PATENT SPECIFICATION

668,419

Date of Application and filing Complete Specification Aug. 15, 1949.
No. 21190/49.
Application made in Germany on Oct. 1, 1948.
Complete Specification Published March 19, 1952.
(Under this application, a Specification was laid open to public inspection under Section 91 (4) of the Patents and Designs Acts. 1907 to 1946 on Aug. 28, 1950)

2968

Index at acceptance:—Classes 1(i), F3b1; and 2(iii), B1g, C3a13a3(a1c: j2).

COMPLETE SPECIFICATION

Process for the Manufacture of Products including Oxygen-containing Organic Compounds by the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Nordrhein-Westfalen, Germany, a German 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 manufacture of products including oxygen-containing organic compounds by the hydrogenation of carbon monoxide.

The life of precipitated iron catalysts used in the hydrogenation of carbon monoxide, particularly in the treatment of gases rich in carbon monoxide (for example, water gas) may, as is known, be increased to an extraordinary degree if, after their precipitation from, for example, the appropriate nitrate solutions, the catalysts are carefully washed. This washing is for the purpose of removing as far as possible the residue of the alkali-metal compound (generally sodium carbonate) used in the precipitation, or the alkali-metal compounds (for example, sodium nitrate) which result from the decomposition of the iron salts. If the alkali-metal compounds referred to, or even only one of them, remain in appreciable amount in the catalyst, if that is to say, the catalyst is badly washed, not only is its reduction made considerably more difficult, but also the working of the catalysts in the subsequent synthesis is unsatisfactory. Their life, in comparison with well washed catalysts, is greatly reduced.

It has now been observed that an incompletely washed iron catalyst, the alkali-metal content of which, calculated as potassium monoxide (K_2O), lies between 3% and 20%, preferably between 5% and 10%, of the weight of iron present in the catalyst, yields large quantities of products containing oxygen, for example, alcohols, esters, aldehydes and the like, when used in the hydrogenation of carbon monoxide. Well washed iron catalysts show, in contrast to this, a marked decline in the formation of oxygen-containing compounds, whilst partially washed iron catalysts, that is to say, iron catalysts from which the alkali-metal compounds have not been wholly removed, render possible the formation of a relatively high proportion of oxygen-containing compounds.

If iron catalysts are thoroughly washed out in accordance with present-day practice, it is not possible to impart to them through a subsequent addition of alkali-metal compounds by way of impregnation, properties as effective as the kind which are characteristic of those catalysts which still contain some of the alkali-metal compounds remaining from the stage of catalyst precipitation.

In the manufacture of the iron catalyst to be used according to the invention, the washing of the precipitated catalyst mass is so regulated, that the final catalysts contain such quantities of alkali-metal compounds that, when calculated as potassium monoxide (K_2O), their weight is from 3% to 20% of the weight of the iron present in the catalyst, the iron being determined as metallic iron. It is particularly advantageous if, using this method of calculation, the K_2O content of the finished catalyst is 5%—10%.

In many types of iron catalyst it is advantageous to incorporate, by subsequent impregnation, further quantities of alkali-metal compounds, in addition to the alkali-metal compounds remaining after the washing of the precipitated catalyst mass. This impregnation can be effected by means of potassium hydroxide, potassium carbonate, sodium carbonate or other compounds of elements of sub-

group A (the alkali-metals) of Group I of the periodic system.

It is advantageous to carry out the process according to the invention at a synthesis pressure of about 10 atmospheres absolute pressure. It is, however, possible, according to the invention, even at normal atmospheric pressure, to obtain greater quantities of oxygen-containing products in the synthesis. The greatest yields of oxygen-containing compounds are obtained when the synthesis is carried out above 20 atmospheres absolute pressure.

Because of the high alkali-metal content of the iron catalysts used the synthesis results in a so-called bed consumption ratio, in which the synthesis gas, for example water-gas, is converted with an increased consumption of carbon monoxide as compared with that of the hydrogen. To avoid this disadvantage, it is advantageous in the method according to the invention, to use a synthesis gas which is particularly rich in carbon monoxide. In this manner, not only is there created a theoretical possibility of increased yield per cubic metre of reaction gas, but also, in addition, an increased formation of oxygen-containing compounds is obtained.

The iron catalysts produced and used according to the invention may, in addition to the usual activators such as copper, zinc or calcium, contain other elements or compounds which favour the formation of products containing oxygen. Such further activators are preferably compounds of vanadium, cerium and tungsten, and also, other elements or compounds of the fourth to seventh groups of the periodic system.

Example.

700 c.c. of a solution of the nitrates of iron, 1.25 grams of copper and 2.5 grams of calcium calculated as CaO, were added with intensive stirring to 700 c.c. of a boiling solution of sodium carbonate containing 95 grams of Na_2CO_3. 2.5 grams of kieselguhr were added immediately after the addition of the iron-containing solution and after intensive stirring of the mixture for 1 minute, the precipitate was filtered off under suction. The filter cake was then washed until the quantity of sodium compounds remaining in the cake corresponded to an alkali-metal content, calculated as potassium monoxide (K_2O), of 8 parts per 100 parts of iron. The filter cake was then dried and afterwards reduced at a temperature of 300° C.

The catalyst so obtained was used in a synthesis operated at a temperature of 220° C. and at an absolute pressure of 10 atmospheres, water-gas being passed over the catalyst at the rate of 100 litres per litre of catalyst per hour. The products obtained contained 30% to 40% of oxygen-containing compounds, which compounds consisted chiefly of alcohols.

When the catalyst in question was washed substantially free from sodium compounds and was then used in a synthesis operation under the same synthesis conditions as described above, the alcohol content of the products decreased and was about 3%—5%.

When the catalyst obtained upon substantial elimination of sodium compounds, was subsequently impregnated with potassium carbonate to an extent to give a K_2O content of about 8% relative to the content of iron and was afterwards used in a synthesis operation, the products of the synthesis contained about 10%—15% of oxygen-containing compounds. It will be noted that even this yield of oxygen-containing compounds is far less than that obtainable with the use of catalysts which, according to the invention, have not been completely freed from their content of alkali-metal compounds.

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 manufacture of products including oxygen-containing organic compounds by the hydrogenation of carbon monoxide, in which the hydrogenation is effected in the presence of an iron catalyst which has been obtained by precipitation from solution by an alkali-metal compound, the precipitated catalyst mass obtained having been incompletely washed so that the catalyst contains an alkali-metal content of from 3% to 20% by weight of the iron present in the catalyst, the alkali-metal content being calculated as potassium monoxide, the iron being determined as metal.

2. A process according to claim 1, in which the alkali-metal compound, calculated as potassium monoxide, is present to the extent of from 5% to 10%.

3. A process according to claim 1 or claim 2, in which the incompletely washed precipitate is impregnated with an alkali-metal compound.

4. A process according to claim 3, in which the precipitate is impregnated with potassium carbonate or sodium carbonate.

5. A process according to any one of the preceding claims, in which the hydrogenation is effected at an absolute pressure within the range 1—20 atmospheres, preferably at about 10 atmospheres.

6. A process according to any one of claims 1 to 4, in which the hydrogenation is effected at an absolute pressure greater than 20 atmospheres.

7. A process according to any one of the preceding claims, in which a synthesis gas containing more carbon monoxide than hydrogen, is used.

8. A process according to any one of the preceding claims, in which the iron catalyst contains copper and/or zinc and/or calcium as activators.

9. A process according to claim 8, in which the iron catalyst also contains as activators, elements of the fourth to the seventh Groups of the periodic system, preferably vanadium, cerium or tungsten, or compounds of such elements.

10. A process for the manufacture of organic compounds by the hydrogenation of carbon monoxide in the presence of an iron catalyst containing an alkali-metal compound, substantially as hereinbefore described with reference to the example.

11. A process for the manufacture of products including oxygen-containing organic compounds by the hydrogenation of carbon monoxide substantially as hereinbefore described.

Dated this 15th day of August, 1940.

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

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Index at accept

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ERRATA

SPECIFICATION No. 668,419.

Page 1, line 39, *for* " overved " *read* " observed "
Page 2, line 17, *for* " bed " *read* " bad "
Page 2, line 45, *after* " iron " *insert* " copper and calcium containing 25 grams of iron "

THE PATENT OFFICE,
12*th August*, 1952.

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