PATENT SPECIFICATION

702,246

Date of Application and filing Complete Specification April 1, 1952.
No. 8322/52.
Application made in Germany on April 5, 1951.
Application made in Germany on July 13, 1951.
(Patent of Addition to No. 679,785 dated Sept. 6, 1950).
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Index at acceptance :—Class 1(1), F3B1.

COMPLETE SPECIFICATION

Improvements in or relating to Iron Catalysts

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Company, and LURGI GESELLSCHAFT FUER WAERMETECHNIK M.B.H., of Frankfurt am Main, 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 method for the production of iron catalysts, particularly of iron catalysts for use in the hydrogenation of carbon monoxide.

In the co-pending Application No. 22006/50 (Serial No. 679,785) there is described a method for the production of an iron catalyst for use in the hydrogenation of carbon monoxide, the catalyst so produced being effective to give a high degree of conversion of the synthesis gas with a load, or space velocity of the synthesis gas which is several times the normal load or space velocity.

The iron catalyst contains no carrier substance or only small amounts of a carrier substance and the method of its production which is described and claimed in the co-pending application comprises precipitating, with intensive stirring, a hot solution of iron nitrate with a hot solution of an alkali-metal hydroxide or of an alkali-metal carbonate to give a solution having a pH value within the range 6.8—7.2 upon completion of the precipitation washing the precipitate to reduce its content of alkali-metal compounds, calculated at K_2O, to a maximum of 0.5 parts by weight of K_2O per 100 parts by weight of iron, converting the precipitate into a homogeneous, aqueous suspension, adding a solution of an alkali-metal silicate to the suspension to give 20 to 25 parts by weight of SiO_2 per 100 parts by weight of iron, treating the suspension with nitric acid to yield, after filtration, a catalyst mass having a ratio of alkali-metal oxide, calculated as K_2O, to SiO_2 of from 1 : 4 to 1 : 5; moulding the catalyst mass, drying the moulded catalyst and then reducing the dried and moulded catalyst at a temperature within the range 200°—350° C. with a reducing gas at linear velocities of the reducing gas of from 1 to 2 metres per second to yield a catalyst containing from 30% to 50% of its total content of iron in the form of metallic iron.

In the specific example described, the alkali-metal silicate used was potassium silicate, the solution being of commercial composition ($K_2O : SiO_2 = 1 : 2.6$ approximately). The impregnated suspension was then treated or neutralised with dilute nitric acid to give the desired ratio of $K_2O : SiO_2$, after which the suspension was filtered, the excess alkali being removed as potassium nitrate in the filtrate.

It has now been found that the method of the co-pending Application No. 22006/50 (Serial No. 579,785) for the production of such an iron catalyst for the catalytic hydrogenation of carbon monoxide, especially at a high gas load, which catalyst may contain small amounts of carrier materials and may contain copper and other activating metals in the usual amounts, can be improved. In the course of the preparation according to the co-pending application hereinbefore referred to, an iron hydroxide suspension was admixed with a quantity of potassium silicate solution sufficient to give 20—25 parts by weight of SiO_2 for every 100 parts by weight of iron contained in the suspension, followed by a treatment with nitric acid in such a manner as to produce a ratio of 1 : 4 to 1 : 5 of K_2O to SiO_2 in the catalyst mass remaining after filtration. In the method according to the present invention a part of the total SiO_2 is added in a form other than as an alkali-metal silicate, such as in the form of an activated bleaching earth or fuller's earth, the amount of alkali-metal silicate added being only that required to give the catalyst its necessary content of alkali, thereby eliminating the subsequent treatment with nitric acid.

In carrying out the method of the invention, a quantitative determination of the amount of SiO_2 present in, for example, a bleaching earth, is first made, followed by a calculation of that quantity of SiO_2 in the form of, for example, activated bleaching earth, which must also be added to the catalyst mass in excess of the SiO_2 present in the alkali-metal silicate used for impregnation. The quantity of bleaching earth corresponding to this amount of SiO_2 is stirred up, in the conventional manner, with the catalyst mass immediately upon precipitation, whereupon the impregnation with the alkali-metal silicate may be carried out in the form of a direct impregnation without subsequent neutralisation. This not only improves the activity of the catalyst, but reduces the material cost for the catalyst and eliminates the step of the neutralisation used according to the invention claimed in Application No. 22006/50 (Serial No. 679,785). Moreover, the mechanical strength of such catalysts is further improved as compared with that of catalysts described in Application No. 22006/50 (Serial No. 679,785).

A suitable material for use in the method of the invention is SiO_2 in the form of an earth or clay, for example, an activated bleaching earth known under the name "Tonsil". Other siliceous materials may however be used, such, for example, as Sterchamol, Filtrol (Registered Trade Mark), Superfiltrol, and ceramic masses such as clay.

It has also been observed that the composition of the bleaching earth, fuller's earth, or other siliceous materials used, has an appreciable influence on the behaviour of the catalyst during the synthesis. The composition of the primary products obtained in the synthesis is also dependent on the composition of the earth or clay or other siliceous material used.

It has been found that particularly advantageous synthesis results may be obtained with these catalysts when using in their preparation bleaching earths which have a rather low aluminium oxide content of less than 10% by weight, preferably less than 5% by weight, in addition to a rather high CaO content of more than 5% by weight, preferably more than 10% by weight.

A high aluminium oxide content in the catalysts according to the invention results in an increased formation of methane in addition to the formation of products having a somewhat lower olefin content. Conversely, a correspondingly higher content of calcium oxide results not only in a reduced methane formation, but in an increased proportion of unsaturated aliphatic hydrocarbons.

The invention is illustrated in the following example.

1000 litres of a hot solution containing per litre approximately 40 grams of iron in the form of $Fe(NO_3)_3$ and 0.2 grams of copper in the form of $Cu(NO_3)_2$ were admixed with 1050 litres of a hot solution containing approximately 100 grams of Na_2CO_3 per litre, while vigorously stirring the mixture. The stirring of the mixture was continued until the carbon dioxide, which is evolved, had escaped. Immediately thereafter, the mixture was stirred up with 6.8 kilograms of an activated bleaching earth known under the name "Tonsil". The "Tonsil" had a content of SiO_2 of 65.6%, so that, approximately 4.47 kilograms of SiO_2 were thereby added to the catalyst. A p_H value of 7 was maintained during and after the precipitation.

The precipitated catalyst mass was then immediately freed from the mother liquor in a filter press and subsequently washed with hot condensate water for approximately 70 minutes. Thereafter, the residual content of alkali, calculated as K_2O, in the catalyst mass was 0.45% based on the total iron present.

The precipitated catalyst mass was then directly impregnated with a dilute potassium silicate solution in such a manner that 5.57 parts of K_2O and 15 parts of SiO_2 (this being the composition of the approximately 20% solution of commercial potassium silicate used) for every 100 parts of Fe were introduced into the catalyst mass. The impregnation was carried out in such a manner that, by carefully kneading in the potassium silicate solution, the distribution in the precipitated catalyst slurry was as uniform as possible. The catalyst mass was then carefully dried to a water content of 60% and moulded in an extruding press into cylindrical grains of 5 mm. size. After short-time re-drying in a belt dryer, the catalyst grains were finally dried in a drying chamber for 24 hours at a temperature of 105° C. to a water content of 4%.

Since the quantity of SiO_2 added to the catalyst by the "Tunsil" was 4.47 kilograms, and the quantity of SiO_2 added by the direct impregnation with potassium silicate was 6 kilograms, the total quantity of SiO_2 was 10.47 kilograms in 40 kilograms of Fe, that is, 26% calculated on Fe. The quantity of K_2O was 2.23 kilograms corresponding to 5.77%

based on Fe. and the $K_2O:SiO_2$ ratio was 1:4.5.

By crushing and sieving the dried mass, a finished grain size of 5 mm. was obtained. This catalyst was reduced in a reduction apparatus for 75 minutes at a temperature of 320. C. using 95 cubic metres of a gas mixture consisting of 75 parts of hydrogen and 25 parts of nitrogen. The flow rate during the reduction was 1.4 metres per second, measured in the cold state. The reduction value of the catalyst after the reduction, that is to say, the percentage of the total iron content of the catalyst present as metallic iron, was approximately 30.

When this catalyst was charged into a synthesis reactor of 12 metres length and consisting of smooth tubes of 32 mm. diameter and was used in a synthesis at a pressure of 30 atmospheres, with a recycle ratio of 1:3 and a gas load of 500 volumes of water gas per volume of catalyst per hour, a conversion of 60% $CO+H_2$ was obtained at a reaction temperature of 227° C.

When the same catalyst was prepared according to the method described in Application No. 22006/50 (Serial No. 679,785) without the addition of "Tonsil", but merely by potassium silicate impregnation and subsequent neutralisation, and reduced and operated under the same reduction and synthesis conditions respectively, a reaction temperature of 233° C. was required to obtain the same conversion.

With the catalyst according to the invention, the methane formation was correspondingly lower, the yield of high boiling hydrocarbons was higher and the catalyst life was appreciably increased.

What we claim is:—

1. A modification of the method for the production of an iron catalyst, for use in the catalytic hydrogenation of carbon monoxide, according to Patent Application No. 22006/50 (Serial No. 679,785), which comprises adding part of the SiO_2 in a form other than as an alkali-metal silicate, the amount of alkali-metal silicate added being only that required to give the catalyst its necessary content of alkali, thereby eliminating the treatment with nitric acid.

2. A method according to Claim 1, in which part of the SiO_2 is added in the form of an earth or clay.

3. A method according to Claim 1, in which that part of the SiO_2 which is added in a form other than as an alkali-metal silicate, is added in the form of an activated bleaching earth or activated fuller's earth.

4. A method according to Claim 2 or Claim 3, in which the Al_2O_3 content of the earth or clay is less than 10% by weight.

5. A method according to Claim 4, in which the Al_2O_3 content of the earth or clay is less than 5% by weight.

6. A method according to any one of Claims 2 to 5, in which the CaO content of the earth or clay is greater than 5% by weight.

7. A method according to Claim 6, in which the CaO content of the earth or clay is greater than 10% by weight.

8. A method according to Claim 1, in which the alkali-metal silicate is potassium silicate.

9. A method according to Claim 8, in which the SiO_2 added other than as potassium silicate, is supplied by the addition of activated fuller's earth or activated bleaching earth.

10. A method according to Claim 9, in which the Al_2O_3 content of the activated earth is less than 10% by weight and the CaO content of the activated earth is greater than 5% by weight.

11. A method according to Claim 9, in which the Al_2O_3 content of the activated earth is less than 5% by weight and the CaO content of the activated earth is greater than 10% by weight.

12. A method for the production of an iron catalyst, substantially as hereinbefore described.

13. A method for the production of an iron catalyst, substantially as hereinbefore described in the example.

14. An iron catalyst whenever produced according to the method of any preceding claims.

15. A process for the catalytic hydrogenation of carbon monoxide whenever carried out in the presence of the iron catalyst claimed in Claim 14.

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

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ERRATUM

SPECIFICATION No. 702,246.

Page 1, line 73, *for* "(Serial No. 579,785)"
read "(Serial No. 679,785)"

THE PATENT OFFICE,
19*th March*, 1954.

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was then treated or neutralised with dilute nitric acid to give the desired ratio of $K_2O:SiO_2$, after which the suspension was filtered, the excess alkali being removed as potassium nitrate in the filtrate.

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