AMENDED SPECIFICATION

Reprinted as amended in accordance with the decision of the Assistant Comptroller, acting for the Comptroller-General, dated the twenty-third day of October, 1936, under Section 11 of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: Oct. 31, 1934. No. 31282/34.

449,603

Complete Specification Left: Nov. 13, 1935.

Accepted: June 30, 1936.

3638

PROVISIONAL SPECIFICATION

Improvements in or relating to the Preparation of Catalysts for Liquid and Vapour Phase Hydrogenation Processes, Ammonia and Methanol Synthesis Processes and other Industrial Purposes

I, HAROLD PARK STEPHENSON, of 14, St. Mary Axe, London, E.C.3, a British Subject do hereby declare the nature of this invention to be as follows:—

This invention relates to the preparation of catalysts for liquid and vapour phase hydrogenation processes, ammonia and methanol synthesis processes and other industrial purposes and has for its object to provide cheaply and efficiently a good carrier for catalysers for a large number of industrial purposes.

In the preparation of catalysts for liquid and vapour phase hydrogenation processes, ammonia and methanol synthesis processes and other industrial purposes in accordance with this invention I incorporate the initial powder of the metals, metal oxides, metal salts or neutral salts forming the basis of the catalysers in a coal-oil mixture, and then subject it to a carbonizing process yielding a semi-coke or coke which contains the catalytic agents in an exceedingly fine and evenly distributed form simultaneously presenting them distributed over a very large surface for chemical reactions.

The semi-coke or coke thus produced may be introduced into the apparatus in the form in which it may be employed in the form in which it is produced, or it may be crushed or pulverised to powder form. If it is desired it may also be pelletted by the mixture of a suitable binder.

A catalyst produced in the above described manner may be produced in any suitable form by modifying the container to the requisite dimensions. Thus, rectangular, semi-circular or cylindrical or other shape can be produced at will, and provide a highly porous carrier.

The catalysts when prepared in the manner indicated may be subjected to further treatment by reduction with hydrogen with or without pressure, or they may be oxidised with or without pressure, as the reaction for which they are prepared may demand.

It will be evident that the details of the invention may be varied in many ways without departing from the scope thereof.

Dated this 31st day of October, 1934.
MEWBURN, ELLIS & CO.,
70 & 72, Chancery Lane, London, W.C.2,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Preparation of Catalysts for Liquid and Vapour Phase Hydrogenation Processes, Ammonia and Methanol Synthesis Processes and other Industrial Purposes

I, HAROLD PARK STEPHENSON, of 14, St. Mary Axe, London, E.C.3, a British Subject 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 preparation of catalysts for liquid and vapour phase hydrogenation processes, ammonia and methanol synthesis processes and other industrial purposes and has for its object to provide cheaply and efficiently a good carrier for catalysers for a large number of industrial purposes.

In the processes of my previous Patent Applications Nos. 431,063, 24920/34 (Serial No. 448,028) and 24923/34 (Serial No. 448,029), I may add a catalyst to the coal-oil mixtures to be carbonised solely for the purpose stated in the specifications, namely, to increase the yields of low boiling hydrocarbons, and part of this catalyst may be found in the resultant coke, depending upon the volatility of the particular material selected. I have now found that a coke prepared in this way by selection of a suitable catalyst becomes a particularly efficient carrier for a large number of catalysts to be used in chemical reactions of a type entirely different from that described in the aforesaid specifications.

In the preparation of catalysts for liquid and vapour phase hydrogenation processes ammonia and methanol synthesis processes and other industrial purposes, to which the catalyts herein described are applicable, in accordance with this invention I incorporate catalytic substances or the initial material or proto-catalysts of the metals, metal oxides, metal salts or neutral salts forming the basis of the catalysers in a mixture of coal and mineral oil containing at least 50% of coal and then subjecting the material to a carbonising process yielding a semi-coke or coke which contains the catalytic agents in an exceedingly fine form and evenly distributed over a very large surface. The metallic compound in those cases where it is water-soluble may, of course, be added to the coal-oil mixture in the form of an aqueous solution.

The admixture of oil and coal according to the present invention produces a coke which has the following special advantages as a carrier for catalysts in that it is

(a) more porous and therefore presents a larger surface of contact;
(b) more friable, with the result that it is more easily ground;
(c) softer whilst in a plastic state during the heating process so that it more readily takes the shape of the containing vessel, which may, itself, be shaped to any given requirements.

The semi-coke or coke based catalytic material thus produced may be used in the subsequent reaction in any preferred form, namely, in that in which it is produced, or it may be crushed or pulverised to powder form. If it is desired it may also be pelletted by the mixture of a suitable binder.

A catalyst produced in the above described manner may be produced in any suitable form by modifying the container to the requisite shape and dimensions. Thus rectangular, semi-circular or cylindrical or other shape can be produced at will, and provide a highly porous carrier.

The proto-catalysts when prepared in the manner indicated may be subjected to further treatment by reduction with hydrogen with or without pressure, or they may be oxidised with or without pressure, as the reaction for which they are prepared may demand.

The material used in producing the catalyst-mass should as far as possible be free from anti-catalytic substance such as sulphur and chlorine, and substances likely to contain these elements, so as to produce a catalyst which maintains its activity in a satisfactory manner. In general it is found that it is advantageous to use not more than 112 lbs. of metallic compound per ton of coal carbonised.

The following examples illustrate the present process, but it is to be understood that the invention is in no way limited to the details given in these examples;

Example I.

PREPARATION OF IRON OR IRON OXIDE CATALYSTS.

(a) A mix in the following ratio was subjected to carbonisation at a temperature of 600° C.
1 ton coal
115 gallons Persian fuel oil
22.4 lbs. iron oxide

The iron-oxide catalyst thus produced was in a form suitable for use, being extremely porous and therefore having a large surface area. If a metallic iron catalyst is required, reduction of the oxide can be carried out in the catalytic reaction chamber, using pure hydrogen and a temperature of 400—450° C.

(b) Similarly, carbonisation of a mix in the ratio:
1 ton coal
115 gallons Persian fuel oil
112 lbs. iron oxalate

produced a useful porous catalyst, the oxalate being decomposed to the oxide during the process.

Other iron salts which give the oxide on decomposition, such as the precipitated hydroxide or carbonate, the nitrate or acetate, can be substituted in the above mixtures.

Reduction of the oxide follows if necessary.

Example 2.

PREPARATION OF NICKEL OR NICKEL OXIDE CATALYST.

A mix in the following ratio was subjected to carbonisation at a temperature of 600° C.

1 ton coal
115 gallons Persian fuel oil
22.4 lbs. nickel oxide.

Reduction may be carried out at temperatures up to 600° C.

A catalyst so prepared was used for the hydrogenation of ethylene, a mixture of ethylene and hydrogen being passed over the reduced catalyst at a temperature of 200° C., resulting in the well known reaction

$$C_2H_4 + H_2 = C_2H_6$$

Nickel catalysts can also be obtained by the addition of nitrate or formate, or precipitated hydroxide or carbonate, to the coal-oil mix, followed by decomposition and reduction.

Example 3.

PREPARATION OF COPPER OR COPPER OXIDE CATALYST.

A mix in the following ratio was subjected to carbonisation at a temperature of 600° C.:

1 ton coal
115 gallons Persian fuel oil
22.4 lbs. copper oxide

Reduction may be carried out at temperatures of approximately 200° C.

Copper powder, the precipitated hydroxide or carbonate, or the nitrate can be substituted for the copper oxide in the above mix.

Similarly iron catalysts prepared as above with the addition of promoters such as molybdenum, uranium, nickel, metals of the alkali, alkali-earth, or rare-earth groups etc., produced in this way can be employed in ammonia synthesis, and similarly catalysts for the synthesis of methyl alcohol from carbon monoxide and hydrogen, can be prepared on a coke base, made from coal and oil according to the present invention, by the addition of zinc oxide, or zinc oxide and chromate.

In the above examples a Persian fuel oil of specific gravity approximately 0.895 is employed. It must be understood, however, that this is merely one example of the many petroleum oils of a widely different character, Venezuelan Topped oil, Rumanian Residual oil and the like, which are capable of applciation in the process. Heavy coal tar distillates such as anthracene oil, creosote etc., are particularly suited for this purpose.

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 preparation of finely divided catalysts for use in chemical reaction in which the catalyst is prepared by incorporating the catalytic substance or the proto-catalyst in a mixture of coal and mineral oil containing at least 50% of coal and then subjecting the material to a carbonising process yielding a semi-coke or coke so that the catalyst is obtained in an exceedingly fine form evenly distributed over a very large surface.

2. A process for the preparation of a catalyst for use in chemical reactions in which the catalyst is prepared by incorporating the initial material or proto-catalyst of the metals, metal oxides, metal salts, or neutral salts forming the bases of the catalysers in a mixture of coal and mineral oil containing at least 50% of coal and then subjecting the material to a carbonising process yielding a semi-coke or coke so that the proto-catalyst is in an exceedingly fine form evenly distributed over a very large surface and then reducing the finely divided proto-catalyst so prepared by means of hydrogen or other reducing gas with or without the application of increased pressure.

3. A process according to Claim 2 in which the reduction of the proto-catalyst takes place in situ in the apparatus in which the catalytic reaction is carried out.

4. A process according to Claim 1, in which the catalyst-mass produced according to the method claimed in Claim 1 is finely ground before use.

5. A process according to Claim 2 or Claim 3 in which the proto-catalyst-mass produced according to Claim 1 is finely ground before conversion into the catalyst.

6. A process according to Claim 1 in which the catalyst produced according to the methods claimed in Claim 1 or Claim 4 is pelletted or made up into any suitable form with or without admixture of a suitable binder.

7. A process for the preparation of a catalyst according to Claim 2 or Claim 3 or Claim 5, in which the finely divided proto-catalyst dispersed throughout the coke or semi-coke mass is pelletted or made up into suitable shapes with or without the addition of a suitable binder before being reduced to form the catalyst.

8. A process according to any of the preceding claims in which the metallic material or materials are used in the proportion of not more than 112 lbs. per ton of coal.

9. A process according to any of the

preceding claims in which the metallic material or materials are incorporated with the coal-oil mixture in the form of a solution.

10. A process according to any of the preceding claims in which the metallic compound used is iron oxide or iron oxalate.

11. A process according to Claims 1 to 8, in which the metallic compound used is nickel oxide, carbonate, nitrate or formate.

12. A process according to Claims 1 to 9 in which the metallic compound used is copper oxide, precipitated hydroxide, carbonate, or nitrate.

13. A process according to Claims 1 to 10, in which an iron catalyst is prepared with the addition of promoters such as molybdenum, uranium, nickel, metals of the alkali, alkali-earth, or rare-earth groups.

14. A process for preparing a catalyst substantially as herein described.

15. Catalysts when prepared according to the methods or processes herein particularly described and ascertained or their obvious chemical equivalents.

Dated this 13th day of November, 1935.

MEWBURN, ELLIS & CO.,
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Chartered Patent Agents.

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