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, of Homberg, Niederrhein, Germany, a German Joint Stock 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 the production of iron catalysts for use in the synthesis of hydrocarbons by the hydrogenation of carbon monoxide, and particularly to the production of such catalysts where natural, alkaline earth compounds are used for precipitation of the catalysts, and as a solid support or carrier for the catalysts.

It has been proposed to use natural alkaline earth compounds, such as minerals containing the oxides, hydroxides or carbonates of magnesium, calcium, strontium or barium, alone or in admixture in a finely divided or finely ground state as precipitating agents for solutions of iron salts in the production of iron catalysts for use in the hydrogenation of carbon monoxide. In such processes, the alkaline earth metal or metals which pass into solution during the precipitation of the iron salts, will pass wholly or partly into the catalyst according to whether an equivalent or a smaller quantity of alkali is used for their re-precipitation.

However, in the use of minerals from the same deposits or beds and also of minerals from different deposits or beds, catalysts have frequently been obtained the activity of which was unsatisfactory, even though complete analysis showed that the minerals differed but slightly from each other in their content and relative proportions of alkaline earths or other alkaline earth compounds.

Numerous experiments have now disclosed the surprising fact that it is not so much the quantity of the accompanying substances in the mineral which is important but the chemical form in which such substances are present.

SiO_2 may be considered to be one of the essential constituent substances of the minerals. If the SiO_2 is present in the form of a silicate, for example as aluminium silicate and/or magnesium silicate, of which at least a considerable proportion is dissolved in the solution of the iron salt or salts at the temperatures employed during the precipitation of the catalysts, then catalysts of low activity are obtained. On the other hand, highly active catalysts are obtained if the SiO_2 is present in a form in which it is dissolved only with difficulty, for example in the form of SiO_2 as such.

According to the invention, a process for the production of a supported iron catalyst comprises precipitating an aqueous solution of an iron salt the acid radical of which is capable of forming a water-soluble alkaline earth metal salt, the precipitant used being a mineral of the alkaline earth group in a solid, finely divided form, which mineral yields the alkaline earth metals in the form of their oxides on heating and which contains not more than 1% of silicates (estimated as SiO_2) soluble in the precipitation solution, and thereafter precipitating the alkaline earth metal salts from the solution by the addition of a suitable alkali-metal compound.

In most cases, a high content of Al_2O_3 in the mineral indicates the presence of admixtures or substances which impair activity. By calcining the minerals, the soluble silicates contained in the minerals are rendered insoluble so that the catalytic properties of the catalysts produced therewith are, in many cases, considerably improved. If calcining alone is not sufficient to bring the unstable or soluble constituents of the minerals into an insoluble state, catalysts of improved catalytic properties may nevertheless be obtained by using such minerals as precipitating agents which have been calcined with the addition of an appropriate additive such, for example, as iron nitrate or a solution thereof, in an amount, for example, of 1%—3% of Fe $(NO_3)_3$ calculated on a CO_2-free mineral, which additive

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is effective to convert the soluble silicates into an insoluble form. The presence in the mineral of up to 1% of silicates (estimated as SiO_2) which are soluble in the precipitation solution, is not prejudicial to the activity of the catalysts produced from such a mineral.

It is known that precipitated iron catalysts for use in the synthesis of hydrocarbons from carbon monoxide and hydrogen, generally require the addition of an alkali-metal compound in order to develop an adequate or full activity. The average length of the chain of the hydrocarbon molecules produced increases with the content of the alkali-metal compound. However, precipitated iron catalysts which are free from alkali-metal compounds give, at the relatively high temperatures needed for an adequate or sufficient conversion of carbon monoxide, an increased or even a predominant formation of methane and a separation of carbon. On the other hand, if catalysts produced according to the invention are used without the addition of an alkali-metal compound, an optimum conversion is obtained at slightly elevated temperature as compared with weakly alkali-impregnated catalysts according to the invention, and it is surprising that the formation of methane and the separation of carbon are not increased. When using iron catalysts according to the invention, which are free from alkali-metal compounds, low-boiling hydrocarbons are predominantly obtained and solid paraffin wax is substantially absent.

The invention is illustrated in the following example:—

EXAMPLE 1.

A crude dolomite having the following composition by weight: 29.82% CaO, 18.10% MgO, 43.30% CO_2, 0.97% Al_2O_3, 0.79% Fe_2O_3, and 7.02% insoluble residue consisting essentially of SiO_2, was calcined at 1000° C. and subsequently reduced to a particle size of less than 0.5 millimetres. The calcined dolomite contained 0.77% by weight of silicates (estimated as SiO_2) soluble in the nitrate solution described below.

100 parts by weight of iron in the form of a 10% aqueous solution of ferric nitrate were mixed with 5 parts of copper in the form of an aqueous solution of cupric nitrate and heated to about 95° C. 80 parts by weight of the calcined dolomite were then gradually added with stirring to the hot nitrate solution. A sodium carbonate solution containing 100—110 grams of the salt per litre, at a temperature of about 95° C., was then added as quickly as possible while stirring, and the temperature was increased to 100° C. for a few minutes, after which the mixture was immediately filtered and washed free of nitrate ions with distilled water. The appropriate amount of sodium carbonate necessary for the precipitation of the alkaline earth metals from their nitrate solutions was determined by prior titration of the iron and copper nitrate solution with the sodium carbonate solution, litmus being used as the indicator, and the end-point being taken as that at which the blue colour developed just became constant.

Where an alkalized catalyst had to be prepared, the precipitated mass, which was filtered as dry as possible, was converted into a uniform paste by the addition of an aqueous solution of potassium carbonate; it is preferred to use up to 3% of potassium carbonate, calculated on the iron in the precipitate.

Thereafter the catalyst mass was slowly dried at temperatures not exceeding 100° C.

Before use in the synthesis, the catalyst may be reduced in known manner with carbon monoxide and/or hydrogen.

A synthesis gas containing carbon monoxide and hydrogen in a volume ratio of 1:2 was passed, at normal pressure and at a temperature of 245° C., over the catalyst prepared in the manner described above, but without alkalization. The synthesis gas contained 10% by volume of nitrogen, but was free from carbon dioxide, nitrogen being substantially the only inert constituent present. The quantity of synthesis gas put through per hour was 4 litres per 25 grams of catalyst. During an operating period of three months, a gas contraction of 52% and a carbon monoxide consumption of 93% were obtained. The total amount of the hydrocarbons produced was 192 grams per normal cubic metre of $CO+H_2$.

EXAMPLE 2.

The precipitant used in this Example was a marble which contained less than 1% by weight of silicates (estimated as SiO_2) soluble in the solution used for the preparation of the catalyst. The marble was therefore suitable for use as a precipitant without prior calcination.

A solution of ferric nitrate and cupric nitrate containing 100 parts by weight of iron and 3.5 parts by weight of copper was heated to boiling and 120 parts by weight of the marble hereinbefore referred to was added to the solution in small portions, the marble being in a finely divided form. Upon completion of the addition of the ground marble, an aqueous sodium carbonate solution containing 100 grams of the salt was added with stirring and heating. The mixture was rapidly filtered and the precipitate was washed free of nitrate ions with distilled water. The washed catalyst mass was then dried at 80° C.

The dried catalyst was then used in synthesis with a gas rich in carbon monoxide. The CO/H_2 ratio in the gas was 1.6:1 by volume, the inert constituents in the gas being carbon dioxide (6% by vol.) and nitrogen (5% by vol.). At a pressure of 10 atmospheres and at a space velocity of 100 litres of synthesis gas per litre of catalyst per hour, a carbon monoxide consumption of 93% with a gas contraction of 51.5% was obtained over an operating period of three months with the use of a synthesis temperature of 240°—250° C. The yield of hydrocarbons was 190 grams per normal cubic metre of $(CO + H_2)$.

What we claim is:—

1. A process for the production of a supported iron catalyst, which comprises precipitating an aqueous solution of an iron salt the acid radical of which is capable of forming a water-soluble alkaline earth metal salt, the precipitant used being a mineral of the alkaline earth group in a solid, finely divided form, which mineral yields the alkaline earth metals in the form of their oxides on heating and which contains not more than 1% by weight of silicates (estimated as SiO_2) soluble in the precipitation solution, and thereafter precipitating the alkaline earth metal salts from the solution by the addition of a suitable alkali-metal compound.

2. A process according to claim 1, in which when the mineral in its natural state contains more than 1% of silicates which are soluble in the precipitation solution, the mineral is calcined to bring its content of such silicates within the specified limit.

3. A process according to claim 2, in which an additive such as ferric nitrate, effective to convert silicates soluble in the precipitation solution into an insoluble form, is added to the mineral prior to the calcination.

4. A process according to any one of the preceding claims, in which the catalyst is not impregnated with an alkali or alkali-metal compound.

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

6. A process for the production of an iron catalyst for use in the hydrogenation of carbon monoxide substantially as hereinbefore described.

7. A process for the catalytic hydrogenation of carbon monoxide, which is effected in the presence of an iron catalyst produced according to any one of the preceding claims.

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