PATENT SPECIFICATION

688,640

Date of Application and filing Complete Specification: May 9, 1950.

No. 11528/50.

Application made in Germany on June 4, 1949.

Complete Specification Published: March 11, 1953.

Index at acceptance:—Class 2(iii), B1g.

COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German company, and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK MBH, of Frankfurt a.M.-Hedderheim, Germany, a German company, 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 a process for the catalytic hydrogenation of carbon monoxide.

In carrying out such a process in the presence of certain catalysts of the iron group, it is known to use synthesis gases containing acetylene or other hydrocarbons having a triple bond. Thus according to one prior process, increased olefine yields are obtained with such synthesis gases in the presence of cobalt catalysts. To a certain extent, the acetylene hydrocarbons included in the synthesis gas may be replaced by ethylene and other hydrocarbons having a double bond.

In B.I.O.S. Final Report No. 447, there is described an experiment in which a synthesis gas containing 90% water-gas and 10% acetylene was passed at a temperature of 200°—210° C. and at a pressure of 10 atmospheres, over an iron catalyst of the composition Fe 100: CaO 10: Kieselguhr 100. The total yield from this prior process was 26 grams per normal cubic metre, the $(CO + H_2)$ conversion being 8%.

It has now been found that appreciably higher conversions can be obtained with synthesis gases containing acetylene, or other gaseous hydrocarbons having a triple bond, in the presence of an unsupported iron catalyst.

According to the invention, a process for the catalytic hydrogenation of carbon monoxide comprises passing a synthesis gas which contains acetylene or other gaseous hydrocarbons having a triple bond, in addition to carbon monoxide and hydrogen, over an unsupported iron catalyst. It is advantageous to use an unsupported iron catalyst which has been impregnated with an alkali-metal salt of a non-volatile acid. The preferred alkali-metal salts used in the impregnation of the catalyst, are phosphates and silicates, particularly potassium phosphate and/or potassium silicate.

As is usual, the iron catalyst is reduced prior to its use in the synthesis. Such reduction is advantageously carried out at a temperature of about 250° C. with a mixture of nitrogen and hydrogen, the mixture being passed over the catalyst for approximately sixty minutes at a flow velocity within the range 1 to 2 metres per second, preferably about 1.4 metres per second. This high flow velocity has proved to be particularly advantageous for uniformly reducing the whole catalyst mass.

As compared with a process for the catalytic hydrogenation of carbon monoxide in the presence of an iron catalyst where the synthesis gas does not contain acetylene, the process according to the invention makes possible a reduction of about 20° C. in the synthesis temperature.

It is known that with iron catalysts the synthesis temperature has a direct relation to the catalyst load or space velocity and to the formation of hydrocarbons of high molecular weight. A greater proportion of higher hydrocarbons is obtained only if a low synthesis temperature is used. In these circumstances, however, the permissible space velocity is low and the $(CO + H_2)$ conversion hardly exceeds 40%—50%. Even though higher synthesis temperatures increase the conversion, they result in an increase in the formation of methane and a reduction in the formation of hydrocarbons of high

molecular weight.

In the process according to the invention, if 0.5%—10% acetylene are added to the synthesis gas, conversions of 65%—70% may be obtained at synthesis temperatures of 195° C.—200° C., the methane formation remaining below 7%. If acetylene is not added, a total conversion of only 40%—50% is obtained at these temperatures. It is appreciated that at an increased synthesis temperature of 220° C.—225° C. a ($CO + H_2$) conversion of 65%—70% is obtained, but on the other hand, there is a methane formation of 12%—16%.

It is preferred to use a synthesis gas which contains the acetylene, or other gaseous hydrocarbon having a triple bond, in an amount constituting from 0.5—1% by volume.

A further advantage of the process according to the invention lies in the fact that, due to the lower synthesis temperature, a high yield in hydrocarbons boiling above 320° C. is obtained. Approximately 80% of the synthesis products consist of hydrocarbons boiling above 320° C., including the wax which may be extracted from the catalyst.

When acetylene is added according to the process of the invention, not only may the temperatures at which the iron catalysts are placed on stream be reduced by about 20° C. but the temperature, which is gradually increased during the course of the synthesis, may be kept about 20° C. lower than the temperatures normally required with a synthesis gas free from acetylene. This results in a considerable increase in the life of the catalyst, since the temperature interval over which the synthesis temperature may be gradually increased, is increased by about 20° C.

A relatively high impregnation of the iron catalyst with an alkali-metal salt of a non-volatile acid is particularly advantageous. The alkali-metal salt or salts (calculated as K_2O) present in the catalyst, may amount to 1—10% K_2O, preferably about 3% K_2O, of the total iron content of the catalyst.

The acetylene added to the synthesis gases may be replaced by other gaseous hydrocarbons having a triple bond, for example, vinylacetylene, allylene and similar compounds. Part of the acetylene may be replaced by hydrocarbons having a double carbon bond, for example, ethylene.

The invention is illustrated by the following example:—

From a solution of the corresponding nitrates, a catalyst mass containing 100 parts of iron and 5 parts of copper was precipitated. After thorough washing, the precipitated catalyst slurry was impregnated with normal potassium orthophosphate (KH_2PO_4) in such manner that the finished catalyst contained 3 parts K_2O per 100 parts iron.

The precipitated catalyst mass was dried and then reduced at a temperature of 250° C. with a hydrogen-nitrogen mixture, the mixture being passed over the catalyst at a flow velocity of 1.4 metres per second for a period of 60 minutes. The finished catalyst had a reduction value equivalent to 40% free iron.

When this catalyst was loaded with 100 normal litres of water gas per litre per hour, a ($CO + H_2$) conversion of 50%—55% was obtained at a synthesis temperature of 200° C. The methane formation amounted to approximately 11% of the liquid synthetic products. The synthetic products, including the wax obtained upon extraction of the catalyst, contained approximately 20% of hydrocarbons boiling above 320° C.

When water gas containing 1.5% by volume of acetylene was passed over the same catalyst, at the same space velocity and at the same temperature of 200° C., the ($CO + H_2$) conversion was increased to 70%—72%. The methane formation was reduced to approximately 7%. Approximately 80% of the synthetic products, including the wax obtained upon extraction of the catalyst, consisted of hydrocarbons boiling above 320° C.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide, in which a synthesis gas which contains acetylene or other gaseous hydrocarbons having a triple bond, in addition to carbon monoxide and hydrogen, is passed over an unsupported iron catalyst.

2. A process according to Claim 1, in which the iron catalyst is impregnated with an alkali-metal salt of a non-volatile acid.

3. A process according to Claim 1 or Claim 2, in which, for the reduction of the iron catalyst prior to use in the synthesis, a hydrogen-nitrogen mixture is passed over the catalyst for a period of approximately sixty minutes at a temperature of about 250° C. and at a flow velocity of from 1 to 2 metres per second.

4. A process according to Claim 3, in which the flow velocity of the hydrogen-nitrogen mixture is about 1.4 metres per second.

5. A process according to any one of the preceding claims, in which the synthesis gas contains 0.5%—10%, preferably 0.5%—1% by volume of acetylene or other gaseous hydrocarbons having a

triple bond.

6. A process according to any one of Claims 2 to 5, in which the alkali-metal content, calculated as K_2O, of the catalyst, constitutes from 1%—10% by weight of the total iron content of the catalyst.

7. A process according to Claim 6, in which the alkali-metal content is about 3% by weight.

8. A process according to any one of the preceding claims, in which part of the acetylene is replaced by ethylene or other gaseous hydrocarbons having a double carbon to carbon bond.

9. A process according to any one of the preceding claims, in which the iron catalyst is impregnated with potassium phosphate and/or potassium silicate.

10. A process according to any one of the preceding claims, in which the synthesis gas consists of a mixture of water gas and acetylene.

11. A process according to any one of the preceding claims, in which the synthesis is effected at temperatures approximately 20° C. below the corresponding temperatures required when an iron catalyst is used with a synthesis gas free from acetylene.

12. A process for the hydrogenation of carbon monoxide in the presence of an unsupported iron catalyst, substantially as hereinbefore described.

13. A process for the conversion of a mixture containing carbon monoxide, hydrogen and acetylene, substantially as hereinbefore described with reference to the example.

14. Hydrocarbons whenever prepared by the process claimed in any one of the preceding claims.

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.