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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Synthesis of Alcohols.

We, THE COMPAGNIE DE BETHUNE, of Bully les Mines, Pas de Calais, France, a body corporate organized under the laws of France, 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 has reference to the synthesis of alcohols, particularly methyl-alcohol.

It has long been known that hydrogen when acting on carbonic oxide may produce two different reactions: the first resulting in methane according to the formula:

$$CO+3H_2=CH_4+H_2O$$

the second in oxygenated hydrocarbon compounds and especially alcohols by the process:

$$CO+2H_2=CH_3OH \text{ and}$$
$$nCO+2nH_2=C_nH_{(2n+2)}O+(n-1)H_2O.$$

In addition to the influence of pressure and temperature which intervenes in both cases, but especially in the second owing to equilibrium of the system, it is necessary to have a suitable catalyser to direct the reaction one way or the other.

Thus with metals such as iron, nickel, cobalt, only methane will be obtained and not alcohol.

To obtain alcohols from carbon monoxide and hydrogen, catalysers will be selected which can produce dehydrogenation of the alcohol; for we know that the same catalyser employed in suitable conditions of pressure and temperature can always give the inverse reaction.

Such, in the case of methyl alcohol, are most of the irreducible metallic oxides noted by Sabatier in his work "Catalysis in Organic Chemistry" and amongst them may be mentioned, uranous oxide (French: L'oxyde uraneux), tungsten oxide vanadious oxide (French l'oxyde vanadeux), zinc oxide, glucinum oxide, chromium oxide, titanic oxide etc., these oxides being preferably mixed with each other or with metals, so as to increase their catalytic activity, in the well-known way.

Preparation of these catalysers constitutes the feature of most of the processes hitherto invented for the synthesis of methyl-alcohol from carbon monoxide and hydrogen, and thus it is that the most commonly used preparation is made with a mixture of oxides such that the most basic oxide will predominate, or with a body such as basic zinc chromate. This catalyser is obtained either from melted potassium bichromate in presence of zinc oxide and in the required proportion or from commercial zinc oxide or zinc yellow. As these catalysers are in the form of powder or particles they must be united by means of some appropriate binding material and then placed on a suitable support, pumice stone, asbestos, etc.

The mode of preparing these oxides exerts considerable influence on their activity. When employed just as they are or in the form of insoluble compounds such as zinc chromate, for example, they must be finely ground to acquire a proper state of division. Moreover the agglomeration of these powders in a form both porous and resisting (the only one compatible with the employment of very great pressure) can only be obtained imperfectly.

The present invention consists essentially in employing as a catalysing agent for the synthesis of alcohols and especially of methyl alcohol, not the aforesaid metal oxides but their formates, these being deposited by crystallisation from their solution on a porous support such as charcoal or active carbon. It is found that these porous substances not only act as absorbers but also to some extent, as catalytic accelerators.

Contrary to what occurs with oxide mixtures, the proportions of which must be mutually well defined, these mixtures of formates can be made in any proportions, and in depositing from their solution by crystallisation on a very porous support, they acquire a state of extreme division which heightens their catalytic activity. It is also necessary to avoid salts which are decomposed by heat with production of gases noxious to the catalyser and it has been noted that the formates fulfil these conditions.

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As examples, the following are given:

EXAMPLE 1.

This is an example of working with a known catalyser, viz., commercial ZnO. Pure commercial ZnO, in the proportion of 52 grammes is agglomerated with distilled water. This paste is laid on 150 grammes of pumice stone which is then dried at a temperature of 120° C. The grains are covered with a slightly adhering crust of ZnO. Over the catalyser thus prepared the following mixture is passed at the rate of 2000 litres per hour:

CO - - - 8.2 per cent.
H_2 - - - 74.6 per cent.
CH_4 - - - 1.6 per cent.
N_2 - - - 15.6 per cent.

under a pressure of 800 kilos per square centimetre at a temperature of 300° C. The production of alcohol is significant.

The following are examples in which catalysers according to this invention are employed:—

EXAMPLE 2.

100 grammes of crystallized zinc formate are dissolved in 350 grs. of boiling water. 150 grs. of active carbon are heated to redness in a closed crucible and put into the solution, whereupon the solution is evaporated to dryness. Only very little zinc formate is left on the sides of the receptacle. The grains of carbon are coated with a thin adhering film and the main part of the salt is absorbed in the pores of the carbon.

Put into action, in the conditions of Example 1, this catalyser gives an average of 70 cm³ per hour of methyl alcohol titrating Gay Lussac.

EXAMPLE 3.

50 grammes of zinc formate and 50 of chromium formate are dissolved in 350 grammes of boiling water; 150 grammes of active carbon are heated to redness in a closed crucible and put into the solution. This solution is then evaporated to dryness; only traces of salts are left on the sides of the receptacles. The grains of carbon have acquired an olive tint; there is no superficial crust.

Put into action in the conditions of Example 1, such a catalyser gives an average of 146 cm³ per hour of methyl alcohol titrating 85°, G.L.

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 synthesis of alcohols, particularly methyl alcohol from gaseous mixtures containing carbon monoxide and hydrogen, in which a catalyser is employed consisting initially of a metallic formate or formates, the corresponding oxide or oxides of which are not reducible either by carbon monoxide or by hydrogen under the conditions of temperature, pressure and concentration necessary for the synthesis, such formates being deposited by crystallization (from a solution) on a porous support, substantially as described.

2. In a process for the synthesis of alcohols according to Claim 1, the employment of active carbon or charcoal as a support for the formates indicated, substantially as described.

3. A process for the production of alcohols carried out substantially as herein described.

Dated this 15th day of July, 1927.
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