. ing about 55% of methanol, the remainder of the condensate
21. being substantially pure water. Increase of pressure and
22. increase of space velocity over the figures given in the
23. example increase the total amount of condensate per hour
24. whereas an increase in the percentage of carbon monoxide
25. produces an increase in the percentage of methanol in
26. the condensate.

27. If pure carbon monoxide is employed as the
28. carbon oxide the percentage may be advantageously increased

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1. to 20% , the hydrogen being correspondingly diminished.

2. Now having described our invention we claim
3. the following as new and novel.
4. 1. A methanol catalyst comprising zinc oxide
5. and ferric hydroxide.
6. 2. A methanol catalyst comprising 97 - 75%
7. zinc oxide and 3 - 25% ferric hydroxide.
8. 3. A methanol catalyst comprising zinc oxide
9. and ferric hydroxide, the ferric hydroxide being formed
10. by precipitation in aqueous solution from a soluble
11. ferric salt.
12. 4. A methanol catalyst comprising 97 - 75%
13. zinc oxide and 3% - 25% ferric hydroxide, the ferric
14. hydroxide being formed by precipitation in aqueous
15. solution from a soluble ferric salt.
16. 5. A methanol catalyst comprising 750 grams
17. of zinc oxide and 82 grams of ferric hydroxide, the
18. ferric hydroxide being formed by precipitation in aqueous
19. solution from a soluble ferric salt.
20. 6. A process for the preparation of a methanol
21. catalyst which comprises precipitating ferric hydroxide
22. from an aqueous solution of a ferric salt on zinc oxide.
23. 7. A process for the preparation of a methanol
24. catalyst which comprises precipitating from 3 - 25% of
25. ferric hydroxide from an aqueous solution of a ferric
26. salt on 97 - 75% of zinc oxide.
27. 8. A process for the preparation of a methanol
28. catalyst which comprises mixing zinc oxide with an

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1. aqueous solution of a ferric salt, precipitating ferric
2. hydroxide by adding ammonium hydroxide, filtering,
3. washing, and drying the resultant mass.
4. 9. A process for the preparation of a
5. methanol catalyst which comprises dissolving 313 grams
6. of ferric nitrate in 25 liters of water, adding 750
7. grams of zinc oxide, precipitating the iron as ferric
8. hydroxide by adding ammonium hydroxide, and recovering
9. the resultant mass in dry form.
10. 10. A process for the production of synthetic
11. methanol which comprises passing a mixture of hydrogen
12. and carbon oxides at a pressure in excess of 50
13. atmospheres and at a temperature of 350 - 450° C. over
14. a catalyst initially containing zinc oxide and ferric
15. hydroxide, cooling the reacted gases, and recovering the
16. resultant methanol.
17. 11. A process for the production of synthetic
18. methanol which comprises passing a mixture of hydrogen
19. and carbon oxides at a pressure in excess of 50
20. atmospheres and at a temperature of 350 - 450° C. over
21. a catalyst initially containing 97 - 75% zinc oxide and
22. 3 - 25% ferric hydroxide, cooling the resultant gases,
23. and recovering the resultant methanol.