PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to Catalysts

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German joint-stock Corporation, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described

hydrogenation carried out under normal, or increased pressure. The reduction can, for example, be undertaken by means of hydrogen, carbon monoxide or other reducing gases or mixture of gases. Whilst cobalt catalysts can be reduced for syn-

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ERRATA

SPECIFICATION NO. 665218

Page 1, line 51, *for* "mixture" *read* "mixtures"

Page 2, line 49, *for* "carbon" *read* "carbonate"

THE PATENT OFFICE,
5th May, 1952

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metallic iron and iron oxides in the relative proportions of 25—35% metallic iron, 50—61% ferrous oxide and 25—4% ferric oxide.

During manufacture it is necessary, by means of appropriate investigations, to determine accurately the Fe, FeO and Fe_2O_3 content of the reduced catalyst. An iron catalyst working well at normal atmospheric pressure, and containing 50—200 parts of kieselguhr, as carrier constituent, for every 100 parts of (iron + iron oxides) should contain approximately 25—35% of the 100 parts in the form of metallic iron. As soon as the free iron content is appreciably above or below this value, the synthesis properties become appreciably worse.

Of great influence on the synthesis properties of the iron catalyst according to the invention, is the nature of its reduction. It is well known that with iron catalysts the preliminary treatment with reducing gases has a decisive influence on their behaviour in carbon monoxide

tion of the reduction is also of considerable importance. If the above mentioned speeds of flow are maintained, the reduction should continue for approximately 30 to 60 minutes.

It is advantageous that the new iron catalyst should be impregnated with an alkali-metal compound, in particular with potassium hydroxide or potassium silicate in a quantity which (calculated as the alkali-metal monoxide) lies between 0.5% and 5% K_2O, preferably between 1% and 3% K_2O. An impregnation with acid potassium orthophosphate or other alkali-metal salts of non-volatile mineral acids, is of particular advantage. In this way the activity of the catalyst is increased, the methane formation is diminished, and the formation of paraffin wax is considerably augmented. Impregnations which are in excess of 5% K_2O produce an excessive formation of paraffin wax which would necessitate an almost daily extraction of the catalysts. The K_2O contents given are determined in relation to the

[*Price* 2/-]

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COMPLETE SPECIFICATION

Improvements relating to Catalysts

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German joint-stock Corporation, 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:—

For the optimum working of an iron catalyst it is more than usually important that the metallic iron (Fe), ferrous oxide (FeO) and ferric oxide (Fe_2O_3) in its content be brought into the right proportion to each other. It has now been discovered that iron catalysts (i.e. catalysts by means of which carbon monoxide hydrogenation can be carried out at roughly atmospheric pressure) which work particularly well at normal pressure, are obtained if there is present, in addition to the usual carrier substances and activators, a content of metallic iron and iron oxides in the relative proportions of 25—35% metallic iron, 50—61% ferrous oxide and 25—4% ferric oxide.

During manufacture it is necessary, by means of appropriate investigations, to determine accurately the Fe, FeO and Fe_2O_3 content of the reduced catalyst. An iron catalyst working well at normal atmospheric pressure, and containing 50—200 parts of kieselguhr, as carrier constituent, for every 100 parts of (iron + iron oxides) should contain approximately 25—35% of the 100 parts in the form of metallic iron. As soon as the free iron content is appreciably above or below this value, the synthesis properties become appreciably worse.

Of great influence on the synthesis properties of the iron catalyst according to the invention, is the nature of its reduction. It is well known that with iron catalysts the preliminary treatment with reducing gases has a decisive influence on their behaviour in carbon monoxide hydrogenation carried out under normal, or increased pressure. The reduction can, for example, be undertaken by means of hydrogen, carbon monoxide or other reducing gases or mixture of gases. Whilst cobalt catalysts can be reduced for synthesis at both normal and medium pressure under practically similar conditions, the synthesis properties of iron catalysts are to a great extent dependent on the conditions under which the reduction of the catalyst mass is carried out.

With iron catalysts according to the invention, the reduction must be carried through at temperatures below 300° C. and preferably at a temperature between 200° C. and 240° C. During the reduction it is necessary to operate at a speed of flow of the reduction gases attaining approximately 1.3—1.5 m/sec., calculated when the gases are cool. The duration of the reduction is also of considerable importance. If the above mentioned speeds of flow are maintained, the reduction should continue for approximately 30 to 60 minutes.

It is advantageous that the new iron catalyst should be impregnated with an alkali-metal compound, in particular with potassium hydroxide or potassium silicate in a quantity which (calculated as the alkali-metal monoxide) lies between 0.5% and 5% K_2O, preferably between 1% and 3% K_2O. An impregnation with acid potassium orthophosphate or other alkali-metal salts of non-volatile mineral acids, is of particular advantage. In this way the activity of the catalyst is increased, the methane formation is diminished, and the formation of paraffin wax is considerably augmented. Impregnations which are in excess of 5% K_2O produce an excessive formation of paraffin wax which would necessitate an almost daily extraction of the catalysts. The K_2O contents given are determined in relation to the total iron content of the catalyst.

The activity of the catalysts manufactured and reduced, according to the invention is the best obtainable after many experiments on the effect of the various known reduction methods. In a carbon monoxide hydrogenation carried out between 200° C. and 220° C. in which 100 volumes of synthesis gas per volume of catalyst per hour were passed through the reactor, iron catalysts of this kind converted up to 70%—75% of the gas mixture employed. As the synthesis gas, water-gas was used. As the iron catalyst did not have a typical consumption of the water-gas, that is to say, not in accordance with the calculated synthesis, but due to secondary reactions—particularly a conversion which occurred in the reaction—which consumed more carbon monoxide than satisfied the pure synthesis equation, the 70%—75% conversion mentioned above presents in fact a practically complete, that is to say 92%—97% treatment of the carbon monoxide present in the synthesis gas.

The life of the iron catalysts according to the invention is considerable and amounts to at least 10,000—12,000 working hours.

As carrier substance, kieselguhr, aluminium oxide, magnesium oxide and similar substances may be used. As activators Cu, CaO, ZnO and similar metal compounds are suitable. The catalysts may, however, also be manufactured without carrier substances.

EXAMPLE 1.

From an appropriate solution containing iron nitrate, copper nitrate and calcium nitrate, a catalyst was produced by precipitation with an aqueous solution of sodium carbonate of a concentration of about 11% at a hydrogen ion concentration pH = 9.2 with the addition of kieselguhr. The nitrate solution contained 40 grams of iron, 2 grams of copper and 4 grams CaO per litre. The iron is precipitated as the carbon and bicarbonate but immediate hydrolysis occurs with the formation of the hydroxide and the evolution of carbon dioxide. The relative proportions of the metal nitrates and kieselguhr were such that the catalyst contained 100 parts Fe, 5 parts Cu, and 10 parts CaO to 100 parts kieselguhr. After a subsequent washing out of the residual alkali content, an impregnation with small quantities of KOH was carried out, and the catalyst mass dried at 120° C.

When hydrogen at 225° C. with a linear speed of 1.35 m/sec. was passed over the catalyst for a period of 40 minutes, the free iron (Fe) content, in relation to the total content of iron and iron oxides, amounted to 30%, the content of ferrous oxide being 58% and that of ferric oxide 12%.

During the synthesis operation, 100 volumes of water gas were passed over one volume of the catalyst per hour. The synthesis temperature amounted to 220° C. The $(Co+H_2)$ conversion attained 65%—68% with a resultant consumption ratio of 1 part by volume of carbon monoxide to 0.65 parts by volume of hydrogen. The CO conversion was in excess of 90%.

When the catalyst was reduced at a temperature of 300° C. instead of 225° C. a conversion of only about 45% $(CO+H_2)$ could be obtained in the subsequent synthesis.

When the catalyst was reduced with a speed of flow of gas of 45 cm/sec. instead of 1.35 m/sec. a conversion of only about 50% $(CO+H_2)$ could be obtained in the subsequent synthesis.

EXAMPLE 2.

From an appropriate solution containing iron nitrate, copper nitrate and calcium nitrate, an iron catalyst was produced by precipitation with an aqueous solution of sodium carbonate of a concentration of about 11% at a hydrogen ion concentration pH = 7.3 with the addition of kieselguhr. The solution of nitrates contained 40 grams of iron, 2 grams of copper and 1.2 grams CaO per litre. The iron is initially precipitated in the form of the carbonate and the bicarbonate but immediate hydrolysis occurs with the formation of the hydroxide and the evolution of carbon dioxide. The relative proportion of the metal nitrates and the kieselguhr were such that the catalyst contained 100 parts Fe, 5 parts Cu, and 3 parts CaO to 50 parts of kieselguhr. The precipitated mass was washed out and then impregnated with 1% K_2O in the form of potassium silicate (calculated on the Fe content). Finally it was dried at 115° C.

When, in the reduction, hydrogen with a linear speed of flow of 1.4 m/sec. was passed over the catalyst for a period of 40 minutes, at a temperature of 225° C., the free iron content, relative to the total content of iron and iron oxides, amonuted to 33%, the content of ferrous oxide being 61% and that of ferric oxide 6%.

When the catalyst was used at 220° C. with water gas for synthesis, and 100 volumes of gas were passed over one volume of the catalyst per hour, a conversion of 65% to 70% $(Co+H_2)$ was obtained. The consumption ratio lay in the region of 0.65 and gave a CO conversion of over 95%.

When, in the reduction, the gas speed was reduced from 1.4 m/sec. to 40 cm/sec.

then, in the subsequent synthesis, the conversion fell to from 50% to 55% (CO+H$_2$).

When, during the reduction, the temperature was maintained at 300° C. instead of 225° C. then the conversion in the subsequent synthesis fell to 55% (CO+H$_2$).

When, during the reduction, the temperature of 225° C. was decreased to 180° C. then, in the synthesis, a conversion of only about 45% (Co+H$_2$) was obtained.

EXAMPLE 3.

From a hot aqueous solution containing iron nitrate and copper nitrate, a catalyst without carrier substance was precipitated by means of a hot aqueous solution of sodium carbonate of a concentration of about 11% at a hydrogen ion concentration of pH=7.1. The nitrate solution contained 45 grams of iron and 2.2 grams of copper per litre. The iron is initially precipitated as the carbonate and bicarbonate but hydrolysis occurs immediately with the formation of the hydroxide and the evolution of carbon dioxide. The relative proportions of the two nitrates were such that the catalyst contained 5 parts copper per 100 parts iron. After a thorough washing, the catalyst was so impregnated with acid potassium ortho-phosphate (KH_2PO_4) that, in the finished state, 1 part K_2O was present in the form of this potassium salt, per 100 parts Fe.

The catalyst was dried at 110° C. and then reduced for 60 minutes at 235° C. by means of a mixture of hydrogen and nitrogen. The speed of flow of the gas amounted (measured cold) to 1.4 m/sec. After this treatment the finished catalyst contained 32% free iron, relative to the total content of iron and iron oxide, the content of ferrous oxide being 60% and that of ferric oxide being 8%.

In the use of the catalyst so obtained, 100 litres of water gas were passed over one litre of catalyst per hour at a temperature of 210° C. The (CO+H$_2$) conversion reached 73%, corresponding to a carbon monoxide conversion of 93.5%. The methane formation amounted to about 8%.

When, in the manufacture of the catalyst, the reduction temperature was raised from 235° C. to 300° C., the catalyst, under the same synthesis conditions, showed a somewhat lesser conversion, and an increase in methane formation to about 14%.

As a result of lowering the reduction temperature from 235° C. to 200° C. and retaining the speed of flow of the gas of 1.4 m/sec., the conversion diminished from 73% to 51%. When the speed of flow of the reduction gases was lowered to 0.35 m/sec., the conversion at the same reduction temperature fell to about 58%.

In the step of impregnating the catalyst, it has been found advantageous to use a solution of the alkali-metal compound of a strength of 5—10%.

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 production of iron catalysts, particularly for the hydrogenation of carbon monoxide, in which a solution of iron nitrate and a solution or solutions of nitrates of suitable activators are precipitated to yield the hydroxides and/or carbonates of iron and of the activators, the hydroxides and/or carbonates being thereafter reduced in a stream of reduction gas at a temperature below 300° C., and preferably within the range 200° C.—240° C., for a period of 30—60 minutes, the rate of flow of the reduction gas being within the range 1.3—1.5 metres per second.

2. A process according to claim 1, in which the hydroxides and/or carbonates are precipitated on to a carrier substance such as Kieselguhr, aluminium oxide and magnesium oxide.

3. A process according to claim 1 or claim 2, in which the precipitation is effected by means of an aqueous solution of sodium carbonate.

4. A process according to any one of the preceding claims, in which the catalyst, prior to treatment with the reduction gas, is impregnated with an alkali-metal compound.

5. A process according to claim 4, in which the compound is an alkali-metal salt of a non-volatile mineral acid.

6. An iron catalyst for the hydrogenation of carbon monoxide at approximately atmospheric pressure, in which the iron is in the form of iron and iron oxides in proportions relative to each other of 25%—35% of metallic iron, 50%—61% of ferrous oxide and 25% to 4% of ferric oxide, the catalyst being impregnated with 0.5%—5%, preferably 1%—3% of an alkali-metal, calculated as the monoxide, relative to the total iron content of the catalyst, and produced according to the process of claim 4 or claim 5.

7. A process for the production of an iron catalyst, substantially as hereinbefore described.

8. A process for the production of an iron catalyst, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

Dated this 15th day of June, 1949.

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Agents for the Applicants.

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