# PATENT SPECIFICATION

**692,234**

Date of Application and filing Complete Specification: April 17, 1951.
No. 8973/51.
Application made in Germany on April 20, 1950.
Complete Specification Published: June 3, 1953.

Index at acceptance:—**Classes 1(i),** F3b1; **and 2(iii),** B1g.

## COMPLETE SPECIFICATION

## Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company, of Oberhausen-Holten, Germany; and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK m.b.H., a German Company, of Frankfurt a.Main-Heddernheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the catalytic hydrogenation of carbon monoxide to hydrocarbons with or without oxygen-containing organic compounds and particularly to the preparation of an unsupported or carrier-free catalyst for use in the hydrogenation of carbon monoxide.

Cobalt, nickel or iron catalysts which are used in the catalytic hydrogenation of carbon monoxide are treated with reducing gases prior to their use as it is not possible to obtain adequate activity of the catalyst without this reduction. Carbon monoxide and/or hydrogen containing gas mixtures are used in this pre-treatment, which is called catalyst reduction or catalyst formation. The step of catalyst reduction is conventionally effected outside the synthesis reactor, since prior to the present invention the reduction of an unsupported catalyst could only be accomplished in relatively thin layers at a temperature of approximately 300° C. Hitherto, all efforts to reduce unsupported carbon monoxide hydrogenation catalysts in the synthesis reactors have been unsuccessful.

The pre-treatment in the synthesis reactor itself has been technically impossible for two reasons.

First, the hydrogenation of carbon monoxide, that is to say, the synthesis proper, is effected at normal and medium pressures and at temperatures which are generally within the range 180° C.—220° C. In the process, about 80 to 120 volumes of the synthesis gas per volume of the catalyst are passed through per hour. During the catalyst reduction a gas temperature of nearly 300° C. is required. The conventional synthesis reaction may only be used for temperatures up to about 250° C., since the heat exchange installation, that is to say, the cooling jackets or tubes in the reactor, are built for a maximum steam pressure of about 30 kg. per sq. cm. During the reduction of the catalyst, the water under pressure circulating within the heat exchanger would be heated to a temperature of nearly 300° C. which would result in a steam pressure of nearly 85 kg. per sq. cm. Conventional synthesis reactors are not constructed to withstand such pressure.

Second, apart from these structural difficulties, it has been impossible to effect the reducing treatment in the synthesis reactor itself because a certain constancy in the catalyst pre-treatment is required and because of the height of the catalyst layer to be maintained in the reactor. The reduction of an unsupported catalyst has hitherto been performed with a catalyst layer of a height of only 20 to 40 cms. because no uniform reduction has been possible with layers of catalyst of a greater height. A still further obstacle lies in the fact that the unsupported catalyst, during its reduction, shrinks considerably, sometimes to the extent of 50% of its volume.

In the hydrogenation of carbon monoxide the catalyst, after its precipitation from a solution of one of its salts, is moulded whilst it is still relatively moist; it is then dried at a temperature of about 110° C. When a catalyst tube of a length of 4 to 5 metres is filled with the moulded unsupported catalyst which has been dried in the usual manner at a temperature of about 110° C., a shrinkage of up to 50% of the original height of the catalyst column occurs if the treatment with the reducing gases is effected in the reactor. Thus, if the pretreatment takes place in the synthesis reactor, the reactor would only contain unsupported catalyst to the extent of about 50% of its capacity, which is uneconomical.

It has now been found that, in the catalytic hydrogenation of carbon monoxide for the production of hydrocarbons with or without oxygen-containing organic compounds, the non-uniform reduction of the unsupported catalyst in layers of more than 50 cms. in height and the excessive shrinkage of the columns of unsupported catalyst may be largely or wholly avoided in the process according to the invention.

According to the invention, a process for the catalytic hydrogenation of carbon monoxide comprises the use of a cobalt, nickel or iron catalyst which is unsupported and which, prior to use in the hydrogenation, has been dried for a period of from 6 to 24 hours at a temperature within the range 150°—350° C. and has thereafter been reduced in layers or columns of more than 100 centimetres in height with a gas mixture containing carbon monoxide and/or hydrogen at a flow velocity of approximately 100—200 centimetres per second (760 mm. Hg. and 0° C.).

The invention further comprises a cobalt, nickel or iron catalyst free from supporting material for use in the hydrogenation of carbon monoxide, which catalyst has been dried for a period of from 6 to 24 hours at a temperature within the range 150°—350° C. before being reduced or activated.

After the unsupported catalyst has been moulded and then partially dried at a temperature of about 100°—110° C., it is dried thoroughly for a period of 6 to 24 hours at a temperature within the range of 150°—350° C., preferably 175°—350° C., before its reduction and "formation" with gas mixtures containing carbon monoxide and/or hydrogen. After this thermal treatment for thorough drying, the catalyst is placed in the synthesis reactor in layers or columns of a height of more than 100 cms. and preferably in layers or columns of a height of 400 to 1,000 cms. The thorough drying may, if desired, be carried out in the synthesis reactor. These layers or columns of the catalyst in the synthesis reactor are then reduced with gas mixtures containing carbon monoxide and/or hydrogen at flow velocities of about 100 to 200 cms./sec. (760 mm. Hg and 0° C.).

The thorough drying of the unreduced, unsupported catalyst at temperatures within the range 150° C. to 350° C. prevents or greatly reduces the subsequent shrinking during the reduction of the unsupported catalyst within the synthesis reactor. By operating with reducing gases having a linear speed of 100 to 200 cms./sec. it is possible to reduce catalyst columns of a length of 5 to 10 metres in a uniform manner in 60 to 120 minutes. With speeds for the reducing gas of about 20 to 40 cms./sec., such as are usual in the methods of treatment hitherto used, it is impossible to obtain a uniform reducing action over the entire column of the unsupported catalyst.

The reduction of the unsupported catalyst, according to the invention, may be effected with water gas, hydrogen, carbon monoxide or other gas mixtures which contain carbon monoxide and hydrogen in any desired ratio. It has been found particularly advantageous to remove, as completely as possible, water vapour and carbon dioxide from the reducing gases prior to their use. Under the conditions hereinbefore described, the reducing pre-treatment of unsupported cobalt and iron catalysts may be effected at considerably lower temperatures than have hitherto been used, for example, the reduction may be effected at temperatures between 150° and 250° C. Higher reduction temperatures may also be used. The lower reduction temperatures are, however, particularly advantageous if the catalyst is to have a lower reduction value and is to be used for the production of hydrocarbons.

There are no technical difficulties involved in using high gas flow speeds during the reduction of the catalyst within the synthesis reactor, as the synthesis is now conventionally carried out at considerably higher gas speeds than were formerly used. For this reason the capacity of the gas blowers at present in use is always great enough to permit a speed of the reduction gas of about 200 cm/sec. (760 mm. Hg and 0° C.) to be obtained without any difficulty.

In the reduction or formation of the unsupported catalysts according to the process of the invention, which is particularly suitable for iron catalysts, the subsequent carbon monoxide hydrogenation may be carried out with approximately 10 to 20 times the normal gas load, that is to say, with 1000 to 2000 volumes of gas per volume of catalyst per hour, and it is preferred that more than 500 volumes of gas be used per volume of catalyst per hour. Even with such high space velocities, a satisfactory removal of the heat of reaction is obtained with the use of uniformly boiling liquids as cooling media, and even with synthesis tubes or pipes having a diameter of between 20 and 60 mm., if the rates at which the synthesis gases are passed over the catalysts are greater than 50 cm./sec., and preferably greater than 200 cm./sec. (760 mm. Hg., 0° C., and calculated on the empty tube cross section). The rates correspond to the aforesaid gas loads of the catalyst. At these high gas speeds, turbulence occurs within the gaseous phase which is sufficient to carry the heat of reaction to the walls of the tubes or pipes quickly and effectively. From the walls of the tube the heat is effectively removed by the latent heat absorbed in the vaporisation of the cooling medium. Homogeneity of the cooling medium ensures, disregarding small hydrostatic differences, an adequate removal of the heat of reaction at all levels of the catalyst column. Damage through over-heating of the catalyst is thus completely avoided.

Many liquids which boil within the temperature range of the synthesis at pressures which may be readily controlled, are suitable for use as the cooling media according to the invention. Water has been found to be the best medium. However, its use is often impossible because the pressure of steam at synthesis temperatures of about 270° C. exceeds 50 kg. per sq. cm. This steam pressure requires the walls of the cooling system to be of such strength that their construction is uneconomical. By the use of appropriate cooling media which boil within the range 200°—300° C. at ordinary atmospheric pressure or at pressures of up to 20 kg. per sq. cm., operation with comparatively thin walls is possible. The following cooling media have been found particularly suitable for this purpose: ethylene glycol, aniline, nitrobenzene, and aliphatic or aromatic hydrocarbons of suitable molecular weight and boiling point. When selecting the cooling medium, however, particular care must be taken that its boiling point is such that vaporisation occurs under the operating conditions, as sufficient and efficient removal of the heat of reaction is only possible with such vaporisation.

It has been found particularly advantageous to carry out the carbon monoxide hydrogenation according to the invention with a recycling of the exit gases. When operating in this manner, 0.5 to 10 volumes, preferably 1 to 4 volumes, of recycled gas per volume of fresh gas are used. The synthesis pressure may be maintained between 10 and 100 kg. per sq. cm., the optimum gas pressures being between 15 and 30 kg. per sq. cm. The internal diameter of the synthesis tubes or pipes may be as large as 20 to 60 mm, since a sufficiently rapid removal of the heat of reaction takes place by reason of the turbulence of the fast flowing synthesis gases.

The process according to the invention has the advantage of eliminating the use of a separate reduction installation which is, at present, required for the production of unsupported catalysts, and which is, in most cases, of a large size. This is possible as the reducing pre-treatment of the unsupported catalysts may be carried out in the synthesis reactor itself. This process also facilitates the transportation of the catalyst to and its introduction into the synthesis reactor, as this can be done without the necessity of having an oxygen-free protective gas atmosphere, since the non-reduced catalyst does not become hot when handled in the open.

The flow velocities of the gases were measured under the conditions of operation in which the gases were used, and were then converted to flow velocities at N.T.P. It is these converted values of the flow velocities which are used in the specification and claims and the abbreviation "760 mm. Hg. and 0° C." is to be understood as indicating this fact.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide with the use of a cobalt, nickel or iron catalyst which is unsupported, in which the catalyst, prior to use in the hydrogenation, is dried for a period of 6 to 24 hours at a temperature within the range 150°—350° C. and is thereafter reduced in layers or columns of more than 100 centimetres in height with a gas mixture containing carbon monoxide and/or hydrogen at a flow velocity of approximately 100—200 centimetres per second (760 mm. Hg. and 0° C.).

2. A process according to claim 1, in which the catalyst is moulded and pre-dried at a temperature of about 100°—110° C. before being dried for 6—24 hours at 150°—350° C.

3. A process according to claim 1 or claim 2, in which the catalyst is dried at a temperature within the range 175°—250° C.

4. A process according to any one of the preceding claims, in which the cata-

lyst is dried in layers of a height of 400 to 1000 centimetres.

5. A process according to any one of the preceding claims, in which the gas mixture used for the reduction of the catalyst is substantially free from water vapour and carbon dioxide.

6. A process according to any one of the preceding claims, in which the catalyst is dried and reduced within the hydrogenation reactor.

7. A process according to any one of the preceding claims, in which the dried and reduced catalyst is fixedly provided in tubes having a diameter of 20—60 mm. through which synthesis gas is passed at flow velocities of more than 50 centimetres per second (760 mm. Hg, 0° C., and calculated on the cross-section of an empty tube) and in amounts greater than 500 volumes of synthesis gas per volume of catalyst per hour, the heat of reaction being removed by indirect heat exchange with a substantially uniformly boiling liquid.

8. A process according to claim 7, in which the flow velocities of the synthesis gas are greater than 200 centimetres per second.

9. A process according to claim 7 or claim 8, in which more than 1000 volumes of synthesis gas are passed over unit volume of the catalyst per hour.

10. A process according to any one of claims 7 to 9, in which the synthesis gas is passed over the catalyst at a pressure within the range 10—100 kg. per sq. cm., preferably at a pressure within the range 15—30 kg. per sq. cm.

11. A process according to any one of claims 7 to 10, in which the synthesis gas consists of 1 volume of fresh gas with 0.5—10 volumes of recycled gas, preferably 1—4 volumes of recycled gas.

12. A process according to any one of claims 7 to 11, in which the substantially uniformly boiling liquid has a boiling point within the range 200°—300° C. at a pressure not greater than 20 kg. per sq. cm.

13. A process according to claim 12, in which the liquid is ethylene glycol, aniline, nitrobenzene, or one or more aliphatic and/or aromatic hydrocarbons.

14. A process according to any one of the preceding claims, in which the cobalt, nickel or iron in the catalyst is obtained by precipitation from a salt solution.

15. A cobalt, nickel, or iron catalyst free from supporting material for use in the hydrogenation of carbon monoxide, which has been dried for a period of 6 to 24 hours at a temperature within the range 150°—350° C. before being reduced or activated.

16. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described.

17. Hydrocarbons and oxygen-containing organic compounds whenever produced by the process of any one of claims 1 to 14 and 16.

EDWARD EVANS & CO.,
14—18, High Holborn, London, W.C.1,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1953.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

RESERVE COPY,

# PATENT SPECIFICATION

# 692,234

*Date of Application and filing Complete Specification: April 17, 1951.*
*No. 8973/51.*
*Application made in Germany on April 20, 1950.*
*Complete Specification Published: June 3, 1953.*

## CORRECTION OF CLERICAL ERROR

## SPECIFICATION NO. 692,234

The following correction is in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the first day of August, 1953.

Page 1, line 40, *after* "pre-treatment" *insert* "of an unsupported catalyst".

THE PATENT OFFICE,
*29th August, 1953*

DB 32968/1(7)/3494 150 8/53 R

in and by the following statement:—

The invention relates to the catalytic hydrogenation of carbon monoxide to hydrocarbons with or without oxygen-containing organic compounds and particularly to the preparation of an unsupported or carrier-free catalyst for use in the hydrogenation of carbon monoxide.

Cobalt, nickel or iron catalysts which are used in the catalytic hydrogenation of carbon monoxide are treated with reducing gases prior to their use as it is not possible to obtain adequate activity of the catalyst without this reduction. Carbon monoxide and/or hydrogen containing gas mixtures are used in this pre-treatment, which is called catalyst reduction or catalyst formation. The step of catalyst reduction is conventionally effected outside the synthesis reactor, since prior to the present invention the reduction of an unsupported catalyst could only be accomplished in relatively thin layers at a temperature of approximately 300° C. Hitherto, all efforts to reduce unsupported carbon monoxide hydrogenation catalysts in the synthesis reactors have been unsuccessful.

The pre-treatment in the synthesis reactor itself has been technically impossible for two reasons.

First, the hydrogenation of carbon monoxide, that is to say, the synthesis proper, is effected at normal and medium pressures

[F

that is to say, the cooling jackets or tubes in the reactor, are built for a maximum steam pressure of about 30 kg. per sq. cm. During the reduction of the catalyst, the water under pressure circulating within the heat exchanger would be heated to a temperature of nearly 300° C. which would result in a steam pressure of nearly 85 kg. per sq. cm. Conventional synthesis reactors are not constructed to withstand such pressure.

Second, apart from these structural difficulties, it has been impossible to effect the reducing treatment in the synthesis reactor itself because a certain constancy in the catalyst pre-treatment is required and because of the height of the catalyst layer to be maintained in the reactor. The reduction of an unsupported catalyst has hitherto been performed with a catalyst layer of a height of only 20 to 40 cms. because no uniform reduction has been possible with layers of catalyst of a greater height. A still further obstacle lies in the fact that the unsupported catalyst, during its reduction, shrinks considerably, sometimes to the extent of 50% of its volume.

In the hydrogenation of carbon monoxide the catalyst, after its precipitation from a solution of one of its salts, is moulded whilst it is still relatively moist; it is then dried at a temperature of about 110° C. When a catalyst tube of a length of 4 to 5 metres is filled with