PATENT SPECIFICATION

678,963

Date of Application and filing Complete Specification: April 6, 1950.

No. 8684/50.

Application made in Germany on May 7, 1949.

Complete Specification Published: Sept. 10, 1952.

3001

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

COMPLETE SPECIFICATION

Process for the Pre-Treatment of Iron-Containing Catalysts for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, 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:—

Iron catalysts, such as are used, for example, for the hydrogenation of carbon monoxide at medium or high gas pressures, are pre-treated with reducing gases before being used. In this manner, a more or less extensive reduction, and/or a "formation" of the catalyst is attained according to the kind of gas used, which considerably affects its activity. Gases suitable for the reduction process proper are those consisting mainly of hydrogen. In contrast to this, for catalyst "formation", carbon monoxide-containing gases are required, and in certain cases, even the use of pure carbon monoxide is desirable. In the art, the reduction of a catalyst is generally understood to mean a pre-treatment with pure hydrogen. However, when a pre-treatment is carried out with carbon monoxide or with a gas containing carbon monoxide, which pre-treatment is also a reduction at first, the term "formation" is used to designate this pre-treatment because of the subsequent reaction of the iron with excess carbon monoxide with the production of carbides.

Up to the present, in the reducing pre-treatment of iron catalysts low gas velocities have been used, which at atmospheric pressure amounted to approximately 2–40 cm. per second. Furthermore, treatment of catalysts had hitherto to be effected with layers of catalyst of relatively little thickness in order to obtain uniform catalyst characteristics.

It has now been found that the pre-treatment of iron catalysts can be effected with greater economy and that catalysts having improved synthesis characteristics can be obtained, when the catalysts are pre-treated, according to the invention, in static layers of a thickness of about 100 centimetres or more with gases containing hydrogen and/or carbon monoxide at high linear velocities of 50–500 centimetres per second.

The linear velocity of the gas used in the pre-treatment is preferably within the range 100–200 centimetres per second and the thickness of the catalyst layer is preferably within the range 80–400 centimetres.

At the low gas velocities hitherto used, considerable differences occur between the reduction value of the catalyst in the upper and lower layers of the catalyst with layer thickness of about 100 cm. These differences do not disappear even if the reduction period is considerably extended. This fact adversely affects the synthesis behaviour of iron catalysts.

The "reduction value" of the catalyst signifies the percentage of the iron, present in the catalyst, which is in the metallic state.

If the increased gas velocities according to the invention are used, practically the same reduction value is obtained within a short time, for example, after only 30 minutes, both in the upper and in the lower parts of a catalyst layer of 100 cms. thickness. The layer thickness of the catalyst can be still further increased, if required, so that this kind of reducing pre-treatment of catalysts is economically of great advantage.

A futher disadvantage in the low velocity of the reduction gases used hitherto consists in that, when the reduction gases are, for example, passed downwardly through a bed of catalyst, the activity of the catalyst in the lower layers of the bed is adversely affected and its life is reduced. This undesirable effect is due to the high partial pressure of water vapour in the reduction gases, which water vapour is produced in the reduction of the catalyst. When using gas velocities in accordance with the invention, the partial pressure of the water vapour remains so low throughout the whole thickness of the cata-

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lyst bed, that no adverse effect is produced on the lower layers in the bed.

Iron catalysts pre-treated according to the process of the invention have the advantage that in the hydrogenation of carbon monoxide the synthesis temperature can be considerably lowered without reducing the extent of conversion of the synthesis gas. In the hydrogenation of carbon monoxide, iron catalysts require, as their period of use increases, a gradual increase in the reaction temperature. The lower starting temperature of catalysts pre-treated according to the invention provides an increased useful temperature difference over which the reaction temperature may be gradually increased, as referred to above. This increase in the range over which the temperature may be raised is of great importance for increase in the life of the catalyst.

Furthermore, by means of the iron catalysts pre-treated according to the invention, the formation of hydrocarbons of high molecular weight, particularly the production of synthetic products boiling above 320° C., can be considerably increased. At the same time, a considerable reduction in the formation of methane takes place; in some cases there is a decrease to less than half the quantities usually formed with known iron catalysts. There is also an improvement in the CO/H_2 consumption ratio of the synthesis gases passed through.

If water gas is used as the synthesis gas, and only passed once over the catalyst, that is to say, used without re-cycling, frequently no useful gas-consumption is obtained with iron catalysts which have been reduced in the manner hitherto usual. In the majority of such cases considerably less hydrogen is used up than is present in the gas mixture. Iron catalysts pre-treated according to the invention do not have this disadvantage, but show a considerably increased hydrogen consumption so that water gas can be usefully consumed in a single passage over the catalyst.

The fact that a lowering of the synthesis temperature can be attained is of particular advantage with catalysts which yield substantial amounts of oxygen-containing products, that is to say, catalysts which have a comparatively high alkali content of 1%–10%, preferably from 4%–8% (calculated as K_2O and based on the total iron content of the catalyst). The formation of oxygen-containing organic compounds is improved by low synthesis temperatures, so that iron catalysts, pre-treated according to the invention, effect an increased yield of oxygen-containing products.

With iron catalysts pre-treated according to the invention, the catalyst load or space velocity also can be increased far above the load of 100 volumes of synthesis gas per volume of catalyst per hour which is the normal load used hitherto. In order to convert the synthesis gas to the same extent, it is necessary to increase the synthesis temperature accordingly. With the pre-treatment of iron catalysts hitherto usual, such an increase in the synthesis temperature has nearly always resulted in a high increase in methane formation which, in some circumstances, increased to such an extent that the synthesis became uneconomical. In contrast to this, the new catalysts treated according to the process of the invention keep the methane content of the synthesis products within economic limits at increased loads.

In order to obtain catalysts with particularly good characteristics, care should be taken that the gases used in the reducing pre-treatment contain neither carbon dioxide nor water vapour.

The invention is illustrated by the following examples.

EXAMPLE 1

A catalyst containing 5 parts copper per 100 parts iron was precipitated, with an aqueous solution of sodium carbonate, from an aqueous solution which contained corresponding quantities of iron and copper in the form of nitrates. After careful washing, the precipitated mass was impregnated with potassium silicate to yield a mass containing 3 parts of K_2O and 7.5 parts of S_1O_2 per 100 parts of iron. The impregnated mass was dried and then reduced in a layer 100 cms. in thickness, with a gas mixture which consisted of three parts by volume of hydrogen and one part by volume of nitrogen. The gas velocity was 140 cms. per second, calculated under normal conditions, and the temperature was 300° C. After a reduction period of 90 minutes the catalyst had a reduction value which corresponded to approximately 40% free iron.

If a catalyst, pre-treated in this manner, is used for the synthesis with water gas at a load of 100 litres of gas per litre of catalyst per hour and 10 kg/cm² pressure, a conversion of 65% $(CO + H_2)$ is obtained at 209° C. The methane formation amounts to approximately 6%. The liquid products contain approximately 65% hydrocarbons boiling above 320° C.

If an iron catalyst of the same composition is reduced, in the manner hitherto usual, with a gas velocity of only 40 cms. per second, then considerably more time is needed to obtain an equally high reduction value. These catalysts only give a conversion of 60% in the subsequent synthesis with water gas at the normal load of 100 litres of gas per litre of catalyst per hour, in spite of the synthesis temperature being increased to 215° C. The methane formation then amounts to 7%–8%.

Only 59% of hydrocarbons boiling above 320° C. are contained in the liquid synthetic products.

EXAMPLE 2

An iron catalyst produced and pre-treated according to Example 1, which had received a somewhat higher impregnation with alkali-metal silicate (4.5 parts K_2O and 10.5 parts S_iO_2 per 100 parts Fe.), was loaded in the synthesis operation with 300 litres water gas per litre of catalyst per hour. This load was approximately three times as high as the usual normal load.

At a synthesis temperature of 226° C. and a synthesis pressure of 10 kg/cm² the $(CO + H_2)$ conversion amounted to 65%. 60% of the liquid synthetic products boiled above 320° C. The methane formation was approximately 7%.

If an iron catalyst of the same composition is reduced in the usual manner, that is to say, with a gas velocity of approximately 30–40 cms. per second (measured linearly), the reaction temperature has to be increased to 238° C. in order to obtain the same conversion. Under such conditions the methane formation amounts to 10%–11%. The yield of hydrocarbons boiling above 320° C. was reduced to approximately 55% of the liquid synthetic products.

What we claim is:—

1. A process for the pre-treatment of an iron catalyst which is particularly suitable for use in the hydrogenation of carbon monoxide, with a reducing gas containing hydrogen and/or carbon monoxide, in which the catalyst is pre-treated in a static layer of a thickness of about 100 centimetres or more with a linear velocity of the gas of from 50 to 500 centimetres per second.

2. A process according to claim 1, in which the linear velocity of the gas is within the range 100–200 centimetres per second.

3. A process according to claim 1 or claim 2, in which the reducing gas used for the pre-treatment is substantially free from water vapour.

4. A process according to any one of claims 1 to 3, in which the reducing gas used for the pre-treatment is substantially free from carbon dioxide.

5. A process according to any one of claims 1 to 4, in which the catalyst subjected to the pre-treatment contains an alkali-metal compound which, calculated as the equivalent quantity of K_2O, is present to the extent of 1–10%, preferably 4–8%, by weight of the iron in the catalyst.

6. A process for the pre-treatment of an iron-containing catalyst, substantially as hereinbefore described.

7. A process for the pre-treatment of an iron-containing catalyst, substantially as described in Example 1 or Example 2 with reference to the invention.

8. An iron-containing catalyst suitable for use in the hydrogenation of carbon monoxide, whenever pre-treated by the process claimed in any of the preceding claims.

9. A process for the hydrogenation of carbon monoxide, in which there is used an iron-containing catalyst as claimed in claim 8.

10. Hydrocarbons and other products, whenever prepared by the process claimed in claim 9.

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Redhill: Printed for Her Majesty's Stationery Office, by Love & Malcomson, Ltd.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.