PATENT SPECIFICATION

709,263

Date of Application and filing Complete Specification Oct. 20, 1949.

No. 27022/49.

Application made in Germany on Dec. 23, 1948.

Complete Specification Published May 19, 1954.

Index at acceptance :—**Classes 1(1),** F3B1 ; **and 2(3),** B1G.

COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Joint-Stock 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:—

The invention relates to a process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide.

In the hydrogenation of carbon monoxide at atmospheric pressure (synthesis at normal pressure), the use of iron catalysts is known. These catalysts nearly always contain, in addition to iron, small amounts of copper, and frequently also appropriate activators, for example calcium or zinc. Catalysts of this type always contain a more or less appreciable amount of one or more alkali-metals, for example in the form of sodium carbonate, sodium hydroxide, potassium hydroxide or potassium carbonate.

The quantity of alkali-metal compound present, which is usually expressed as K_2O, is of fundamental importance. If small quantities of the alkali-metal compound are used, for example 0.5%—1%, expressed as K_2O and based on the total iron content of the catalyst, the proportion of hydrocarbons of high molecular weight in the products is relatively small. On the other hand, the amount of methane formed is fairly high. If the quantity of alkali-metal compound, expressed as K_2O, is increased to 5%—10%, then an appreciably higher yield of hydrocarbons of high molecular weight occurs, whilst the methane formation decreases. These catalysts quickly become coated with paraffin wax during the reaction; this results in a speedy reduction of their activity and often necessitates the extraction of the catalysts at short intervals.

In the catalytic hydrogenation of carbon monoxide, particular importance is often attached to products having a low content of hydrocarbons of high molecular weight. It has now been found that this object can be achieved at normal pressure or at a pressure only a few atmospheres higher, with the use of precipitated iron catalyst, if the catalysts are impregnated with an alkali-metal acid salt of a non-volatile acid, particularly the potassium salt, instead of with an alkali-metal hydroxide or an alkali-metal carbonate, the quantity of the alkali-metal acid salt (calculated as K_2O) in the finished catalyst being from 1% to 5% by weight of the total iron content of the catalyst. Prior to use in the synthesis, the catalysts are reduced with hydrogen.

By the term " alkali-metal acid salt ", as used in the specification and the appended claims, is to be understood an alkali-metal salt of an acid the replaceable hydrogen of which is only replaced in part by the alkali-metal. As hereinbefore stated, the acid is non-volatile.

Catalysts with particularly good properties are obtained when the impregnation is carried out by means of an alkali-metal silicate, being an acid salt as hereinbefore defined, a primary alkali-metal phosphate and/or a primary alkali-metal borate. By contrast, secondary phosphates are not so suitable, since their acid component is not sufficiently pronounced, and therefore, if they are used for the impregnation of the catalysts, their use, after reduction, results in a higher formation of hydrocarbons of high molecular weight.

If the impregnation of the catalysts is carried out with an alkali-metal silicate, being an acid salt as hereinbefore defined, a K_2O/SiO_2 ratio in the catalyst within the approximate range of 1:3 to 1:6 is particularly advantageous. With an increase in the silicate components beyond this, the catalyst shows, after reduction, a marked decrease in activity. Increase of the alkali-metal components in such a manner that for each part K_2O there are precipitated less than 3 parts SiO_2, results in an appreciably greater formation of paraffin wax.

The precipitated iron catalysts according to the invention, under severe synthesis conditions, for example when working at the highest possible conversion by the use of appropriate reaction temperatures, show after reduction only a small formation of paraffin wax; nevertheless, suprisingly enough, the methane formation also remains relatively low. Also, under less severe conditions of operation, no particularly large quantities of paraffin wax are produced; under these conditions the methane formation decreases still further.

To obtain the highest possible yield of hyrocarbons of low boiling point, the molecular size of which lies, for example between C_5 and C_{12}, the iron catalysts to be used according to the invention are reduced with hydrogen at relatively low temperatures, preferably at temperatures within the range 220°—250° C., with the use of high gas velocities, the gas velocities being preferably within the range 1 to 1.5 metres per second. Reduction under conditions outside these preferred ranges results in the production of iron catalysts which are either of a lower activity or which cause an increase in the formation of methane during synthesis. If water-gas is used instead of hydrogen for the reduction of the catalysts, an increase then occurs in the formation of hydrocarbons of high molecular weight.

The precipitated iron catalysts according to the invention are best prepared completely without, or with only a small content of the usual supporting materials such, for example, as kieselguhr.

The invention is illustrated by the following examples:—

EXAMPLE 1.

A catalyst containing 100 parts of iron and 5 parts of copper was precipitated hot, in known manner, from the appropriate nitrate solutions by means of a solution of sodium carbonate. Immediately after the precipitation, the mother solution was filtered off, and the alkali-metal compounds still present in the filter cake were washed out with condensate water until the residual alkali-metal compound or compounds, expressed as K_2O present in the filter cake comprised approximately 0.8% by weight of the iron. The filter cake, still moist, was then impregnated with a solution of waterglass, the waterglass being an alkali-metal acid salt as hereinbefore defined. The solution contained approximately 3 parts SiO_2 per part of K_2O. After this impregnation, the moist catalyst mass contained 25% by weight of SiO_2, calculated on the total iron present. Excess alkali-metal was washed out by neutralization with dilute nitric acid and subsequent filtration, leaving 5 parts by weight of K_2O per 100 parts of the total iron in the mass and a K_2O/SiO_2 ratio of 1:5.

The catalyst mass was then dried for 24 hours at 110° C., and thereafter sieved to a particle size of between 1 mm. and 3 mm. The subsequent reduction was carried out by means of hydrogen at at 225° C. for a reduction period of 60 minutes, at a gas-flow velocity of 1.2 metres per second. The catalyst produced in this way had a reduction value of 30% free iron, that is to say, 30% of the iron in the catalyst was in the metallic state.

This catalyst was used in a synthesis reactor for the conversion of water-gas, 100 volumes of water-gas per volume of catalyst being passed through per hour at a temperature of 220° C. In this way a conversion ($CO+H_2$) of 72%—74% was attained corresponding to a 95%—98% carbon monoxide consumption. The methane formation approximated to 7%—8% of the total conversion. The consumption ratio (CO/H_2) amounted to approximately 1:0.7. The yield per normal cubic metre of ideal gas reached 142 grams of synthesis products, excluding methane. About 15% of these synthesis products consisted of C_3—C_4 hydrocarbons (boiling below 30° C.), 45—55% consisted of C_5—$_{10}$ hydrocrabons (boiling range 30°—180° C.), 18—20% consisted of C_{11}—C_{18} hydrocarbons (boiling range 180°—320° C.) and the remaining 10—20% consisted of hydrocarbons having more than eighteen carbon atoms in the molecule and boiling above 320° C.

In comparison with this, an iron catalyst which had, instead of a silicate impregnation according to the invention, been given a corresponding impregnation with KOH, attained a yield of 138 grams per normal cubic metre of ideal gas. The composition of the synthesis products was similar to that given earlier in this Example. However, as a consequence of the high amount of free alkali, the conversion fell to 47%, whereupon extraction of the catalyst was necessary to restore it to its state of full activity.

When the catalyst was impregnated according to the invention in such manner that it contained at almost the same K_2O/SiO_2 ratio, only 1% of the alkali-metal compound (expressed as K_2O and relative to the total iron content of the catalyst), then, with approximately the same conversion, a methane formation of about 14% occurred. The yield fell, in this instance, to 130 grams of synthesis products per normal cubic metre of ideal gas. This yield was, however, maintained only at the beginning of the run, since the methane formation, even after a relatively small time on stream, rose to about 15%—20%, whereupon the yield fell still further to 120 grams per normal cubic metre of ideal gas. The composition of the synthesis products containing more than two carbon atoms in the molecule, obtained by means of this catalyst, was similar to that given earlier in this example.

In a comparative test a catalyst was used which contained a greater quantity of alkali-metal acid salt than the catalysts employed in the process according to the invention. The catalyst used was impregnated with a waterglass solution which contained 3 parts by weight of SiO_2 per part of K_2O to give a catalyst containing by weight, 25 parts of SiO_2 and 8.3 parts of K_2O per 100 parts of the total iron. The synthesis product obtained in this comparative test contained large quantities of hydrocarbons of high molecular weight and this fact necessitated extraction of the catalyst after a short period of operation.

When the catalyst according to the invention was reduced with water-gas instead of hydrogen then, in this case, also, there was an increased yield of paraffin wax. Furthermore, the catalyst had a shorter life than when the reaction was carried out with hydrogen.

When the amount of SiO_2 in the catalyst was increased, the catalysts exhibited under similar working conditions, an appreciable lowering in activity, with the result that the conversion fell to about 60%—63%.

Example 2.

A catalyst mass was precipitated by quickly pouring a boiling solution containing, in the form of nitrates, 50 grams of iron and 2.5 grams of copper per litre, into a boiling solution of sodium carbonate; the sodium carbonate solution contained 100 grams of sodium carbonate per litre. The precipitated catalyst mass was filtered, and the precipitate was carefully washed with hot condensate water. The washed precipitate contained 0.5 parts of the alkali-metal compound or compounds, expressed as K_2O, per 100 parts of iron. Thereupon, the precipitate was immediately impregnated with a solution of primary potassium phosphate (KH_2PO_4) containing determined amounts of free phosphoric acid, the impregnation being so effected to give the finished catalyst 4 parts of alkali-metal compounds, expressed as K_2O, per 100 parts of iron. The catalyst mass was then dried at a temperature of 105° C. and thereafter moulded and sieved to a particle size of from 2 mm. to 4 mm.

The reduction of the catalyst with hydrogen was effected with a linear gas velocity of 1.5 metres per second at a temperature of 230° C. for a period of sixty minutes. The reduction value of the catalyst was then 29%.

The catalyst was then used in synthesis with water-gas under normal pressure at a temperature of 217° C. and with a space velocity of 100 v/v/hr. A $CO+H_2$ conversion of 73% was obtained in the synthesis, which corresponded to a CO conversion of over 90%. The methane formed amounted to 6%. 144 grams of synthesis products, other than methane were obtained per normal cubic metre of ideal gas. The composition of these products was similar to the composition of the products obtained in Example 1.

Throughout the specification and the appended claims, the alkali-metal compound or compounds in the catalyst is or are expressed as K_2O and the content of alkali-metal compounds, expressed as K_2O is calculated with reference to the total amount of iron, in elementary and combined form, in the catalyst. Thus where the only alkali-metal compound present in the catalyst is that introduced as NaH_2PO_4 and the catalyst was impregnated with 5.1 parts by weight of this compound for every 100 parts by weight of the total amount of iron in the catalyst, the quantity of alkali-metal compound in the catalyst is expressed as 4 parts of K_2O per 100 parts of iron or as 4%.

Similarly, where the alkali-metal acid salt used for the impregnation of the catalyst is an alkali-metal silicate, the alkali-metal component is always expressed as K_2O in the ratio alkali-metal component/SiO_2. Thus where the alkali-metal acid salt is sodium silicate and the finished catalyst contains 1 part by weight of Na_2O for every 6 parts by weight of SiO_2, the K_2O/SiO_2 ratio of the finished catalyst is 1:4 approximately.

In Patent Specification No. 672,259 there is claimed a process for the synthesis of hydrocarbons or mixtures of hydrocarbons and oxygenated hydrocarbon derivatives by the catalytic hydrogenation of carbon monoxide with the aid of catalysts which contain iron, alkali-metal compounds (preferably oxygen-containing potassium compounds) and difficulty reducible non-volatile reactive acid anhydrides as therein defined, characterised in that the ratio by weight of alkali-metal compound (calculated in terms of alkali-metal oxide) to non-volatile reactive acid anhydride in the catalyst is selected to be between 1:2.5 and 1:7.0. The term "reactive acid anhydrides" used therein is defined as intended to denote a group of compounds comprising those oxides which are capable of reacting directly at elevated temperatures with alkali metal carbonates or alkali metal hydroxides to form alkali metal salts.

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 the synthesis of hydrocarbons by the hydrogenation of carbon monoxide in the presence of a precipitated iron catalyst at normal or slightly elevated pressures with reduced formation of methane and of hydrocarbons of high molecular weight, in which the iron catalyst, which may contain the usual activators, has been impregnated with an alkali-metal acid salt (as hereinbefore defined) of a non-volatile acid, to an extent such that the quantity of alkali-metal acid salt, calculated as K_2O, in the finished catalyst constitutes from 1% to 5% by weight of the total iron content of the catalyst, the catalyst having been reduced with hydrogen at high gas velocities and at relatively low temperatures prior to use.

2. A process according to Claim 1, in which the acid salt is an alkali-metal silicate, a primary alkali-metal phosphate or a primary alkali-metal borate.

3. A process according to Claim 2, in which an alkali-metal silicate is used, the K_2O/SiO_2 ratio of the finished catalyst being within the range 1:3 to 1:6.

4. A process according to any one of the preceding claims, in which the linear velocity of the hydrogen in the reduction of the catalyst is within the range 1—1.5 metres per second.

5. A process according to any one of the preceding claims, in which the reduction of the catalyst with hydrogen is effected at a temperature within the range 220°—250° C.

6. A process according to any of the preceding claims, in which the alkali-metal salt is a potassium salt.

7. A process according to any one of the preceding claims, in which the catalyst is unsupported.

8. A process for the production of hydrocarbons, substantially as hereinbefore described in accordance with the invention in Example 1.

9. A process for the production of hydrocarbons substantially as hereinbefore described with reference to Example 2.

10. A process for the production of hydrocarbons, substantially as hereinbefore described.

11. Hydrocarbons whenever produced by the process of any preceding claim.

EDWIN 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.—1954.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.**

PATENT SPECIFICATION

709,263

Date of Application and filing Complete Specification Oct. 20, 1949.
No. 27022/49.
Application made in Germany on Dec. 23, 1948.
Complete Specification Published May 19, 1954.

Index at acceptance:—**Classes 1(1), F3B1; and 2(3), B1G.**

COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

ERRATA

SPECIFICATION No. 709,263

Page 2, line 98, *for* "C_5—$_{10}$" *read* "C_5—C_{10}"
Page 3, line 33, *for* "reaction" *read* "reduction"
Page 4, line 19, *for* "non" *read* "iron"

THE PATENT OFFICE,
14th September, 1954.

---

sium carbonate.

The quantity of alkali-metal compound present, which is usually expressed as K_2O, is of fundamental importance. If small quantities of the alkali-metal compound are used, for example 0.5%—1%, expressed as K_2O and based on the total iron content of the catalyst, the proportion of hydrocarbons of high molecular weight in the products is relatively small. On the other hand, the amount of methane formed is fairly high. If the quantity of alkali-metal compound, expressed as K_2O, is increased to 5%—10%, then an appreciably higher yield of hydrocarbons of high molecular weight occurs, whilst the methane formation decreases. These catalysts quickly become coated with paraffin wax during the reaction; this results in a speedy reduction of their activity and often necessitates the extraction of the catalysts at short intervals.

In the catalytic hydrogenation of carbon monoxide, particular importance is often attached to products having a low content of hydrocarbons of high mole-

Catalysts with particularly good properties are obtained when the impregnation is carried out by means of an alkali-metal silicate, being an acid salt as hereinbefore defined, a primary alkali-metal phosphate and/or a primary alkali-metal borate. By contrast, secondary phosphates are not so suitable, since their acid component is not sufficiently pronounced, and therefore, if they are used for the impregnation of the catalysts, their use, after reduction, results in a higher formation of hydrocarbons of high molecular weight.

If the impregnation of the catalysts is carried out with an alkali-metal silicate, being an acid salt as hereinbefore defined, a K_2O/SiO_2 ratio in the catalyst within the approximate range of 1:3 to 1:6 is particularly advantageous. With an increase in the silicate components beyond this, the catalyst shows, after reduction, a marked decrease in activity. Increase of the alkali-metal components in such a manner that for each part K_2O there are precipitated less than 3 parts SiO_2, results in an appreciably greater formation of paraffin wax.