[Second Edition.]

PATENT SPECIFICATION

Application Date: Dec. 23, 1926. No. 32,483 / 26.

Complete Left: Sept. 23, 1927.

Complete Accepted: June 25, 1928.

293,056

740

PROVISIONAL SPECIFICATION.

Improvements in the Production of Methanol and other Alcohols and Preparation of Catalysts therefor.

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:—

It is known that compositions containing zinc and chromium oxides are good catalysts for the production of methanol, etc., from carbon monoxide and hydrogen under pressure, and a variety of catalysts embodying these elements has been suggested. We have now found that such compositions are particularly effective when they contain the chromium and zinc in the form of basic carbonates.

This use of basic carbonates is believed to be broadly novel. In referring to these compositions as compounds, we do so for brevity; the invention does not depend on their existence as true compounds but on the nature of the ingredients and in some cases, on the proportion of such ingredients and the method of preparation. Joint alkaline precipitation is an important but not the invariable feature of our invention. The invention also includes the novel methods of preparing catalysts as hereafter described.

Compounds such as

$$5ZnO.2CO_2.4H_2O;$$
$$ZnCO_3.7ZnO.2H_2O;$$
$$ZnCO_3.3ZnO.2H_2O;$$
$$ZnCO_3.2ZnO.2H_2O;$$
$$ZnCO_3.ZnO.H_2O$$

and the like are very suitable as a source of the zinc part of the catalyst, while basic chromium carbonates such as

$$4Cr_2O_3.CO_2.H_2O;$$
$$2Cr_2O_3.CO_2.6H_2O:$$
$$10Cr_2O_3.7CO_2.8H_2O;$$

may supply the chromium part (see Mellor's "A comprehensive Treatise on Inorganic and Theoretical Chemistry", 1923, vol. 4, pp. 645—646; Friend's "Textbook of Inorganic Chemistry", 1926, vol. 7, part 3, p. 95).

According to our invention we prepare a catalyst containing both zinc and chromium substantially all in the basic carbonate state. This composition may then be used as such in the catalytic apparatus.

Our invention further includes the process of preparing our improved catalysts as follows:—A strong solution of sodium bichromate or chromate is mixed with sulphuric acid or other strong acid and the mixture is treated with granulated zinc metal. Reduction of the bichromate takes place with the production of chromium sulphate. When the reduction is finished, or slightly before, a solution of soda ash is added. The precipitate thrown down consists of a mixture of basic zinc and chromium carbonates and is separated, washed and dried. It is then made into pellets or other suitable form and introduced in the catalytic apparatus. In this preparation the exact composition of the precipitate as regards the basicity of the carbonates depends upon many factors, such as concentration of solutions, temperature and amount of soda ash added. We prefer to proportion the zinc and chromium so that the precipitate contains 70—80 atoms of zinc to 30—20 atoms of chromium. All the zinc and chromium are precipitated from solution. The solution may be boiled together with the precipitate so as to free it as much as possible from absorbed alkali salts.

Other methods or preparation than the above may be employed. For instance, chromium oxide may be dissolved in sulphuric acid and the solution mixed with a solution of zinc sulphate, precipitation with soda ash following as before.

The reduction of the sodium bichromate by means of zinc in the presence of sulphuric acid may also be effected electrochemically by making the zinc metal one electrode of a cell having an inert material such as carbon for the other electrode and a solution of bichromate and sulphuric acid as electrolyte. By taking current from this cell the bichromate is reduced and the spent electrolyte eventually contains the requisite amount of zinc and chromium sulphate for the precipitation with soda ash. This method of preparation has the advantage that the free energy of the reactants is made to manifest itself as useful electrical energy instead of as heat

AMENDMENT — SEE LAST PAGE

The zinc electrode may also be amalgamated to prevent direct attack by the acid, as in an ordinary bichromate cell.

Catalysts prepared according to this invention are characterised by yielding high yields of methanol of very high purity. If alkali salts are allowed to remain in the catalysts, or if separate additions of such are made, they become suitable for the production of higher alcohols. When through poisoning these catalysts become less efficient they may be regenerated by dissolving up in sulphuric acid and reprecipitating the complex carbonates with soda ash.

Dated this 22nd day of December, 1926.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in the Production of Methanol and other Alcohols and Preparation of Catalysts therefor.

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:—

This invention relates to the production of catalysts suitable for the hydrogenation of carbon monoxide to methanol and other alcohols. Among numerous catalysts for this purpose it has been proposed to employ compositions of zinc and chromium with 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.

According to the present invention we adopt a method for the production of the above catalysts which includes the step of heating a mixture containing zinc and chromium each in the form of basic carbonate. Mixtures of oxides prepared as such do not come within the scope of the invention.

The basic carbonates employed are referred to as compounds for the sake of brevity, as the invention does not depend upon their existence as true compounds but upon the nature of the starting material for their preparation, upon the proportions of the ingredients and upon the method of preparation.

Compounds such as

$$5ZnO.2CO_2.4H_2O\ ;$$
$$ZnCO_3.7ZnO.2H_2O\ ;$$
$$ZnCO_3.3ZnO.2H_2O\ ;$$
$$ZnCO_3.2ZnO.2H_2O\ ;$$
$$ZnCO_3.ZnO.H_2O$$

and the like are very suitable as a source of the zinc part of the mixed catalyst, while basic chromium carbonates such as

$$4Cr_2O_3.CO_2.H_2O\ ;$$
$$2Cr_2O_3.CO_2.6H_2O\ ;$$
$$10Cr_2O_3.7CO_2.8H_2O\ ;$$

may supply the chromium part (see Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1923, vol. 4, pp. 645—646; Friend: "Textbook of Inorganic Chemistry", 1926, vol 7, part 3, page 95).

According to the invention basic zinc carbonate may be mixed with basic chromium carbonate, or the basic carbonates may be co-precipitated. The composition of matter containing basic carbonates is then subjected to heat and is thereby converted into the improved catalyst. We use the term catalyst as referring either to the freshly made basic carbonate mixture or the mixture of oxides obtained therefrom by heating.

The compounds are prepared by precipitation, the precipitates being well washed and dried and preferably pelleted before introduction into the catalytic apparatus.

The following examples illustrate the method of preparation of our improved catalysts.

EXAMPLE 1.

A strong solution of sodium bichromate or chromate is mixed with sulphuric acid and the hot mixture (90° C.) is heated with granulated zinc metal to effect reduction of the bichromate to chromium sulphate. When the reduction is finished a solution of soda ash (5—10 per cent. excess) is added; the precipitate thrown down consists of a mixture of basic zinc and chromium carbonates, which is separated, washed well with hot water and dried. It is then made into pellets and introduced into the catalytic apparatus.

In this preparation exact composition of the precipitate as regards the basicity of the carbonates depends upon many factors, such as concentration of solutions, temperature and amount of soda ash added. We prefer to proportion the zinc and chromium so that the precipitate contains 70—80 atoms of zinc to 30—20 atoms of chromium. In some cases the amount of zinc may not be sufficient to effect reduction of all the chromium and additional reducing agents may then be used e.g. SO_2.

EXAMPLE 2.

A solution of sodium bichromate in aqueous sulphuric acid is placed as electrolyte in a cell having a zinc negative pole and a carbon positive pole. By taking current from the cell the bichromate is reduced and the spent electrolyte eventually contains the requisite amount of zinc and chromium sulphate for the precipitation with soda ash, which follows as before. This method of preparation has the advantage that the free energy of the reactants is made to manifest itself as useful electrical energy instead of as heat. The zinc electrode may also be amalgamated to prevent direct attack by the acid.

EXAMPLE 3.

Basic chrome liquor of commerce, which consists of a solution of chromium sulphate made by reduction of chromates by SO_2 or by molasses, is used as a source of chromium. A suitable amount of zinc sulphate is added to the liquor and the mixed basic carbonates precipitated as before.

Catalysts prepared according to this invention are capable of yielding direct methanol of a high degree of purity. If alkali salts are allowed to remain in the catalyst, or if separate additions of such are made, they become suitable for the production of higher alcohols. When, through poisoning, these catalysts become less efficient, they may be regenerated by dissolving up in sulphuric acid and reprecipitating the complex carbonates with soda ash.

We do not, in the present application claim anything claimed in our co-pending Application No. 28,689/26, which claims (inter alia) the use of mixtures of normal or basic zinc carbonate with a chromium compound.

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. Method of making catalysts for the production of alcohols particularly methanol from carbon monoxide and hydrogen which consists in heating a mixture of basic zinc carbonate and basic chromium carbonate.

2. Method of making catalysts for the production of alcohols, particularly methanol, from carbon monoxide and hydrogen which includes the step of precipitating basic zinc and chromium carbonates from a mixed solution of zinc and chromium salts.

3. Method as claimed in Claim 2 in which the chromium salt is obtained by reduction of sodium bichromate, in the presence of an acid.

4. Method as claimed in Claim 3 in which zinc is used as the reducing agent.

5. Method as claimed in Claim 4 in which the zinc forms the negative pole of a bichromate cell.

6. Method as claimed in Claims 1—5 in which the catalysts contains 70—80 atoms of zinc to 30—20 atoms of chromium.

7. Catalysts whenever prepared by the methods claimed in Claims 1—6.

8. Methods of preparing catalysts substantially as described.

9. Process of preparing alcohols from carbon monoxide and hydrogen, in which the gases are led over catalysts prepared as claimed in the preceding claims.

Dated this 22nd day of September, 1927.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 56A.—125/10/1928.]

SPECIFICATION No. 293,056.

Page 3, line 50, *after* "28,689/26" *insert* "(290,399)"