PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A process for the production of Iron Catalysts for the Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Joint Stock Company, of (22A) Homberg, Niederrhein, Germany, 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 production of a highly active iron catalyst which contains kieselguhr and an alkaline earth metal in addition to copper and an alkali-metal.

It has hitherto been usual in the precipitation of iron catalysts containing kieselguhr and an alkaline earth, to add the kieselguhr to the nitrate solution, the iron catalyst being then precipitated by the addition of such a quantity of an alkali-metal carbonate or an alkali-metal hydroxide that a pH value of 7—8 was obtained. After washing, the catalyst was then dried at a temperature of about 110° C.

When used at normal pressure, the activity and life of catalysts so produced do not exceed those of carrier-free or unsupported catalysts. Thus they give a yield of about 60—70 grams of hydrocarbons having more than one carbon atom per molecule, per normal cubic metre of $CO+H_2$, and have a life of from 4 to 6 weeks.

Also, when used at a gauge pressure of 10 atmospheres, they do not exhibit any better properties than the catalysts having no carrier or support; on the contrary, they tend to give an increased formation of methane and, owing to their relative lack of firmness or toughness, their life is short.

It has now been found that an iron catalyst containing kieselguhr, copper, an alkali-metal and an alkaline earth metal, of an unusually high activity and of long life is obtained if the following measures are used in its production:—

1. The solution of the iron, copper and alkaline earth metal nitrates is added batchwise to the alkali-metal carbonate solution or alkali-metal hydroxide solution in which the kieselguhr is suspended.
2. The quantity of the nitrate solution added is increased with each batch; for example, the total nitrate solution may be added in batches in the following quantities—5%, 10%, 15%, 20%, 23%, and 27%.
3. The second and every succeeding batch of nitrate solution is not added until the evolution of carbon dioxide, consequent upon the addition of the preceding batch has ceased. Commercial grades of alkali-metal hydroxides generally contain minor proportions of alkali-metal carbonate and when solutions of such hydroxides are used for the precipitation, carbon dioxide is generally evolved. This would not be the case if the alkali-metal hydroxides were pure.
4. Upon completion of the precipitation, the catalyst slurry or sludge is brought to the boil within 5—20 minutes, preferably within 8—12 minutes, and the boiling then continued for a further 2—7 minutes, preferably 3—5 minutes.
5. In the precipitation, an excess of 5%—40%, preferably 10%—30%, of the alkali-metal compound is used relatively to the quantity of the alkali-metal compound required to reach the end or equivalent point.
6. The nitrate solution has added thereto from 5% to 40%, preferably 10% to 25%, of HNO_3 based on the weight of the nitrate solution.
7. The concentration of the nitrate solutions is not lower than 2% and preferably not lower than 5%.
8. The catalyst is dried at temperatures below 80° C., preferably below 60° C.

These measures may be applied singly or together. Each individual measure improves the properties of the catalyst but only when all the measures are applied, is a catalyst of optimum activity obtained.

The effects of these measures are hereinafter described in detail.

The solution of alkali-metal carbonate or alkali-metal hydroxide is normally introduced into the nitrate solution more or less rapidly in one stream, or at intervals. By such an acid type of precipitation, reproduction of the properties of an iron catalyst containing kieselguhr and an alkali is particularly irregular. For the most part, the iron catalysts obtained are of a dark colour and of little toughness or hardness, and their efficacy hardly differs from that of known catalysts. Only when the iron catalyst containing kieselguhr and an alkaline earth is precipitated in alkaline solution, that is to say, when the nitrate solution is added to the solution of the alkali-metal, and that in batches, is it increasingly assured that catalysts substantially uniform in their properties are obtained. However,this is ensured only when the first batch added is small and the subsequent batches added are successively increased so that the precipitation is effected in about five to seven steps, that is to say, the nitrate solution is added in about five to seven batches, each batch of which is greater than the preceding batch. It is important, in this batchwise addition of the nitrate solution to the alkali solution, that the individual batches be added quickly and then to wait until the evolution of carbon dioxide is complete.

When these conditions are strictly observed, there will always be obtained catalysts which are distinguished by their light colour and great hardness or toughness; it is these characteristics which are necessary for good activity.

Furthermore, the measures hereinbefore referred to under heading 4 are important for the reproduction of the properties of the iron catalyst. If the catalyst slurry or sludge is brought to the boil too quickly, it froths or foams very strongly, whilst if it is brought to the boil too slowly, it hardly froths at all. In both instances, a catalyst of dark colour is obtained, the activity of which differs in no wise from that of an unsupported or carrier-free catalyst. This also applies to the boiling process itself. When the catalyst slurry or sludge is, for example, boiled for one minute only, although it will be light in colour, its activity will be poor. On the other hand, when the catalyst slurry or sludge is boiled for too long a period, it is of a dark appearance and its activity is also low. It is only when the stated periods are observed that a catalyst of good activity is ensured. With an iron catalyst precipitated under the conditions hereinbefore set forth under headings 1—4 and without prior reduction of the catalyst, a yield of 105—115 grams per normal cubic metre of $CO+H_2$ is obtained with a hydrogen-rich synthesis gas under normal pressure at a temperature of 225° C.—235° C. as compared with a former yield of 60—70 grams per normal cubic metre of $CO+H_2$.

The measures hereinbefore set forth under headings 5—8 were found when attempts were made to increase the activity of the iron catalyst by varying the conditions under which precipitation was effected. Nothing can be found in the literature about the use of metal nitrate solutions which also contain nitric acid. With respect to the use of excess alkali, it is only known to use so much alkali that the precipitated solution has a pH of 8. The measure given under heading 5 uses an amount of alkali which is considerably in excess of that required to neutralise the acid solution of the metal nitrates. Iron catalysts have, hitherto, been dried almost exclusively at a temperature of about 110° C. and no reference can be found in the relevant literature that it is of particular advantage to carry out the drying at a lower temperature.

When the conditions hereinbefore set forth under headings 5—8 are also applied in the production of an iron catalyst, the activity of the catalyst is greater than that of similar, previously known catalysts. When used with a hydrogen-rich synthesis gas, such catalysts convert 90% of the carbon monoxide at a temperature of 185° C.—225° C. and at normal pressure. The life of the catalyst is increased to 7—8 months and the yield, according to the synthesis conditions, increases to 120—160 grams per normal cubic metre of $CO+H_2$.

An iron catalyst precipitated according to the invention is not only able to work up under normal pressure a hydrogen-rich synthesis gas, but it is also able to work up watergas at temperatures of 205° C.—235° C. to produce a yield of 135—165 grams per normal cubic metre of $CO+H_2$, 25%—50% of hydrocarbons being obtained with boiling points above 320° C., according to the degree of alkalisation.

It is thus also possible to use these iron catalysts successfully in the Fischer-Tropsch plants which have been designed for use with cobalt catalysts, the synthesis with the iron catalysts being carried out under the same synthesis conditions as are used with cobalt catalysts. Though the weight of the yield obtained in this manner without the use of additional operating means amounts only to 90% of that obtained with cobalt catalysts, the monetary value of that lower yield may exceed by 20%—60% the value of the higher yield obtained with cobalt catalysts.

When iron catalysts produced according to the invention are used at a gauge pressure of 10—50 atmospheres, the reaction temperature of 190° C.—220° C. is 20° C.—30° C. lower than that hitherto required. The low-boiling products are distinguished by a high olefin content, whilst the higher boiling products are strongly saturated.

After the catalyst slurry or sludge has been boiled, it is filtered and the precipitate is washed and dried. The catalyst is brought to its desired alkali-metal content at the stage of washing; the precipitate is either incompletely washed thereby reducing its alkali-metal content to the desired level or the precipitate is washed until it is free of, or contains less than the desired quantity of, alkali-metal and is then impregnated with an alkali-metal compound to bring the alkali-metal content to the desired level.

The following example illustrates the measures taken according to the invention.

100 parts of iron, 10 parts of copper and 15 parts of magnesium were present as nitrates in a solution of 6% concentration, the solution containing also 12% of added HNO_3 and being at room temperature. Six portions of the nitrate solution in the following amounts—6%, 12%, 15%, 19%, 22% and 26%, were successively added to a sodium carbonate solution of 14% concentration which contained 16% of sodium carbonate in excess of the equivalent quantity and in which 50 parts of kieselguhr were suspended. The time between the addition of each portion of the nitrate solution was such that the evolution of carbon dioxide, caused by the addition of the previous portion of the nitrate solution, had ceased. The catalyst slurry was then brought to the boil within nine minutes and was then boiled for a further three minutes. After filtering and washing the precipitate, it was alkalised with 2% of potassium carbonate and then dried at 50° C.

Without previous reduction, the catalyst so produced converted 90% of the carbon monoxide of a hydrogen-rich synthesis gas ($1CO:2H_2$) at normal pressure and at a temperature of 215° C.—225° C. The yield of hydrogenation products amounted to 120—130 grams per normal cubic metre of $CO+H_2$. 25%—30% of the synthesis products obtained had boiling points of over 320° C.

When the catalyst was pre-treated or reduced with a hydrogen-rich synthesis gas and then used in synthesis, with recycling, with a synthesis gas of the composition $1CO:2H_2$ at a space velocity of 50, more than 90% of the carbon monoxide was converted at temperatures of 190° C.—205° C. The yield of synthesis products per normal cubic metre of $CO+H_2$, increased to 130—145 grams.

When water-gas was used at normal pressure, even without previous reduction of the catalyst, at temperatures of 225° C.—235° C., a yield of 135—155 grams per normal cubic metre of $CO+H_2$ was obtained, 25%—40% of hydrocarbons being obtained with boiling points above 320° C. The life of the catalyst was at least four to six months.

At a gauge pressure of 10 atmospheres, water-gas gave, even at temperatures of 200° C.—210° C., a carbon monoxide conversion of over 90% with a yield of 165—185 grams per normal cubic metre of $CO+H_2$. The proportion of hydrocarbons boiling above 320° C. increased to 30%—65%.

What we claim is:—

1. A process for the production of an iron catalyst containing copper, an alkali-metal, kieselguhr and an alkaline earth metal as activators or carriers, which comprises precipitating a solution containing iron nitrate, copper nitrate and the nitrate of an alkaline earth metal, by adding the nitrate solution in batches to a solution of an alkali-metal carbonate or an alkali-metal hydroxide in which kieselguhr is suspended, the first batch of the nitrate solution so added being small and the further batches being increased in quantity at each addition, the second and each succeeding batch not being added until evolution of carbon dioxide consequent upon addition of the preceding batch has ceased, bringing the catalyst slurry or sludge to the boil within five to twenty minutes of completion of the precipitation and then boiling the catalyst slurry or sludge for a period of two to seven minutes, following by filtering, washing and drying the precipitate, the catalyst being brought to its desired alkali-metal content by incompletely washing the precipitate and/or by impregnating the washed precipitate with an alkali-metal compound.

2. A process according to claim 1, in which the catalyst slurry or sludge is brought to the boil within eight to twelve minutes of the completion of precipitation.

3. A process according to claim 1 or claim 2, in which the catalyst slurry or sludge is, upon being brought to the boil, boiled for a period of three to five minutes.

4. A process according to any one of the preceding claims, in which the alkaline solution contains 5%—40% of the alkaline material in excess of that required to attain the end or equivalent point.

5. A process according to claim 4, in which the alkaline solution contains an excess of 10%—30% of the alkaline material.

6. A process according to any one of the preceding claims, in which the nitrate solution has added thereto from 5% to 40% of HNO_3.

7. A process according to claim 6, in which 10%—25% of HNO_3 is added.

8. A process according to any one of the preceding claims, in which the concentration of the nitrate solution is not below 2%.

9. A process according to any one of the preceding claims, in which the concentration of the nitrate solution is not below 5%.

10. A process according to any one of the preceding claims, in which the precipitated catalyst is dried at a temperature not exceeding 80° C.

11. A process according to claim 10, in which the catalyst is dried at a temperature not exceeding 60° C.

12. A process according to any one of the preceding claims, in which the nitrate solution is added to the solution of the alkali-metal carbonate or alkali-metal hydroxide in

five to seven batches.

13. A process for the production of an iron catalyst for use in the hydrogenation of carbon monoxide, which includes all of the measures hereinbefore described.

14. A process for the production of an iron catalyst, substantially as hereinbefore described with reference to the Example.

15. An iron catalyst whenever produced by the process of any preceding claim.

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