AMENDED SPECIFICATION.

Reprinted as amended in accordance with the decision of the Assistant Comptroller, acting for the Comptroller-General, dated the 30th day of November, 1928.

PATENT SPECIFICATION

275,345

3357

Application Date: May 12, 1926. No. 12,228/26.

Complete Accepted: Aug. 11, 1927.

COMPLETE SPECIFICATION (AMENDED).

Improvements in or relating to the Production of Methanol and other Oxygenated Organic Compounds.

We, SYNTHETIC AMMONIA & NITRATES, LIMITED, a British Company, of Billingham, Stockton-on-Tees, in the County of Durham, and HAROLD GREVILLE SMITH, a British Subject, of Synthetic Ammonia & Nitrates, Limited, of Billingham, Stockton-on-Tees, 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:—

This invention relates to the production of oxygenated organic compounds by the catalytic reduction of oxides of carbon, particularly to the production of methanol from mixtures of hydrogen and carbon monoxide under high pressure and in the presence of a catalytic agent. We have discovered that a contact mass prepared as having the composition $4\,ZnO.CrO_3$ is a particularly active catalyst for this reaction, and enables one to obtain high yields of methanol at relatively low temperatures, e.g. 300—400° C. and our invention consists in the use of this catalyst as hereinafter described and claimed.

Compositions containing zinc and chromium have previously been proposed, but we find that the particular contact mass of our invention gives results which are unusually satisfactory.

In referring to a catalyst having the composition $4ZnO.CrO_3$, we wish it to be understood as including a basic zinc chromate of the said composition with varying amounts of water; we do not wish to convey the idea that the catalysts remain as such under synthesis conditions, as in fact they do not. But our invention is based upon the fact that a substance prepared as having the composition mentioned becomes a good catalyst under the synthesis conditions.

Our invention may be carried out in the following manner:—Finely divided zinc oxide (ZnO) or zinc hydroxide ($Zn(OH)_2$) is suspended in water and treated at the ordinary temperature with a slight excess of an aqueous solution of chromic acid (CrO_3).

By a slight excess of chromic acid is meant slightly over one molecular proportion of the acid to four molecular proportions of zinc oxide or hydroxide. We prefer to use a thin suspension e.g. 1 molecule of zinc as hydroxide per 10 litres of water and the chromic acid is added as a concentrated solution, the mixture being well stirred. The yellow precipitate of basic zinc chromate is separated and dried. It is then introduced, in any convenient form, e.g. pellets, into the catalytic apparatus and treated with a gaseous mixture of two parts of hydrogen and one part of carbon monoxide at atmospheric pressure and at a temperature of 360° C. After a short time, during which partial reduction or other change of the contact mass is effected, the pressure of the gas mixture is raised to 200 atmospheres, when the production of methanol begins and thereafter continues in satisfactory manner. The further life and efficiency of the catalyst are dependent upon the purity of the reaction gases. Sulphur has little poisonous effect, and as much as 10 to 15 per cent (of the total weight of the contact mass) may be fixed in the catalyst without its undergoing marked diminution of activity. Volatile compounds of iron, cobalt and nickel should be excluded in known manner. The gas rate should be between 20 and 50 cubic metres per hour (gas mixture measured at N.T.P) per kilogram of contact mass. The reduction of the basic

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zinc chromate may also be carried out outside the apparatus. In any case care should be taken that the temperature of the contact mass does not rise too high during reduction.

If alkali salts are intimately mixed with the above described catalyst it becomes especially suitable for the production of oxygenated organic compounds such as higher alcohols than methanol, e.g. butanol, particularly if the gas rate is reduced to say 5 cubic metres per hour per kilogram of catalyst. The contact mass of the composition 4 $ZnO.CrO_3$ as prepared by double decomposition of suitable salts e.g. zinc sulphate and sodium chromate preferably in presence of alkali usually contains absorbed alkali salts and is likewise adapted for the production of higher alcohols. If it is desired to use the catalyst so prepared for the manufacture of methanol alone, it should be thoroughly washed so as to remove as far as possible the alkali salts; and the precipitation should be carried out from a hot solution and with stirring so that the minimum of alkali salt is absorbed.

In general the catalyst is much better when prepared in dilute solution.

Our invention is not limited to the precise operating conditions described in the above example, as deviations from this procedure may be made in accordance with the already established technique of methanol synthesis.

As an example of the value of our selection of the contact mass prepared as having the composition $4ZnO.CrO_3$, the following experiments may be cited:

1. A gaseous mixture containing 40 per cent CO, 50 per cent H and small amounts of nitrogen and carbon dioxide was passed at 200 atmospheres and a temperature of 360—390° C over a contact mass prepared by mixing zinc oxide and chromium oxide in the proportion of 8 moles of ZnO to one mole of Cr_2O_3 (Zn : Cr = 4 : 1). With a gas rate of 1,000 litres per hour and employing 70 cc. of catalyst the yield of methanol was 37 cc. per hour.

2. Under the same experimental conditions as in example 1, a contact mass prepared by the chemical combination of zinc oxide and chromic trioxide and having 70 per cent moles ZnO gave a yield of 29 cc. per hour.

3. Under the same experimental conditions a contact mass prepared as in example (2) but having 90 per cent moles zinc oxide gave a yield of 28 cc. per hour.

4. Under the same experimental conditions the contact mass prepared according to our invention gave a yield of 66 cc. per hour.

We are aware of specification 227,147 and we claim nothing described or claimed therein.

We have not found that formaldehyde is produced in the working of our process, and we make no claim to the production of formaldehyde by such process.

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. Process for the production of oxygenated organic compounds which comprises passing oxides of carbon and hydrogen at elevated temperatures and pressures in contact with a catalyst containing zinc oxide and chromium oxide in the form of the basic zinc chromate substantially of the composition $4ZnO.CrO_3$, or the substance into which the compound is converted under the conditions of the synthesis.

2. Process for the catalytic production of methanol as claimed in claim 1 which consists in passing a mixture of hydrogen and carbon monoxide at elevated temperature and pressures over a contact mass prepared as having substantially the composition $4ZnO.CrO_3$ and being substantially free from soluble alkali salts.

3. Process for the production of oxgenated organic compounds such as higher alcohols than methanol as claimed in claim 1 which consists in passing a mixture of hydrogen and carbon monoxide at elevated temperatures and pressures over a contact mass prepared as having substantially the composition $4ZnO.CrO_3$ and having an admixture of soluble alkali salt.

4. Process for the production of oxygenated organic products, substantially as described.

Dated this 10th day of May, 1926.
W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1929