

PATENT SPECIFICATION

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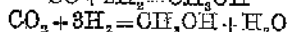
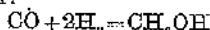
COMPLETE SPECIFICATION

A process for the preparation of Catalysts for the Synthesis of Methanol.

I, GIULIO NATTA, of 18, Via Principe Umberto, Milan, Italy, a subject of the Kingdom of Italy, 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 a process for the preparation of catalysts for the synthesis of methanol by the reaction of carbon oxide with hydrogen under pressure.

Zinc-oxide is actually one of the principal constituents of many known catalysts which promote the following reactions that take place in the synthesis of methanol:



It is however also known that zinc-oxide prepared by ordinary methods, as well as commercial zinc-oxide, are not suitable for carrying out these catalytic reactions on a commercial scale, owing to the fact that its catalytic activity rapidly decreases as the process proceeds. It is also found that as its catalytic activity in useful reactions decreases, its effect in the promotion of secondary and harmful reactions increases in proportion.

Stronger and more lasting activity is sometimes obtained by the addition of promoters (in most cases metallic oxides) but as these are inert or noxious substances, from the catalytic standpoint, in respect of the desired reactions, their function is often simply protective on zinc oxide, and they often cause secondary reactions, as the formation of organic products of higher molecular weight than methanol.

Up to the present time catalysts consisting only of zinc-oxide and having lasting activity, have been unknown; one exception being the zinc oxide obtained from Smithsonite. This, however, is a natural product which cannot easily be obtained in its pure form and which cannot be manufactured artificially in the form of neutral compact and crystalline carbonate.

All the types of zinc-oxide prepared

artificially show a catalytic activity which rapidly decreases in the course of time and further, do not possess properties of mechanical resistance which are desirable for catalysts for use on a commercial basis.

The present invention provides a process for the production of a catalyst for the synthesis of methanol, wherein organic zinc salts whose melting point is lower than their decomposition point, are heated until decomposed. The process may be carried out at a low temperature of 200–350° C. and products can be obtained which have a very strong and lasting catalytic activity.

For instance, zinc acetate (which has a melting temperature of 240°), decomposes at about 280–300° C. and makes an excellent catalyst. After the calcination has been completed, the catalyst which is composed essentially of zinc-oxide, is in the form of an agglomerate and after grinding assumes a granular porous structure with favourable mechanical properties. This particular structure is due to the fact that zinc oxide segregates from a molten mass, the melting temperature of the acetate being 240° and it therefore becomes porous and agglomerated and not in the form of powder like calcinated and precipitated products. On account of this physical structure, no further physical or mechanical treatment is required for the preparation of the catalyst, and no agglomerating agent is necessary nor is it necessary to press the substance into tablet form.

Moreover, products obtained by the calcination of organic zinc salts which decompose before melting, for instance formate and oxalate of zinc, appear in the form of powder and are not so advantageous from the catalytic point of view as products obtained by the calcination of fusible organic zinc salts such as zinc acetate.

For this reason the catalysts proposed in the present invention are preferable to any catalyst obtained by the precipitation of zinc salts with alkali, which have a minor specific activity suitable for use in the synthesis of methanol, but promote

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secondary reactions on account of the presence of traces of alkali which are firmly retained in the precipitates and cannot be removed by simple washing.

5 It is well known that the presence of alkali, or even traces of the same, promotes the formation by synthesis of carbon monoxide and hydrogen, of higher alcohols, aldehydes, acids, ethers, etc.
10 By the use of the present invention however, it is very easy to obtain zinc acetate free from alkali by dissolution of the metal in acetic acid, or much more economically by the dissolution of the mineral calamine carbonate (Smithsonite), lightly calcinated. In order to evaporate the solutions of zinc acetate obtained in this way and after drying in order to eliminate the water of crystallisation, it is sufficient to heat at relatively low temperatures (nearly 300°) for the preparation of the catalyst. The zinc acetate first melts and then decomposes according to the following reaction:

25 $(\text{CH}_3\text{COO})_2\text{Zn} = \text{ZnO} + \text{CO}_2 + \text{CH}_3\text{COCH}_3$
The acetone which is formed according to the preceding reaction can be recovered, thereby further reducing the low cost of production of the catalyst.

30 Preferably the reaction is carried out at the lowest possible temperature, in an atmosphere of inert or reducing gas, at normal pressure or still better, at an increased pressure.

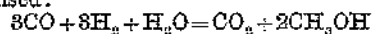
35 If during the preparation of the catalyst, pure zinc acetate is not used and substances are present which do not combine with the zinc oxide, at a low temperature, these substances may have a deleterious effect in the use of the catalyst for example by causing a definite and unfavourable reaction, and especially by promoting secondary reactions, which are not desired. The presence of metals of the iron group, for example, which are often present in the zinc ores, has a harmful effect. These metals may however, be easily eliminated from the neutral solutions of zinc salts by using an excess of zinc-oxide and of metallic zinc in powder form.

50 On the other hand, the presence of oxides, which are not reduced in the conditions in which the catalyst is being used, such as aluminium, chromium, magnesium, calcium, cadmium and silicon oxides is advantageous. Such oxides may accordingly be added, preferably in the form of organic compounds of the respective metal whose melting point is lower than their decomposition point.

The catalysts proposed also favour the reaction of conversion of water gas:

65 $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

which reaction takes place under the same temperatures and pressures as in the synthesis of methanol. Consequently they make it possible to use in the synthesis of methanol water gas with a lower hydrogen content than that which would be required theoretically. This lack of hydrogen may be remedied by adding a small quantity of steam, so that the two inter dependent equilibria allow the following reaction to be realised:



The carbon dioxide developed is easily eliminated on account of its very high solubility in methyl alcohol, under pressure.

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

1. A process for the synthesis of methanol characterised by the use as catalyst of zinc oxide which has been obtained by heating organic zinc salts whose melting point is lower than their decomposition point until they are decomposed.

2. A process according to Claim 1 wherein zinc acetate is heated until decomposed.

3. A process for the synthesis of methanol according to claim 1 or claim 2 wherein organic compounds of other metals whose melting point is lower than their composition point and which yield oxides which cannot be reduced in the conditions in which the catalyst is used are admixed with the zinc salts.

4. A process according to any of the preceding claims wherein the decomposition is effected at the lowest possible temperature.

5. A process according to any of the preceding claims wherein the decomposition is effected under pressure.

6. A process according to any of the preceding claims wherein after heating the resulting agglomerate is ground to a porous granular structure.

7. A process for the synthesis of methanol substantially as herein described and claimed.

8. A process for the synthesis of methanol from carbon monoxide and hydrogen when carried out according to any of the preceding claims.

9. A process for the synthesis of methanol from carbon monoxide hydrogen and steam when carried out according to any of claims 1 to 7.

10. Methanol when prepared according to the process claimed in any of the preceding claims.

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Dated this 10th day of June, 1937.

ERIC POTTER & CLARKSON,
Chartered Patent Agents,
8, Staple Inn, London, W.C.1,
London and Nottingham.

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