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PATENT SPECIFICATION

279,378

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3982

COMPLETE SPECIFICATION.

Improvements in Catalysts for Synthetic Methanol Production.

We, COMMERCIAL SOLVENTS CORPORATION, a corporation organised and existing under the laws of the State of Maryland, United States of America, located at Terre Haute, Vigo County, State of Indiana, United States of America, (Assignees of JOHN CAULFIELD WOODRUFF, a citizen of the United States of America, of 1526, South Sixth Street, Terre Haute, Vigo County, State of Indiana, United States of America, and GROVER BLOOMFIELD, a citizen of the United States of America, of 1806, South Center Street, Terre Haute, Vigo County, State of Indiana, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In Specification No. 271,840 is described an improved catalyst for methanol production comprising one or more difficultly reducible metal oxides, one or more easily reducible metal oxides and a metal halide, and a process of preparing methanol employing the said catalyst, and the present invention is an improvement in or modification thereof.

The present invention consists in the preparation of an improved methanol catalyst of the kind described and claimed in Specification No. 271,840 and comprising zinc oxide, chromium oxide, iron oxide and zinc chloride.

We have found that a catalyst of the above composition has certain peculiar properties which impart thereto commercial characteristics of unusual merit.

The invention also consists in the improvement or modification in the process for the preparation of a methanol catalyst as described and claimed in our parent British Application No. 271,840 which comprises adding an aqueous solution consisting of chromium nitrate ($Cr(NO_3)_3.9H_2O$), ferric nitrate and zinc chloride to an aqueous suspension of zinc oxide, obtaining the resultant mixture in the form of a dry hardened mass, and heating the said mass to convert the nitrates to oxides.

The invention further consists in a method of producing synthetic methanol as described and claimed in Specification No. 271,840 which comprises passing a mixture of hydrogen and oxides of carbon at a pressure in excess of 2000 pounds per square inch and at a temperature above 250° C. over a catalyst initially comprising zinc oxide, chromium oxide, iron oxide and zinc chloride, cooling the reacted gases and recovering the resulting methanol.

To produce the improved catalysts of the present invention it is not necessary that the amount of zinc chloride added bear any exact weight relation to the remaining constituents of the catalyst, though the amount of halide added should preferably be less than that which is chemically equivalent to the amount of the metallic oxide present in the largest molecular proportion in the catalyst.

As illustrative of the present invention a number of examples will be cited which show the possible methods of preparing and employing the catalyst which has been discovered. In order to indicate the efficiency of this catalyst typical results obtained by its use are given below. Modifications of the conditions of the reaction will, of course, modify the results.

For example, an increased space velocity produces an increased hourly yield and an increase in operating pressure has the same effect. A change in the temperature will also effect the rate of conversion of the gases to methanol. Likewise the use of pure carbon monoxide as distinguished from carbon dioxide or a mixture of the two results in an increased methanol percentage in the condensate.

A catalyst prepared by combining 26.7 to 27.3% zinc oxide, 42.9 to 43.9% chromium nitrate ($Cr(NO_3)_3.9H_2O$), 25.6 to 26.1% ferric nitrate and 4.8 to 2.7% zinc chloride in aqueous mixture and converting the nitrates to oxides, has desirable properties. The examples describe the preparation and use of typical catalyst mixtures of such a composition.

EXAMPLE I.

160 grams chromium nitrate ($Cr(NO_3)_3.9H_2O$) are dissolved, with heat,

ing in 60 c.c. water. After the solution has cooled 10 grams zinc chloride and 96 grams ferric nitrate are added. To the resulting cold solution 100 grams zinc oxide are then added with constant stirring. The resulting wet mass is heated in a porcelain evaporating dish to dryness and then placed in a copper crucible in which it is heated over a Fletcher burner to drive off the nitrogen peroxide fumes.

The material thus obtained is crushed sufficiently to pass a 65 mesh screen and to it 8.2 grams zinc chloride dissolved in 60 c.c. water are added. The product thus obtained hardens spontaneously and is olive green in colour.

The yields of methanol condensate obtained with this catalyst when a gas mixture comprising 16—17% carbon monoxide and 84—83% hydrogen is passed through 1 liter of catalyst granules at a space velocity of 20,000—75,000 at a pressure of 2000 pounds per square inch and at a temperature of 400—420° C. will be about 400—950 c.c. of condensate per hour, which analyses 87.6—95.4% by volume of methanol.

EXAMPLE II.

7.2 kilograms chromium nitrate $Cr(NO_3)_3.9H_2O$ and 4.3 kilograms ferric nitrate are dissolved in 5 liters of water by heating in a large porcelain evaporating dish on a steam bath. 450 to 820 grams zinc chloride (which may contain 0.0002% arsenic) are then dissolved in this solution.

Separately there is made up a suspension of 4.5 kilograms zinc oxide (which may contain traces of chlorides and heavy metals slightly in excess of U.S.P. limit) in 11 liters of water. By stirring this suspension well and breaking up by hand any lumps that form, a practically complete suspension is obtained. To this suspension there is slowly added with vigorous stirring the above solution of salts. A thick pasty mass is formed which is spread out in a thin layer to dry and harden. To accelerate this process, a current of air from an electric fan may be allowed to play on the surface of the mass. On the following day, the hardened mass is broken up and placed in a furnace consisting of an alundum tube inside of which is placed a sealed copper vessel which contains the catalyst and through which a current of hydrogen gas or a gas composed of 15—25% carbon monoxide and 85—75% hydrogen is passed. The mass is heated until the temperature registered by a pyrometer placed in the centre of the copper vessel reaches approximately 350° C. and the heating continued at this temperature until nitrogen peroxide fumes are no longer given off.

When a gas mixture comprising 10—60% carbon monoxide and 90—40% hydrogen is passed over this catalyst at a temperature of 400—420° C. at a space velocity of 20,000—40,000 and at a pressure of 3200—3500 pounds per square inch, from 1.5 to 2.5 liters of condensate per hour per liter of contact mass, analyzing 98.0—97.2% by volume of methanol, are obtained.

EXAMPLE III.

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

It will be noted that in both of the herein described specific examples, the catalytic mass, as finally prepared for use, comprises zinc oxide, chromium oxide, iron oxide, and zinc chloride. In the case of Example I, the nitrates of chromium and iron were decomposed to the oxide by simple heating of the dry mass. In the case of Example II, this reduction was accomplished by means of a mixture of carbon monoxide and hydrogen. The effect on the composition is the same in both treatments.

Broad claims relating to the use of mixtures of difficultly reducible oxides with oxides of iron group metals and metallic halides as methanol catalysts have been presented in our Specification No. 271,840 hence only specific claims are presented herein.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An improvement or modification of the improved methanol catalyst described and claimed in our parent British Application No. 271,840 which consists in combining zinc oxide, chromium nitrate, ferric nitrate and zinc chloride in aqueous admixture and converting the nitrates to oxides.

2. Preparation of a methanol catalyst as claimed in Claim 1, by combining 4500 grams of zinc oxide, 7200 grams chromium nitrate ($Cr(NO_3)_3.9H_2O$), 4800 grams ferric nitrate and 450 to 820 grams zinc chloride in aqueous mixture and converting the nitrates to oxides.

3. Preparation of a methanol catalyst

according to Claim 1, by combining 26.7—27.3% zinc oxide, 42.9—43.9% chromium nitrate $Cr(NO_3)_3.9H_2O$), 25.6—26.1% ferric nitrate, and 4.8—2.7% zinc chloride in aqueous mixture, and converting the nitrates to oxides.

4. The modification or improvement in the process for the preparation of a methanol catalyst as described and claimed in our parent British Application No. 271,840 which comprises adding an aqueous solution consisting of chromium nitrate $Cr(NO_3)_3.9H_2O$), ferric nitrate and zinc chloride to an aqueous suspension of zinc oxide, obtaining the resultant mixture in the form of a dry hardened mass, and heating the said mass to convert the nitrates to oxides.

5. A process for the preparation of a methanol catalyst as claimed in Claim 4, which comprises adding an aqueous solution consisting of 42.9—43.9% chromium nitrate ($Cr(NO_3)_3.9H_2O$), 25.6—26.1% ferric nitrate and 4.8—2.7% zinc chloride to an aqueous suspension containing 26.7—27.3% zinc oxide, obtaining the resultant mixture in the form of a hardened mass and heating the said mass in a current of hydrogen to a temperature of approximately 350° C. until nitrogen peroxide fumes are no longer given off.

6. The improvement in or modification of the process for the production of synthetic methanol described and claimed in our parent British Application No. 271,840 which comprises passing a mixture of hydrogen and oxides of carbon at a pressure in excess of 2000 pounds per square inch and at a temperature above 250° C. over a catalyst initially comprising zinc oxide, chromium oxide, iron oxide, and zinc chloride prepared as claimed in Claims 1—5, cooling the reacted gases, and recovering the resultant methanol.

7. A process for the production of synthetic methanol as claimed in Claim 6, which comprises passing a mixture of hydrogen and oxides of carbon at a pressure of 2000 to 3500 pounds per square inch and at a temperature to 385—420° C. over a catalyst initially comprising zinc oxide, chromium oxide, iron oxide, and zinc chloride prepared as claimed in Claims 1 to 5, cooling the reacted gases, and recovering the resultant methanol.

8. The improved methanol catalyst comprising zinc oxide, chromium oxide, iron oxide and zinc chloride when prepared by the process of Claims 1 to 5.

9. The improved process for the production of synthetic methanol substantially as hereinbefore described.

Dated this 20th day of April, 1927.
MARKS & CLERK.

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