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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Methyl Alcohol and to Agents for use therein.

We, British Celanese Limited, a company incorporated in accordance with the laws of Great Britain, of 8, Waterloo Place, London, S.W. 1, Walter Bader, a citizen of the Swiss Republic, and Stanley Joseph Green, a subject of the King of Great Britain, both of the Works of British Celanese Limited, Spondon, near Derby, England, 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 manufacture of methyl alcohol and to catalysts for use therein.

It is known that methyl alcohol can be prepared from gas mixtures containing hydrogen and an oxide or oxides of carbon by leading them over catalysts, under pressure and at a temperature between about 250 and 450° C. A very large number of substances have been proposed as catalysts for this reaction, but it is generally known that only zinc oxide, or mixtures containing zinc oxide are economically successful.

As a rule zinc oxide forms the bulk of the catalysing mixture, its action being enhanced by relatively small amounts of so-called promoters. For this purpose, oxides of chromium are generally favoured, and also small amounts of copper.

It has now been found that the physical condition of the zinc oxide, which depends upon the method of its preparation, is much more important for its activity than the presence of promoters. A zinc oxide, which by itself is only moderately active, certainly becomes activated by the addition of 5—10% of chromic acid, but the effect of the same promoter upon a zinc oxide which is already highly active, is quite small.

Pure zinc oxide can be relatively inactive as a catalyst for the formation of methyl alcohol, and it may show every possible degree of activity, without any apparent chemical reason.

The present invention makes possible the preparation of a highly active pure zinc oxide catalyst which does not require the presence of any promoter, its activity being in fact hardly influenced by a promoter. The use of a chemically pure substance as a catalyst has the advantage that undesirable by-reactions are thereby minimised.

The present invention is based on the discovery that when the zinc oxide catalyst is prepared from precipitated zinc carbonate by heating it at temperatures not higher than that used in the catalytic preparation of methyl alcohol, it is necessary in order to produce a highly active zinc oxide that the zinc carbonate should be precipitated in a highly colloidal and gelatinous form, and that care should be taken to maintain the zinc carbonate in a highly colloidal state during the subsequent washing and drying operations. A similar procedure is necessary when the zinc oxide catalyst is of the type containing a promoter, and especially when it is prepared by a process involving the co-precipitation of a zinc carbonate with a promoter-yielding carbonate. The catalytic activity of the zinc oxide catalyst finally produced depends upon the colloidal character of the zinc carbonate gel; the more colloidal and gelatinous the zinc carbonate gel is, the greater is the catalytic activity of the zinc oxide finally obtained.

Zinc carbonate gels of the character indicated can be obtained by precipitation in very dilute solutions at ordinary or low temperature. They should not be brought to a denser state by filtering or pressing, but, after washing by decantation, the water should be removed by drying. The complete removal of electrolytes from the precipitate is important for the production of zinc oxide catalyst of high activity. In order to increase the voluminous character of the product, the drying of the zinc carbonate gel may be effected by heating under vacuum or reduced pressure.

It is preferred to precipitate the zinc carbonate in the presence of solutions or jellies containing suitable inert protective colloids, e.g. starch, pectin, saponin, hydrated silica etc., or to mix the precipitate, after washing, with solutions or jellies of such bodies. This not only enhances the activity of the zinc oxide finally obtained, but also facilitates the formation of the dried mass into convenient granules. In this case also, the product may be dried by heating under vacuum.

The temperatures used for converting the zinc carbonate gel into zinc oxide lie between about 250° C. and 450° C., and preferably between about 250° C. and 350° or 400° C.

The following example shows one of the many ways in which the invention can be carried out.

EXAMPLE.

A 1% solution by weight of zinc nitrate is poured, at room temperature, into an equivalent solution of sodium carbonate, also of 1% strength, with good agitation. The gelatinous precipitate is thoroughly washed with water by decantation, then mixed with a starch jelly and dried at about 60° C. The dry mass is broken into pieces of about ¼ inch size and charged into the reaction chamber used in the synthesis of methyl alcohol. At the prevailing temperature, e.g. 250° to 300° C., the zinc carbonate gel is converted into a light, fluffy form of zinc oxide displaying a high degree of activity when used as catalyst in the production of methyl alcohol by the hydrogenation of oxides of carbon.

Dilute solutions of any other soluble zinc salt (e.g. zinc sulphate or chloride), or of sodium bicarbonate or any other soluble carbonate or bicarbonate (e.g. potassium or ammonium carbonate or bicarbonate) may be substituted for the zinc nitrate and sodium carbonate in the production of the zinc carbonate gel.

The proportions and concentrations of the reagents may be varied as desired always provided that a zinc carbonate gel of a highly voluminous character is obtained as the result of the reaction.

The zinc carbonate gel may be mixed with solutions or jellies of any suitably inert protective colloids such as starch, pectin, saponin, or hydrated silica, or may be formed in the presence of such solutions or jellies, or it may be prepared and converted into zinc oxide catalyst in the entire absence of such colloids.

As previously explained, it is convenient to effect the conversion of the zinc carbonate gel into zinc oxide during the synthesis of the methyl alcohol. For example, the zinc carbonate gel may be placed in a suitable reaction chamber maintained at a temperature of 250 to 350° C., for example 300° C., through which a mixture containing approximately two parts by volume of hydrogen and one part by volume of carbon monoxide is passed under a pressure of about 80 to 120 atmospheres. As the conversion of the zinc carbonate gel into zinc oxide proceeds, methyl alcohol is produced in quantities which rapidly increase to a maximum.

The conversion of the zinc carbonate gel into zinc oxide may however be effected as an entirely separate operation under conditions similar to or differing from those obtaining in the methyl alcohol synthesis. Thus, for instance, a zinc oxide may be produced from the zinc carbonate gel at low temperature under atmospheric pressure, and used afterwards in the production of methyl alcohol at a higher temperature.

The zinc oxide prepared in accordance with the process forming the subject matter of the present invention may also be employed in admixture with a promoter, or mixed with other catalysts suitable for combining hydrogen with oxides of carbon, or mixed with or distributed over an inert solid carrier, such as pumice or carbon. Such mixtures or preparations may be formed after the conversion of the zinc carbonate gel into zinc oxide, or, in suitable cases, by mixing the added substance with the zinc carbonate gel before or after the drying operation, or by incorporating the added body with the zinc carbonate gel during its formation. In some cases, it is possible to form a suitable mixture by co-precipitation of the carbonates from a solution containing a mixture of salts or compounds. For instance, a zinc oxide containing chromium oxide as promoter can be obtained by precipitating the zinc carbonate gel from a solution containing a zinc salt and a chromium salt, and drying and heating the resulting gelatinous precipitate in the manner previously described. In these modifications of the process, however, all necessary precautions must be observed to prevent loss of the colloidal structure of the zinc carbonate gel during the manufacture of the mixture before the carbonic acid is driven off by the application of heat.

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. A process for the manufacture of a zinc oxide catalyst for use in the synthesis of methyl alcohol from mixtures of hydrogen and oxides of carbon, which comprises precipitating a zinc carbonate gel in a highly colloidal and gelatinous form, washing and drying the zinc carbonate gel under such conditions as to

maintain the same in a highly colloidal state, and heating the zinc carbonate gel at a temperature not exceeding the temperature at which the catalyst is to be employed in the synthesis of methyl alcohol.

2. A process according to Claim 1, which comprises precipitating the zinc carbonate gel in very dilute solution.

3. A process according to Claim 1 or 2, which comprises incorporating a solution or jelly of a protective colloid with the zinc carbonate gel.

4. A process according to Claim 1, 2 or 3, which comprises precipitating the zinc carbonate gel in the presence of a solution or jelly of a protective colloid.

5. A process according to Claim 1, 2, 3, or 4, wherein the zinc carbonate gel is converted into zinc oxide catalyst at a temperature not exceeding 450° C.

6. A process according to Claim 1, 2, 3, 4 or 5, wherein the zinc carbonate gel is converted into a zinc oxide catalyst at a temperature between about 250° C. and 350° or 400° C.

7. Process for the production of a zinc oxide catalyst substantially as described.

8. A process for the synthetic production of methyl alcohol, which comprises heating a mixture containing hydrogen and an oxide of carbon under pressure in the presence of a zinc oxide catalyst prepared in accordance with the process claimed in any of the preceding claims.

9. Process for the manufacture of methyl alcohol substantially as described.

10. A zinc oxide catalyst when prepared or produced by the processes claimed and described or by their obvious chemical equivalents.

11. Methyl alcohol when prepared or produced by the processes claimed and described or by their obvious chemical equivalents.

Dated this 2nd day of May, 1927.
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