[Second Edition.]

PATENT SPECIFICATION

Application Date: May 1, 1937. *No. 8643/37.* **500,182**

2870

Complete Specification Accepted: Feb. 1, 1939.

(*Under this Application, which was originally made under Section 91 of the Patents and Designs Acts, 1907 to 1932, a Specification was laid open to public inspection on Oct. 2, 1937*).

COMPLETE SPECIFICATION.

Process for Producing Catalysts for Benzine Synthesis.

(A communication from abroad from RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a body corporate organized and existing under the Laws of the German State.)

I, WILLIAM EDWARD EVANS, of 40—43, Chancery Lane, London, W.C.2, of British Nationality, 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:—

In large scale benzine synthesis from carbon monoxide and hydrogen the catalysts particularly employed are metals of the iron group (iron, cobalt, nickel) whose active constituents have been precipitated on to kieselguhr. Certain difficulties are involved in the production of such catalysts, as the kieselguhr used as carrier mass gives off when brought into contact with acidic and alkaline reagents soluble constituents which have an extremely prejudicial action on the catalytic substance.

Thus, for example, when kieselguhr is added to the alkaline precipitating solution for the metal catalysts a part of the silicic acid of the kieselguhr dissolves in the form of alkali silicate, and is converted with the heavy-metal salts into insoluble heavy-metal silicates which cannot be reduced to metal, and which prejudicially affect the activity of the catalyst.

Further, such catalysts, when spent, are treated by means of acids. There is then a danger that substances will at the same time be dissolved that are capable of exerting in some measure a very injurious action on the activity of the newly produced catalysts.

Care has thus to be taken that both during the first production of the catalysts as well as during the treatment of spent contact or catalytic masses no injurious constituents are dissolved.

According to the invention, in the production of catalysts of the iron group, suitable for the catalytic conversion of mixtures of carbon monoxide and hydrogen, by precipitation in the presence of a carrier material, which catalysts, on being regenerated are subjected to the action of an acid reagent, the carrier material, selected from those hereinafter defined is heated to incandescence, that is to say, to a temperature of over 1,000° C., to reduce the solubility of or to render insoluble those constituents that are soluble in the acidic and alkaline reagents employed in the preparation or regeneration of the catalyst.

The carrier materials that may be treated according to the process of the invention are kieselguhr, powdered asbestos, chromium oxide, and steatite. The term "carrier material" is thus hereinafter employed as designating only this range of materials.

The process may be modified as found desirable in that the carrier material is first heated to incandescence and then treated with acid, for example, hydrochloric acid, to dissolve out any remaining constituents which are soluble in acids.

In order to obtain a very fine distribution of the carrier materials, they may be mixed with finely divided organic substances such as wood-pulp, cellulose and the like, and then the organic substances can be burned out in order at the same time to obtain fine distribution and conversion to the insoluble condition.

Further, the carrier materials produced as hereinbefore set forth by heat treatment are generally not completely insoluble in relation to alkaline solutions, and the alkaline compounds produced are likewise converted with the metal catalysts to produce heavy-metal compounds which are insoluble and cannot be reduced to metal, and which may considerably affect the activity of the catalyst and even lead to the formation of a completely inactive material.

It is therefore advisable even when using such carrier materials for the purpose of avoiding the damage to the catalysts which has been referred to, to place the carrier masses into the conversion

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vessel only when the precipitation of the catalytically active metals is almost ended, so that the precipitating solution has no longer a strongly alkaline reaction. Thus, when working with alkaline solutions, for example, in the use of kieselguhr or powdered asbestos, the possible damage to the catalyst may be prevented, by reducing the period of contact with the alkaline precipitating solution as much as possible and by first introducing the silicate-containing carrier material into the alkaline solution when the precipitation of the catalytic metals is wholly or almost completed and the solution is no longer strongly alkaline.

In the same way as it is necessary to prevent any of the constituents of the carrier mass from dissolving on the precipitation of the catalytically active substances, care must be taken that during the regeneration of the catalysts which have become inactive no foreign substances shall enter the solution which contains the catalytic metals. Thus there is the danger that the catalyst may have absorbed substances from the vessels or from the contact furnace, for example, through the synthesis gas, these substances also becoming dissolved on the regeneration of the spent catalyst and affecting the catalyst on precipitation. Furthermore in this way foreign substances may enter into solution during regeneration, as, for example, from the material of the vessel employed for carrying out this process (either by being mechanically removed or chemically dissolved) furthermore from the chemicals employed during regeneration, for example, from the nitric acid employed for dissolving the catalysts that have become inactive. Moreover, during the regeneration of the catalysts, constituents which were insoluble on the first production of the catalyst may pass into solution from the carrier mass under the possibly sharper conditions involved in the dissolving of the spent catalysts. These noxious impurities are rendered ineffective by causing them to be removed from the solution containing the catalytic substances by a precipitation by first adding a small quantity of the alkaline precipitating agent. The actual metal catalysts are then, after the removal of the first precipitate, for example, by filtration, precipitated by the further addition of the alkaline precipitating solution. In this case also it is advisable to add to the precipitating mixture the substances to be employed as carrier masses after the precipitation of the metal catalysts is completely or almost completely finished.

EXAMPLE No. 1.

A carrier substance in a condition that is usable according to the invention is secured by drying raw kieselguhr in the atmosphere, calcining it at 600 to 700° C. and then raising it to incandescence at temperatures of 1,000 to 1,100° C. After this heat treatment the total of the impurities soluble in a 25% HNO_3 amounts to about 1%; without heat treatment at the last-mentioned temperatures the quantity of the soluble impurities amounts to about from 8 to 12%.

By the intense heating of the kieselguhr, moreover, the solubility of the kieselguhr in alkaline solvents and precipitating agents is considerably lowered and amounts to only about one-fifth of the solubility of the untreated kieselguhr. The dissolving in alkalies of constituents of the heated kieselguhr can be further reduced by introducing the kieselguhr into the solution to be precipitated only when already the greater part of the active contact substances is precipitated out by the alkaline precipitating agent. The solubility of the kieselguhr in the precipitating solution that has a content of about 1% of soda after the precipitating action has ceased amounts to only 0.3%, while of the non-heated kieselguhr about 1.5% is dissolved by a precipitating solution of the same strength.

EXAMPLE No. 2.

A crude solution obtained by dissolving a spent cobalt contact substance in dilute nitric acid, contained the following impurities (calculated in percentages of cobalt)

Fe_2O_3 – – – – 2.36%
Al_2O_3 – – – – 1.26%
SiO_2 . – – – 0.31%

With this solution the preliminary precipitation was effected in the following manner: while heating to from 50 to 60° C., soda was gradually added while the solution was being continuously stirred, until the P_H value of the solution had reached 6.3. Filtration was then effected from the precipitate obtained, which contained the hydroxides of iron and aluminium as well as the separated out silicic acid. The filtered solution then contained the following impurities (calculated on cobalt)

Fe_2O_3 – – – 0.03%
Al_2O_3 – – – not demonstrable
SiO_2 – – – – traces under 0.01%

The effectiveness of the contact substances produced from the solutions corresponded to the purity of the solutions. During a working period of 165 hours there arose the following difference:

	Maximum yield of oil obtained.
Contact substance from crude unpurified solution – – – –	50 cc. per cu. m. Synthesis gas
Contact substance from a solution purified by a preliminary precipitation – – –	94 cc. per cu. m. Synthesis gas

Highly refractory materials, such as chamotte and porcelain, have before been proposed as carriers for compounds or mixtures of metal oxides of the iron group with certain acid-forming metal oxides, intended for use as catalysts in a process for the manufacture of hydrogen or hydrogen-containing gas mixtures from hydrocarbons such as methane.

It has before been proposed, in connection with carriers for catalytic material intended more particularly for the conversion of mineral oils into oils of lower boiling point, to grind mineral bauxite, adding water to it, to produce a very stiff paste and then raising the temperature gradually until the whole mass is at a red heat, that is to say, a temperature between 900° and 1000° C.

It has also been proposed, in the preparation of catalysts for use in gaseous and liquid phase chemical reactions, to employ carrier materials consisting of silicates of alumina, such as aluminous fireclays, that have been indurated by calcination and have subsequently been treated with mineral acids while in small lump or granular form, the porosity and permeability being increased, where required, by selecting an aluminous fireclay which contains a proportion of carbonaceous coal-like matter and suitably regulating the calcination.

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 producing catalysts of the iron group, suitable for the catalytic conversion of mixtures of carbon monoxide and hydrogen, by precipitating the catalytically active substances in the presence of a carrier material, such catalysts, on being regenerated, being subjected to the action of acid reagents, in which the carrier material as hereinbefore defined is heated to incandescence, that is to say, to a temperature over 1000° C., to reduce the solubility of or to render insoluble those constituents of the carrier material that are soluble in the acidic and alkaline reagents employed in the preparation or regeneration of the catalyst.

2. A process according to claim 1, characterised in that the period during which the carrier material remains in the alkaline solution as used for the precipitation of the active substance is maintained as short as possible, the carrier material being first introduced into the solution after the precipitation of the catalytically active substances has completely or almost completely stopped.

3. A process for the regeneration of catalysts prepared according to claim 1 or claim 2, wherein the soluble constituents that have been dissolved out from the carrier mass by means of acid are removed from the solution by a preliminary precipitation before the precipitation of the catalytically active substances.

4. A process according to claim 1 or claim 2, wherein the carrier material is treated with acid after being heated to incandescence.

Dated this 23rd day of March, 1937.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8138.—50/7/1939.]