[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in Catalysts for the Catalytic Production of Methanol and other Oxygenated Organic Compounds from Oxides of Carbon and Hydrogen.

We, SYNTHETIC AMMONIA & NITRATES LIMITED, a British company, of Billingham, Stockton-on-Tees, in the County of Durham, and REGINALD GEORGE FRANKLIN, a British subject, of the said company's address, do hereby declare the nature of this invention to be as follows:—

Among numerous catalysts for the synthesis of methanol and other organic compounds from hydrogen and carbon monoxide it has been proposed to employ compositions containing zinc and chromium oxides containing various ratios of zinc and chromium, and it has been proposed to prepare these in various ways.

We have now discovered that a very good way to prepare these catalysts is to employ zinc carbonate or basic zinc carbonate as a basis for the preparation of zinc-chromium compositions. Such catalysts are particularly effective when the molecular ratio of zinc to chromium is nine to one (Zn : Cr).

Thus according to the present invention in its preferred form zinc carbonate or basic zinc carbonate is treated with chromic acid in aqueous solution, the product is dried and brought into a suitable form e.g. pellets for introduction into a converter where it is exposed to a gaseous mixture containing carbon monoxide and hydrogen. After reduction of the catalyst, the synthesis of methanol may be carried on in the usual manner.

The following examples illustrate our invention:—

EXAMPLE 1.

700 gms. of zinc sulphate, $ZnSO_4, 7H_2O$, are dissolved in 5 litres of water and a solution of 270 gms. of soda ash (Na_2CO_3) is added to the solution. The mixture is boiled for 10 minutes and then the precipitate is filtered off and washed until the washings are free from sodium sulphate. The moist precipitate of basic zinc carbonate is then digested with a solution of 95 gms. of chromic acid (CrO_3) in 9 litres of water. The precipitate is filtered off, dried and formed into suitable granules or pellets for introduction into the catalytic apparatus.

The zinc carbonate may also be precipitated on a carrier such as asbestos or pumice, by impregnating same with the solution of zinc sulphate and then treating with a soluble carbonate. The zinc-carbonated carrier may then be treated with chromic acid solution as before.

The proportion of chromic acid mentioned above represents a considerable excess, since only about 20% is fixed by the zinc carbonate. The excess, however, is necessary in the method of preparation according to this example, as if smaller proportions are employed a correspondingly smaller amount is fixed by the zinc carbonate.

EXAMPLE 2.

A solution of 40 gms. of zinc sulphate is added to a solution of 15 gms. of soda ash and 11 gms. of sodium bichromate, the total volume of solution being about 9—10 litres. After boiling for several minutes the precipitate is filtered off and washed and dried. It is then suitable for introduction into the catalytic apparatus.

The composition of the precipitate varies with slight changes in the conditions of preparation, and in making our preferred catalyst (having a ratio Zn : Cr of 9 : 1) it is necessary to test the final product to be sure that the desired ratio has been obtained and if not, the preparation must be repeated. The invention also includes catalysts prepared as above and containing more or less chromium e.g. 2% by weight of the finished catalyst.

The precautions advised in our co-pending Application No. 12,228/26 (Serial No. 275,345) with regard to the reduction of the catalyst prior to its mise en marche proper must be observed also with catalysts prepared according to this invention, i.e. the reduction should be carried out as carefully as possible with strict avoidance of overheating.

When the catalyst contains soluble alkali salts as described in our co-pending Application No. 12,228/26 (Serial No. 275,345), and when the gas current is slower and the temperature somewhat higher, higher alcohols and other organic compounds are produced.

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The invention includes the novel catalysts, and their method of production and the synthesis of methanol or other organic compounds by their aid.

Dated this 13th day of November, 1926.
W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered and Registered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in Catalysts for the Catalytic Production of Methanol and other Oxygenated Organic Compounds from Oxides of Carbon and Hydrogen.

We, SYNTHETIC AMMONIA & NITRATES LIMITED, a British company, of Billingham, Stockton-on-Tees, in the County of Durham, and REGINALD GEORGE FRANKLIN, a British subject, of the said company's address, 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:—

Among numerous catalysts for the synthesis of methanol and other organic compounds from hydrogen and carbon monoxide it has been proposed to employ compositions containing or comprising zinc and chromium oxides containing various ratios of zinc and chromium (compare for example Specifications Nos. 227,147 and 275,345), and it has been proposed to prepare these in various ways. On the other hand it has been proposed to make catalysts containing zinc by heating precipitated zinc carbonate.

We have now found that a very good way to prepare such catalysts containing zinc and chromium, is to heat a mixture comprising zinc carbonate or basic zinc carbonate and a chromium compound which may be zinc chromate or basic zinc chromate. When zinc chromates are employed the heating should be done in presence of the reaction gases or hydrogen.

Thus according to the present invention in its preferred form zinc carbonate or basic zinc carbonate is treated with chromic acid in aqueous solution, the product is dried and brought into a suitable form e.g. pellets for introduction into a converter where it is exposed to a hot gaseous mixture containing carbon monoxide and hydrogen. After reduction of the catalyst, the synthesis of methanol may be carried on in the usual manner.

Our preferred catalyst has a ratio Zn : Cr of 9 : 1 but the invention also includes catalysts containing more or less chromium e.g. 2% by weight of the finished catalyst.

The following examples illustrate our invention:—

EXAMPLE 1.

700 gms. of zinc sulphate, $ZnSO_4$, $7H_2O$, are dissolved in 5 litres of water and a solution of 270 gms. of soda ash (Na_2CO_3) is added to the solution. The mixture is boiled for 10 minutes and then the precipitate is filtered off and washed until the washings are free from sodium sulphate. The moist precipitate of basic zinc carbonate is then digested with a solution of 95 gms. of chromic acid (CrO_3) in 9 litres of water. The precipitate is filtered off, dried and formed into suitable granules or pellets for introduction into the catalytic apparatus.

The zinc carbonate may also be precipitated on a carrier such as asbestos or pumice, by impregnating same with the solution of zinc sulphate and then treating with a soluble carbonate. The zinc-carbonated carrier may then be treated with chromic acid solution as before.

The proportion of chromic acid mentioned above represents a considerable excess, since only about 20% is fixed by the zinc carbonate. The excess, however, is necessary in the method of preparation according to this example, as if smaller proportions are employed a correspondingly smaller amount is fixed by the zinc carbonate.

The proportion of chromic acid mentioned above, is found to produce a catalyst of the preferred composition. If a sample of the precipitate however is found to contain too little chromium, the digestion of the zinc carbonate must be repeated with a somewhat stronger solution of chromic acid, since the stronger the chromic acid the more chromium is taken up by the precipitate.

If the precipitate contains too much chromium after digestion, a weaker solution of chromic acid must be used, or alternatively the excess acid is removed by careful washing.

EXAMPLE 2.

A solution of 40 gms. of zinc sulphate is added to a solution of 15 gms. of soda ash and 11 gms. of sodium bichromate, the total volume of solution being about 9—10 litres. After boiling for several minutes the precipitate is filtered off and washed and dried. It is then suitable for introduction into the catalytic apparatus.

In making our preferred catalyst by this method the precipitate at first contains too much chromium and it is washed by decantation until the chromium has fallen to the correct amount. In the washing, zinc and chromium are removed in approximately equal proportions but as the precipitate contains an excess of zinc the correct ratio of 9 : 1 can always be obtained.

The precautions advised in our Specification No. 275,345 with regard to the reduction of the catalyst prior to its mise en march proper must be observed also with such catalysts as are prepared by reduction according to this invention, i.e. the reduction should be carried out as carefully as possible with strict avoidance of overheating.

When the catalyst contains soluble alkali salts as described in our Specification No. 275,345 and when the gas current is slower and the temperature somewhat higher, higher alcohols and other organic compounds are produced.

The invention includes the novel catalysts, and their method of production and the synthesis of methanol or other organic compounds by their aid.

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 of preparing a catalyst containing zinc and chromium suitable for the production of oxygenated organic compounds particularly methanol, from carbon monoxide and hydrogen, which includes the step of heating a mixture comprising zinc carbonate or basic zinc carbonate and a chromium compound.

2. Process of preparing a catalyst containing zinc and chromium suitable for the production of oxygenated organic compounds particularly methanol, from carbon monoxide and hydrogen, which consists in heating a mixture comprising zinc carbonate or basic zinc carbonate and zinc chromate or basic zinc chromate in the presence of the reaction gases or hydrogen.

3. Method of preparing a catalyst as claimed in Claims 1 and 2 which includes the step of causing a soluble acidic chromium compound to react with zinc carbonate or basic zinc carbonate, substantially as described.

4. Method of preparing a catalyst as claimed in Claim 1, which includes the step of precipitating a soluble zinc salt with a bichromate, chromic acid or a chromate, in presence of a soluble carbonate.

5. Method as claimed in Claim 3 in which freshly precipitated zinc carbonate or basic zinc carbonate is treated with an excess of chromic acid in dilute solution.

6. Method as claimed in Claim 4 in which a soluble zinc salt is precipitated with sodium bichromate and soda ash.

7. Catalysts whenever prepared by the methods claimed in any of the preceding claims.

8. Catalyst whenever prepared according to any of the preceding claims in which the atomic ratio of zinc to chromium is 9 to 1.

9. Process of preparing oxygenated organic compounds from carbon monoxide and hydrogen in which the gases are passed over a catalyst prepared as described in any of the preceding claims.

Dated this 11th day of August, 1927.
W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered and Registered Patent Agents.

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