PATENT SPECIFICATION

711,406

Date of Application and filing Complete Specification April 10, 1952.

No. 9317/52.

Application made in Germany on April 16, 1951.

Complete Specification Published June 30, 1954.

Index at acceptance:—Classes 1(1), F3B1; and 2(3), B1G, C3A13A3A1C, C3A13A3B(1: 2), C3A13A3(J2: M).

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 M.B.H., of Frankfurt a.M.—Heddernheim, 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 hydrogenation of carbon monoxide in the presence of a precipitated iron catalyst and to a process for the production of the catalyst.

It is known that, on the one hand, products containing more or less large quantities of oxygen-containing organic compounds, principally alcohols, and on the other hand products consisting almost entirely of hydrocarbons, may be obtained by the hydrogenation of carbon monoxide carried out under atmospheric or elevated pressure, and with the use of catalysts of various compositions. These catalysts include fused catalysts, sintered catalysts and precipitated catalysts.

In the preparation of the precipitated catalysts, iron and, if necessary or desired, activator metals to be added are in general brought into the form of their nitrate solutions. The nitrates are easily soluble and, by precipitation with alkali compounds such, for example, as sodium carbonate or potash, give precipitates which may be readily filtered, and which yield very active catalysts after reduction. It is one of the advantages of the use of the nitrates that the residual alkali remaining in the precipitated catalyst mass after the precipitation, contains no contaminants which cannot easily be removed by carefully washing with water.

A disadvantage of the precipitated catalysts is the high cost of the nitrate solutions used for the precipitation. It is always necessary to dissolve the corresponding metals in excess nitric acid which, owing to the high price of the nitric acid used, adds considerably to the cost of catalysts of this type. Moreover, appreciable losses of nitric acid occur during the process of solution itself. It has been proposed to evaporate the mother liquor separated from the precipitate and to recover the valuable nitrates contained therein; such procedure, however, is expensive.

It has now been found that the catalytic hydrogenation of carbon monoxide may be carried out with the use of iron catalysts precipitated from sulphate solutions. During the precipitation of these catalysts, a part (approximately one third) of the iron is converted into the trivalent form. The precipitate is washed with an aqueous solution of ammonia, of an ammonium salt or of an organic compound derived from ammonia and in the form of an aliphatic amine, preferably of a readily soluble compound of ammonia, and oxidation of the residual iron is carried out during the washing and principally during the drying in such a manner that approximately 70% to 98% of the total Fe is finally present in the trivalent form (Fe^{III}). Iron sulphate is obtained as a cheap waste product in various chemical processes, for example in pickling processes and in the production of titanium white.

The impurities contained in the sulphate obtained from such sources are negligible and have no adverse effect.

According to the invention, a process for the catalytic hydrogenation of carbon monoxide comprises the use of an iron catalyst obtained by the precipitation of a solution of iron sulphate in such manner that from about 10% to 50% of the iron in the precipitate is in the trivalent form, the step of washing the precipitate being carried out with the use of an aqueous solution of ammonia or of an ammonium salt or of an aliphatic amine, preferably an aqueous solution of a readily soluble ammonium compound, whilst further oxidation of the iron in the precipitate from the bivalent to the trivalent form is effected during the washing and drying of the precipitated mass by means of a gaseous oxidising medium so that more than 70% of the iron is in the trivalent form upon completion of the drying.

According to the invention furthermore, a process for the production of an iron catalyst for use in the hydrogenation of carbon monoxide includes the steps of precipitating an aqueous solution of ferrous sulphate by means of an aqueous solution of an alkali-metal hydroxide, carbonate or bicarbonate at a temperature within the range 50°—100° C. whilst passing air through the mixture to convert from 10% to 50% of the iron in the precipitate into the trivalent form, washing the precipitate substantially free from sulphate ions, the washing being effected at least in part, by means of a solution of a readily soluble ammonium compound and drying the precipitated catalyst mass in a stream of heated air to bring more than 70% of the iron in the mass into the trivalent form.

Care has to be taken in the production of catalysts with the use of iron sulphate that practically no sulphur in the form of sulphate is contained in the finished catalyst since, during the reduction of the catalyst, sulphide would form and the hydrogen sulphide produced would immediately poison the catalyst.

It is required in the process for the production of catalysts with the use of iron sulphate that at least a part of the bivalent iron is converted into the trivalent form. In the precipitation preferably 25- 35% of the iron is in the trivalent state. For carrying out the precipitation, the iron sulphate is dissolved in hot water or the solution of iron sulphate is heated. The concentration of the Fe^{II} should be between 5 and 100 grams, preferably between 20 and 60 grams of Fe per litre. The solution is heated with the addition, if necessary or desired, of activators such, for example, as copper, silver or calcium. The alkali solution to be used for the precipitation, for example, an aqueous solution of an alkali-metal hydroxide, carbonate or bicarbonate, is likewise heated. Immediately before starting the precipitation, an oxygen-containing gas, for example, a powerful stream of air, is blown through the hot solution of the alkali-metal compound, for example, sodium carbonate. The purpose of this step is to convert at least part of the ferrous hydroxide formed during precipitation into ferric hydroxide. The flow rate of the air which, if desired, is first passed through a preheater to heat it to temperatures of between 80° C. and 100° C., should be such that approximately 10 to 50, preferably 20 to 30, cubic metres of air per kilogram of iron are hourly blown through the solution. Immediately thereafter, the precipitation is carried out in known manner by adding the heated sulphate solution to the hot alkali solution and the precipitation is completed in approximately 2 to 6 minutes. During the whole time the stream of air is blown through at the rate mentioned above. In this manner, approximately 25% to 35% of the iron is obtained in the trivalent form in the precipitated catalyst mass. During the precipitation the temperatures are about 50° C. to 100° C., preferably 60° C. to 95° C. It is not absolutely necessary, however, for the alkali and iron solutions to be at the same temperatures.

For the preparation of a highly active catalyst with the use of ferrous sulphate, it is important that the alkali adsorbed on the iron hydroxide should be removed as completely as possible, which alkali is now present in the form of sulphate. Washing the precipitated catalyst mass with hot condensate water, such as is effected when employing iron nitrate solutions, will not be sufficient for this purpose. It is necessary to provide ammonia, an ammonium salt or an aliphatic amine in solution in the condensate water used for the washing in order to attain a considerably easier removal of the sulphate ions by ion exchange. For example, ammonium compounds of the type of ammonium nitrate, ammonium carbonate and ammonium acetate have proved to be particularly effective, but various other easily soluble ammonium compounds are also useful for this purpose. NH_3 is also suitable depending on the kind of the catalyst.

It is advantageous to have not too high a concentration of the ammonia, ammonium compound or aliphatic amine in the condensate water used at the beginning, since in the first phase of the washing much of the alkali sulphate adsorbed on the iron hydroxide can be removed by washing with condensate water alone. Only in the last or later phase or phases of the washing is it necessary to add or increase the quantity of the ammonia, ammonium compound or aliphatic amine, for example, ammonium carbonate or nitrate. The concentration of the ammonia, ammonium compound or amine in the wash water may range between 0.2% and 20%; the washing is preferably effected with wash waters containing approximately 0.2% to 2% of ammonia, ammonium compound or amine. The preferred aliphatic amines are primary amines.

A sulphur content in the catalyst of not more than 0.1%, particularly below 0.5%, has been found to have no adverse effect.

The further steps in the preparation of the catalyst from iron sulphate, are practically the same as those known in the art when the catalyst is produced from a solution of iron nitrate. The carefully washed catalyst mass may be impregnated in accordance with the particular kind of synthesis in which it is to be used, moulded, if necessary or desired, and dried at temperatures of about 100°—110° C. to give a finished catalyst having a water content of approximately 3—5%.

It is essential, however, that some or all of these steps be carried out in the presence of an abundant supply of oxidising media, preferably air. Much air may be used at elevated temperature when blowing the washed catalyst mass dry in the filter press, and the final drying in the drier may likewise be carried out with an abundant flow of air, whereby at the end more than 70%, preferably more than 80% of the total iron is present in trivalent form (Fe^{III}). When preparing the catalyst in small quantities with the use, for example, of a suction filter, a good oxidation is obtained by filtering and washing the precipitated catalyst mass in thin layers.

The prepared catalyst particles are freed from dust and splintered grains by sieving and may then be reduced with the use of hydrogen, carbon monoxide, or their mixtures with nitrogen. The reduction temperatures are in the range 150°—350° C., preferably in the range 220°—320° C. A high flow rate of the reduction gases of more than 50 centimetres per second, preferably of more than 1 metre per second, is generally advantageous. The thickness of the layer of catalyst during the reduction may be less than 30 cm., but is preferably between 30 cm. and 100 cm.; it may, however, be considerably greater. If desired, the reduction may even be carried out in the synthesis reactor itself. The catalysts in accordance with the invention may also contain determined quantities of carrier substances such, for example, as kieselguhr, Al_2O_3, Tonsil, activated bleaching earths or fuller's earth.

It has been found that in carrying out the synthesis for the production of oxygen-containing organic compounds, particularly alcohols catalysts prepared in accordance with the invention should contain at least 50%, preferably more than 60%, of their content of iron in the form of metallic iron. For the production of oxygen-containing organic compounds furthermore, the catalysts advantageously contain from 2% to 15%, preferably from 4% to 12%, of alkali (measured as K_2O) in the form of a hydroxide, an oxide or a carbonate or of a salt of another volatile decomposable acid, based on the total iron present in the catalyst.

On the other hand, a higher content of hydrocarbons in the synthesis products may be obtained when using catalysts of corresponding composition prepared in accordance with the invention, and maintaining the content of free iron in the reduced catalyst below 50%, preferably below 30% of the total iron content. Catalysts of this kind are advantageously impregnated with an alkali-metal salt of a non-volatile acid, such as boric acid, phosphoric acid, silicic acid or tungstic acid, the content of the acid component (measured as SiO_2) in the catalyst being more than 1%, preferably more than 10% by weight of the total amount of iron in the catalyst, and the quantity of alkali (measured as K_2O) being from approximately 1% to 10%, preferably from 1% to 7%, by weight of the total amount of iron present in the catalyst.

When using the catalysts in accordance with the invention, the synthesis may be carried out in either single-stage or multi-stage operation and with either once-through passage of the gas or gas recycling. In multi-stage operation, partial removal, between the individual stages, of the carbon dioxide formed is of advantage. The synthesis pressures should be from 1 to more than 100 atmospheres, preferably from 20 to 40 atmospheres. The synthesis temperatures are between approximately 150° C. and 300° C. The gas load may be varied within wide limits, from approximately 10 volumes of gas per volume of catalyst per hour to more than 500 volumes of gas per volume of catalyst per hour. The gas may contain between 0.5 and 2 volumes of hydrogen, and more, per volume of carbon monoxide. The catalyst layer depths may, for example, be 5 metres; they may, however, be more than 5 metres, for example, up to 12 metres approximately.

The invention is illustrated by the following examples.

EXAMPLE 1.

A boiling solution consisting of iron sulphate and copper sulphate, containing 5 parts of copper for every 100 parts of iron and having a concentration of 40 parts of iron in 1000 parts of water, was precipitated by pouring it into a sodium carbonate solution, the temperature of which was 80° C., containing 90 grams of Na_2CO_3 per litre. During the precipitation, a stream of air was blown through the precipitation apparatus, the quantity of air being 600 litres for every 25 grams of iron, the blowing time being 3.5 minutes. Immediately thereafter the precipitated catalyst mass was freed from the mother liquor by subjecting it to suction filtration and was then washed twice with a quantity of boiling condensate water corresponding to twelve times the quantity of iron present. Finally, the catalyst mass was washed three times by suspending it in an aqueous ammonium carbonate solution containing 5—10 grams of ammonium carbonate dissolved in 1500 cc./1500 cc. of washing solution for every 2 grams of iron were used in each of the three washings. After the last washing, the sulphur content of the finished catalyst was only 0.02%. 28% of the total amount of iron was now present as Fe^{III}, the balance being Fe^{II}. The catalyst mass was then impregnated with a potassium carbonate solution in such manner that 8 parts of alkali, measured or calculated as K_2O, for every 100 parts of iron were contained in the mass.

The catalyst mass was dried for 24 hours at a temperature of 110° C. with circulation of air and crushed to a particle size of 2—4 mm. The content of Fe^{III} was now 88%. Thereafter, the catalyst was reduced for one hour at a temperature of 300° C., using a gas mixture consisting of 75% of hydrogen and 25% of nitrogen at a linear gas velocity of 1.4 metres per second, measured in the cold state. The reduction value of the catalyst, that is to say, the proportion of the total iron content of the catalyst present as free iron, was 68%.

This catalyst was then used in the synthesis at a synthesis pressure of 30 atmospheres with a gas load of 100 volumes of water gas per volume of catalyst per hour. A conversion rate of 60% $CO+H_2$ was obtained at a temperature of 205° C. The methane formation was between 4.5% and 6% approximately. The yield of oxygen-containing organic compounds was 50%, based on total liquid product.

Example 2.

A solution consisting of iron sulphate and copper sulphate, containing 2 parts of copper for every 100 parts of iron and having a concentration of 45 parts of iron for every 1000 parts of water, was heated to 90° C. and precipitated by pouring it into a solution of sodium carbonate, the temperature of which was 75° C., and which had a concentration of 68 grams of Na_2CO_3 per litre. The pH value during the precipitation was 7.2. During the precipitation, a stream of air was blown through the precipitation apparatus using 650 litres of air per 25 grams of iron and a blowing time of 4.5 minutes. Thereafter, calcium carbonate in a quantity of 10%, calculated as CaO and based on the iron present, was added while vigorously stirring the mixture. Immediately thereafter the precipitated mass was separated from the mother liquor by subjecting it to suction filtration and washed with a quantity of boiling condensate water corresponding to 12 times the iron present. Finally, the catalyst mass was washed twice by suspending it in a solution of ammonium carbonate containing at first 4 grams, and then 10 grams of ammonium carbonate dissolved in 1500 cc. of solution. The sulphur content after the last washing was 0.05%. 28.5% of the total iron was now present in the form of Fe^{III}, the remainder being Fe^{II}.

The catalyst was then impregnated with a solution of potassium silicate so that 3 parts of K_2O and 7.6 parts of SiO_2 for every 100 parts of iron were contained therein.

The catalyst mass was dried for 24 hours with circulating air at a temperature of 105° C. and crushed to a particle size of 1.5—3 mm. The content of Fe^{III} was now 91%. Thereafter, the catalyst was reduced for 90 minutes at a temperature of 305° C., using a gas mixture consisting of 75% of H_2 and 25% of N_2 at a linear gas velocity of 1.4 metres per second (measured in the cold state). The reduction value of the catalyst was 35%.

The catalyst was used in the synthesis at a synthesis pressure of 10 atmospheres, using a gas load of 100 volumes of water gas ($CO:H_2=1:1.2$) per volume of catalyst per hour. A conversion rate of 66% of $CO+H_2$ was obtained at a temperature of 215° C. The resulting liquid product contained 40% of hydrocarbons boiling above 320° C. Oxygen-containing organic compounds were present only in small quantities.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide with the use of a precipitated iron catalyst, in which the catalyst is precipitated from a solution containing iron sulphate in such manner that approximately 10%—50% of the iron in the precipitate is converted into the trivalent form, the step of washing the precipitate being carried out with the use of an aqueous solution of ammonia or of a ammonium salt or of an aliphatic amine, preferably an aqueous

solution of a readily soluble ammonium compound, whilst further oxidation of the iron in the precipitate from the bivalent to the trivalent form is effected during the washing and drying of the precipitated mass by means of a gaseous oxidising medium so that more than 70% of the iron is in the trivalent form upon completion of the drying.

2. A process according to claim 1, in which the gaseous oxidising medium is air.

3. A process according to claim 1 or claim 2, in which air is blown through the mixed solutions of iron sulphate and precipitant during the precipitation.

4. A process according to any one of the preceding claims, in which 25%—35% of the iron in the precipitate is in the trivalent form.

5. A process according to any one of the preceding claims, in which more than 80% of the iron is in the trivalent form upon completion of the drying.

6. A process according to any one of the preceding claims, in which the concentration of the ammonia or of the ammonium salt or of the aliphatic amine in the wash-water is increased during the course of the washing.

7. A process according to any one of the preceding claims, in which the content of the ammonia or of the ammonium compound or of the alphatic amine in the wash-water is in the range 0.2%—20%, preferably in the range 0.2%—2%.

8. A process according to any one of the preceding claims, carried out to give a high yield of oxygen-containing organic compounds in the synthesis products, in which the catalyst contains 2%—15% of alkali (measured as K_2O), based on the total iron content of the catalyst, in the form of hydroxide, oxide or carbonate or salt of another volatile or decomposable acid.

9. A process according to claim 8, in which the content of alkali (measured as K_2O) is within the range 4%—12%.

10. A process according to any one of the preceding claims, carried out to give a high yield of oxygen-containing organic compounds in the synthesis product, in which at least 50% of the iron in the catalyst is in the metallic state.

11. A process according to claim 10, in which at least 60% of the iron is in the metallic state.

12. A process according to any one of claims 1 to 7 carried out to give a high yield of hydrocarbons in the synthesis product, in which the catalyst is impregnated with an alkali-metal salt of a non-volatile acid such, for example, as boric acid, phosphoric acid, silicic acid or tungstic acid, the content of the acid component (measured as SiO_2) in the catalyst being more than 1% by weight of the total amount of iron in the catalyst and the quantity of alkali (measured as K_2O) being from 1% to 10% by weight of the total amount of iron in the catalyst.

13. A process according to claim 12, in which the content of the acid component (measured as SiO_2) in the catalyst is more than 10% by weight of the total amount of iron in the catalyst and the quantity of alkali (measured as K_2O) is in the range 1%—7% by weight of the total amount of iron in the catalyst.

14. A process according to any one of claims 1 to 7 or according to claim 13, carried out to give a high yield of hydrocarbons in the synthesis product, in which less than 50% of the iron in the catalyst is in the metallic state.

15. A process according to claim 14, in which less than 30% of the iron in the catalyst is in the metallic state.

16. A process according to any one of the preceding claims in which an aqueous solution of ammonium carbonate, ammonium nitrate or ammonium acetate is used in the washing of the precipitate.

17. A process according to any one of the preceding claims, in which the synthesis is effected at a temperature within the range 150°—300° C. and at a pressure in the range 1—100 atmospheres.

18. A process according to claim 17, in which the synthesis is effected at a pressure with in the range 20—40 atmospheres.

19. A process according to any one of the preceding claims, in which the feed gas to the synthesis contains from 0.5 to 2 volumes of hydrogen per volume of carbon monoxide.

20. A process for the production of an iron catalyst for use in the hydrogenation of carbon monoxide, which includes the steps of precipitating an aqueous solution of ferrous sulphate by means of an aqueous solution of ferrous sulphate by means of an aqueous solution of alkali-metal hydroxide, carbonate or bicarbonate at a temperature within the range 50°—100° C., whilst passing air through the mixture to convert 10%—50% of iron in the precipitate into the trivalent form, washing the precipitate substantially free from sulphate ions, the washing being effected at least in part, by means of a solution of a readily soluble ammonium compound, and thereafter drying the precipitated catalyst mass in a stream of heated air, whereby more than 70% of the iron in the mass is brought into the trivalet form.

21. A process according to any one of

the preceding claims, in which the finished catalyst contains less than 0.1% of sulphur.

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

23. A process for the production of an iron catalyst, substantially as hereinbefore described in Example 1 or Example 2.

24. A process for the hydrogenation of carbon monoxide, in the presence of a precipitated iron catalyst, the preparation of the catalyst and the hydrogenation of the carbon monoxide being carried out substantially as hereinbefore described in Example 1 or Example 2.

25. An iron catalyst obtained by the process claimed in claim 20, claim 22 or claim 23.

26. Hydrocarbons and oxygen-containing organic compounds whenever obtained by the process claimed in claim 24 or in any of the claims 1 to 19.

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

PATENT SPECIFICATION

711,406

Date of Application and filing Complete Specification April 10, 1952.
No. 9317/52.
Application made in Germany on April 16, 1951.
Complete Specification Published June 30, 1954.

Index at acceptance :—**Classes 1(1)**, F3B1 ; **and 2(3)**, B1G, C3A13A3A1C, C3A13A3B(1 : 2), C3A13A3(J2 : M).

COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

...tals in excess nitric acid which,

ERRATA

SPECIFICATION No. 711,406

Page 2, line 115, *for* "aliphate" *read* "aliphatic"
Page 3, line 6, *for* "0.5%" *read* "0.05%"
Page 4, line 21, *for* "2 grams" *read* "25 grams"
Page 5, lines 114—115, *after* "of" *delete* "ferrous sulphate by means of an aqueous solution of"
Page 5, line 115, *for* "alkali-" *read* "an "alkali-"

THE PATENT OFFICE,
6th August, 1954.

---

carried out under atmospheric or elevated pressure, and with the use of catalysts of various compositions. These catalysts include fused catalysts, sintered catalysts and precipitated catalysts.

In the preparation of the precipitated catalysts, iron and, if necessary or desired, activator metals to be added are in general brought into the form of their nitrate solutions. The nitrates are easily soluble and, by precipitation with alkali compounds such, for example, as sodium carbonate or potash, give precipitates which may be readily filtered, and which yield very active catalysts after reduction. It is one of the advantages of the use of the nitrates that the residual alkali remaining in the precipitated catalyst mass after the precipitation, contains no contaminants which cannot easily be removed by carefully washing with water.

A disadvantage of the precipitated catalysts is the high cost of the nitrate solutions used for the precipitation. It is always necessary to dissolve the corres-

tion of the residual iron is carried out during the washing and principally during the drying in such a manner that approximately 70% to 98% of the total Fe is finally present in the trivalent form (Fe^{III}). Iron sulphate is obtained as a cheap waste product in various chemical processes, for example in pickling processes and in the production of titanium white.

The impurities contained in the sulphate obtained from such sources are negligible and have no adverse effect.

According to the invention, a process for the catalytic hydrogenation of carbon monoxide comprises the use of an iron catalyst obtained by the precipitation of a solution of iron sulphate in such manner that from about 10% to 50% of the iron in the precipitate is in the trivalent form, the step of washing the precipitate being carried out with the use of an aqueous solution of ammonia or of an ammonium salt or of an aliphatic amine, preferably

[*Price* 2/8]

Price