PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Production of Hydrocarbons by Conversion of Carbon Monoxide with Hydrogen

I, Harold Edwin Potts, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company) of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that the process for the production of hydrocarbons with more than one carbon atom in the molecule by reaction of carbon monoxide with hydrogen can be carried out under atmospheric or higher pressure in the presence of catalysts containing metals of the iron group, or their compounds, or mixtures of these metals or compounds. These catalysts are preferably employed on carriers, such as diatomaceous earth, and usually with additions of activating or stabilising substances. In the preparation of catalysts which contain more than one metal of the iron group usually easily reducible compounds of the catalytic metals are precipitated from a mixed solution of salts of the said metals which are subsequently subjected to a reducing treatment.

My foreign correspondents have now found that in the said process very good yields of solid and liquid hydrocarbon products are obtained under atmospheric or higher pressure when employing iron and nickel containing catalysts, which have been prepared by gradually precipitating reducible iron and nickel compounds by gradual addition to a solution maintained at a p_H value of not less than 8, during the precipitation of a mixed solution of salts of the said metals at a temperature of 40° Centigrade or therebelow, preferably less than 30° Centigrade.

The said gradual precipitation is advantageously carried out in such a manner that it takes more than one hour, preferably more than 3 hours, for example 12 hours or more. Preferably a mixed solution of the metal salts is added to the solution of the precipitating agent, the addition being preferably carried out gradually and continuously in small amounts, for example drop by drop and at room temperature while the solution is advantageously agitated, for example by stirring.

The iron-nickel-precipitate obtained is, if desired after heating to boiling temperature for a short time, washed and then dried, for example, at 110° Centigrade while exposed to the atmosphere or in a stream of carbon dioxide or of other inert gases.

The catalysts according to the process of the present invention may contain activators, such as aluminium oxide, magnesium oxide or other metal oxides which are not reduced under the conversion conditions and such catalysts are prepared similarly. The said activators may be added in different amounts. If the reduction of the catalysts becomes more difficult due to the addition of substantial amounts of the activating substances, this may be compensated by addition of silver before or after the precipitation of the catalyst. The beneficial effect obtained by the gradual precipitation at the said p_H values is particularly clear with catalysts containing activators which are free from carriers. Improved results are, however, also obtained in the present process when employing catalysts on carriers, such as diatomaceous earth.

The ratio of the amount of iron to that of nickel contained in the present catalysts may vary within wide limits; it is preferred not to have more than 2 mols of iron per mol of nickel.

The catalysts according to the present invention are very voluminous and the weight of a certain volume of the present catalysts, that is the bulk density, is much smaller than that of catalysts having the same composition but which have been prepared in the usual manner by rapid precipitation. The present invention thus presents the advantage of a considerably smaller amount by weight of the catalytic metal being required for the same catalyst space. The bulk density of the present catalysts is also much smaller than that of catalysts which have been obtained by gradual precipitation in the inverse way, namely by adding the precipitating agent drop by drop to the mixed solution of the iron and nickel salts. For example, the ratio of the bulk density of an iron-nickel-aluminium oxide catalyst (molal proportion of the constituents 1:1:0.2), prepared according to the present invention from a mixed solution of the nitrates of the said metals by precipitating with a solution of an alkaline metal carbonate, to the bulk density of a catalyst which has also been prepared by gradual precipitation from a similar solution, however, in the inverse way by adding the carbonate solution drop by drop to the mixed solution is 1:3.5 (when substituting magnesium oxide for the aluminium oxide this ratio is 1:3). Although therefore when employing the present catalysts only about one third of the amount by weight of the active metallic component is required compared with catalysts prepared in the inverse way, the yield of solid and liquid hydrocarbons per cubic metre of the carbon monoxide-hydrogen mixture is in both cases about 90 grams per cubic metre. Furthermore with the present voluminous catalysts the danger of local overheating of the catalyst is considerably reduced and consequently the operation is simpler.

When employing the catalysts according to the present invention the operation may be continued during a period of several weeks, before the activity of the catalyst decreases by 10 per cent. of its maximum value.

If after extended periods of operation the present catalysts have suffered activity loss regeneration may be effected by known means, for example, by treatment with hydrogen or extraction with solvents.

The conversion of the carbon monoxide with hydrogen according to the present process may be carried out at temperatures between 160° and 250° Centigrade, advantageously between 190° and 220° Centigrade, however, higher temperatures for example, 300° Centigrade or thereabove, or lower temperatures, for example, 150° Centigrade, may also be employed. The pressure employed in the present process may be atmospheric pressure or thereabout, however, higher pressures, for example 10, 20, 50 or 100 atmospheres or more, may also be used.

The following Example will further illustrate the nature of the present invention, and how the same can be carried out in practice, but it should, however, be understood that the invention is not limited to said Example.

EXAMPLE.

9 litres of an aqueous solution containing 725 grams of iron nitrate $Fe(NO_3)_3.9H_2O$, 480 grams of nickel nitrate $Ni(NO_3)_2.6H_2O$ and 268 grams of aluminium nitrate $Al(NO_3)_3.9H_2O$ are allowed to flow drop by drop in the course of 48 hours into 9 litres of an aqueous solution containing 1010 grams of potassium carbonate. The precipitated mixture is then heated and kept at boiling temperature for 5 minutes. The precipitate is separated by filtration, washed with water and dried at 110° Centigrade while exposed to the atmosphere.

50 cubic centimetres of the unreduced catalyst containing 5.6 grams of iron and nickel, are reduced with hydrogen at 350° Centigrade for 5 hours. After having lowered the temperature to 190° Centigrade synthesis gas ($CO:H_2=1:2$) is then passed over the catalyst at a rate of 4 litres per hour. During a period of several weeks a yield of 90 grams of liquid and solid conversion products per cubic metre of the carbon monoxide-hydrogen mixture is obtained. After the operation has been extended to 6 weeks the decrease in the activity of the catalyst amounts only to less than 10 per cent.

About the same yield is obtained with catalysts having substantially the same composition but which have been prepared in another manner; however, a considerably larger amount of iron and nickel is required in the latter case. The bulk density of a catalyst which has been obtained by gradual precipitation in the inverse way, that is by adding the potassium carbonate solution drop by drop to the solution of the iron-nickel-aluminium nitrate is 3.5 times as high, so that about 20 grams of iron and nickel would be required for the same catalyst space.

The bulk density of a catalyst prepared by a more rapid precipitation, say within a few minutes is still higher, so that with such a catalyst 25 grams of iron and nickel are needed for the same catalyst space.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the production of hydrocarbons with more than one carbon

atom in the molecule by conversion of carbon monoxide with hydrogen in the presence of catalysts containing iron and nickel, which comprises employing catalysts which have been prepared by gradually precipitating reducible iron and nickel compounds by gradual addition to a solution maintained at a p_H value of not less than 8, during the precipitation of a mixed solution of salts of the said metals at a temperature of 40° Centigrade, or therebelow.

2. A process as claimed in claim 1, which is effected by allowing the said solution to flow drop by drop into the solution of the alkaline precipitating agent.

3. In the process as claimed in claim 1, carrying out the precipitation in such a manner that it takes more than one hour, preferably more than 3 hours, for example 12 hours or more.

4. In the process as claimed in any of claims 1 to 3, precipitating the catalyst at a temperature below 30° Centigrade.

5. In the process as claimed in any of claims 1 to 4, employing catalysts which contain as activators metal oxides which are not reduced under the conversion conditions.

6. In the process according to claim 5, employing aluminium oxide as the activator.

7. In the process as claimed in any of claims 1 to 6, employing a catalyst to which silver or a silver compound has been added before or after the precipitation.

8. A process for the conversion of carbon monoxide with hydrogen in the presence of a catalyst containing iron and nickel, which has been prepared by gradual precipitation, substantially as described in the foregoing Example.

9. Hydrocarbons with more than one carbon atom in the molecule, whenever obtained in the processes as claimed in any of the preceding claiming clauses.

Dated this 2nd day of February, 1940.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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