NOTE.—*The application for a Patent has become void.*
This print shows the Specification as it became open to public inspection.

PATENT SPECIFICATION

Convention Date (France): Aug. 6, 1926. **275,600**

Application Date (in United Kingdom): July 25, 1927. No. 19,649 / 27.

Complete not Accepted.

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COMPLETE SPECIFICATION.

Improvements in or relating to Catalysers for the Synthesis of Alcohols.

We, the SOCIÉTÉ ANONYME: COMPAGNIE DE PÉTHUNE, of Bully les Mines, Pas de Calais, France (a French company), 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 catalysers for the synthesis of alcohols, more especially of methyl alcohol.

It is known that active nickel will effect the hydrogenation of carbon monoxide according to the equation:

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

this reaction, which readily takes place under atmospheric pressure, being increased by high pressure. Iron, cobalt, and the metals of the platinum group act in the same manner.

If the reaction is desired to be directed towards the formation of methylic alcohol, according to the equation

$$CO + 2H_2 = CH_3OH$$

the intervention of pressure becomes necessary and there must be employed as catalysers, oxides which are irreducible by hydrogen to metallic state: for instance, oxide of zinc or oxide of chromium. Such oxides can be used either alone, or mixed with one another, or, else, mixed with metals, which, taken separately would be without effect in said reaction. A mixture of zinc oxide and of metallic copper has been proposed for the purpose.

Such catalysers present themselves in the form of insoluble powders which have to be either agglomerated by compression or agglutinated with gum arabic, dextrine (British gum), etc. Catalyzers obtained in this way however have a very slow action, they require the employment of very large catalysing apparatus, and a gas circulation within a closed circuit, all of which involve numerous inconveniences.

Catalysers which are far superior to the above have already been proposed, these being obtained by using formates of metals adapted to give irreducible oxides and depositing them on a highly porous support, say active carbon or charcoal according to the process covered by our co-pending British Patent Application No. 18,797 filed 15th July, 1927.

The activity of the catalyzer is of course a factor of paramount importance.

As a matter of fact the equation

$$CO + 2H^2 \Longleftrightarrow CH^3OH$$

tends the more towards the production of methyl alcohol, the lower the reaction temperature. It is necessary however that the reaction be reasonably speedy in order that the process shall be commercially practicable. Now the function of the catalyser is both to direct the reaction and also to accelerate the speed thereof.

According to this invention it has been discovered that, contrary to what might have been supposed, the adjunction of nickel (hitherto considered as exclusively calculated to catalyse the formation of methane), to the above mentioned catalyzers for methyl alcohol synthesis, brings about a considerable improvement in such catalysers without rendering them more sensitive to the various causes of deterioration or of "poisoning". On the contrary, the active life of catalysers is thereby prolonged, and they withstand better any accidental over-heating. Moreover the re-action temperature can be decreased and the operative yield is increased.

The nickel may be in the form of metal, of oxide or of salts and may be in the proportion of 2 to 10 per unit of the irreducible metal oxides or to soluble salts, such as formates which yield these oxides. These latter may themselves be used alone or mixed together or with other metals which individually would not act as catalysers.

As one example of the carrying out of

the invention, there is dissolved in 350 cubic centimeters of boiling distilled water, 50 grams of zinc formate and 50 grams of chromium formate, and to this is added a nickel salt, say 5 grams of nickel formate. In an open crucible 150 grams of active carbon are brought to a red heat and then immersed in the solution, which is then evaporated to dryness.

Over the catalyzer so obtained, there is passed at the rate of 2000 liters per hour, a gaseous mixture composed of:

CO	8 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 kilograms per square centimeter and at a temperature of 300° C., the gas passing but once over the catalyzer.

Under those conditions there is obtained 280 cubic centimeters of methyl alcohol grading 90° Gay-Lussac per hour, which represents 75 per cent. of the carbon monoxide transformed into methyl alcohol.

The proportion of carbonic oxide in the gaseous mixture may vary considerably without spoiling the catalyzer. In the event of overheating, the activity of the catalyzer is not decreased, and its action goes on in the same conditions as soon as normal temperature is re-established.

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 manufacturing catalysers for the synthesis of alcohols and, more especially that of methyl alcohol by the hydrogenation of carbon monoxide, said process being characterised by the use of nickel in the form of metal, of oxide, or of salts, added in a proportion of 2 to 10 per cent. to metallic oxides irreducible by hydrogen, either alone or mixed together or with other metals which, taken separately, would not catalyse the reaction, substantially as described.

2. A process for manufacturing catalysers for the synthesis of alcohols (more especially of methyl alcohol) by hydrogenation of carbon monoxide, said process being characterised by the use of nickel in the form of metal, of oxide, or of salts added in a proportion of 2 to 10 per cent. to soluble salts of metals yielding oxides non-reducible by hydrogen, the mixture being deposited on a highly porous support, substantially as described.

3. A process for manufacturing catalysers for the synthesis of alcohols (more especially methyl alcohol) by hydrogenation of carbonic monoxide, said process being characterised by the use of nickel taken under the form of metal, of oxide, or of salts reducible to metal in the above set forth experimental conditions, mixed in the proportion of 2 to 10 per cent. with formates of metals giving oxides non reducible by hydrogen, said formates being used either alone or mixed with one another, substantially as described.

4. A catalyser for the production of alcohols (especially methyl alcohol) according to one or other of the preceding claims, comprising nickel or suitable nickel compounds together with suitable irreducible oxides.

5. A catalyser for the production of alcohols, formed or produced substantially as hereinbefore described.

Dated this 25th day of July, 1927.

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