[Second Edition.]

PATENT SPECIFICATION

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474,448

PROVISIONAL SPECIFICATION.

Improvements in Carrying Out the Reaction of Carbon Monoxide with Hydrogen.

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

It has already been proposed in the reaction of carbon monoxide with hydrogen for the preparation of gaseous, liquid and/or solid hydrocarbons or their derivatives, to use catalysts comprising more than one substance, the main constituent being metals of the 8th group of the periodic system. Such catalysts have hitherto been prepared by bringing soluble compounds containing the single components into solution together and then subjecting them in this solution to a common further treatment, for example by precipitating the components together from the solution, drying and reducing, or evaporating the solution and then subjecting the residue to a decomposing thermal treatment.

My foreign correspondents have now found that catalysts of especially good activity for the said reaction are obtained by precipitating from solutions or suspensions of compounds of the metals of the iron group the said metals in the form of their difficultly soluble or insoluble compounds, adding the further components to the precipitated compounds and then subjecting the resulting mixture to a thermal treatment. For example there may be added to the compound of a metal of the iron group which has been precipitated by itself, a compound of another metal which by heating is decomposed with the formation of an oxide which is not reducible to metal with hydrogen at temperatures up to 1000° Centigrade. As metal compounds of the said kind which may be added may be mentioned for example the nitrates, carbonates, hydroxides or salts with organic acids. The resulting mixture is preferably stirred well and then treated with reducing gases at elevated temperature. The procedure may also be that to the precipitated compound of a metal of the iron group there is added the solution of a compound of another metal, the latter then being precipitated in the presence of the first compound.

Of the metals of the iron group, iron itself is of special advantage. It is precipitated, similarly to the other iron metals, preferably in the form of a compound containing oxygen which is reducible to metal with hydrogen, as for example as the hydroxide, carbonate, basic acetate or oxalate.

As additions may be mentioned for example compounds of aluminium, beryllium, manganese, zinc, thorium, cerium, zirconium and other earth metals, in particular their nitrates.

Compounds of the said metals obtained by precipitation methods, in particular the hydroxides, as for example aluminium hydroxide, may, however, be used with equally good results. The salts with organic acids, as for example aluminium acetate, aluminium oxalate and the like have also proved to be suitable additions. Two or more of the said components may also be added to the catalyst. Thus for example good yields are obtained with catalysts which have been prepared by the addition of aluminium hydroxide and manganese hydroxide to precipitate iron hydroxide.

As the third or further component there may also be used a compound of a metal which forms a readily reducible oxide. Thus for example catalysts which contain not only aluminium nitrate, but also copper nitrate as a second additional substance to precipitated iron hydroxide, also give good yields.

The catalysts provided with the additions are then subjected to a thermal treatment, preferably in the presence of reducing gases, as for example hydrogen, gases containing hydrogen or carbon monoxide. The treatment is preferably carried out at high temperatures, as for example at 800° Centigrade, whereby a partial sintering of the catalyst takes place. The thermal treatment may also be carried out in two or more stages, for

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example by first heating the catalysts in the presence of non-reducing gases, as for example nitrogen or air, and then with reducing gases.

The thermal treatment in one or more stages may take place at atmospheric pressure or at pressures of any value, as for example at 2, 5, 10, 50, 100 atmospheres or more. In some cases, when working in two or more stages, it is also advantageous to use different pressures in the single stages.

The reaction of carbon monoxide with hydrogen is carried out at temperatures above 150° preferably between 200° and 450° Centigrade. The proportions of carbon monoxide and hydrogen may be for example 1:1 (calculated by volume), but this ratio may also be varied in favour of hydrogen or carbon monoxide. The hydrocarbon synthesis may be carried out at any desired pressure. It is preferable, however, to use increased pressure, as for example 5, 10, 20, 50, 100 atmospheres or more.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight.

Example 1.

Iron hydroxide is precipitated and filtered off. A suspension of precipitated aluminium hydroxide is added to the still moist iron hydroxide, the amounts being such that there are 5 per cent. of aluminium oxide with respect to metallic iron. The mixture of the hydroxides is then intimately stirred and dried in a drying cabinet and reduced in a stream of hydrogen at 850° Centigrade.

If a mixture of equal parts of carbon monoxide and hydrogen be led over the said catalyst at a pressure of 15 atmospheres at a temperature of 300° Centigrade, there are formed, in addition to small amounts of products containing oxygen, mainly liquid hydrocarbons and small amounts of gaseous and solid hydrocarbons. The amount of liquid and solid products obtained per day is equal to the volume of the catalyst used.

If on the other hand the iron hydroxide is precipitated together with the aluminium hydroxide, filtered off and reduced, the yield of liquid and solid products under the same reaction conditions is considerably less. It amounts to only about one quarter of the volume of the catalyst used per day.

Example 2.

Precipitated iron hydroxide is made into a paste with an aqueous solution of aluminium nitrate. The aluminium nitrate is added in such an amount that there are 10 per cent. of aluminium oxide with respect to metallic iron. The paste is dried in a drying cabinet and treated at 800° Centigrade with hydrogen.

If a mixture of carbon monoxide and hydrogen be led over the catalyst thus prepared under the reaction conditions specified in Example 1, there are obtained in the course of a day about one and a half times the catalyst volume of liquid and solid products.

Dated this 26th day of March, 1936.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION.

Improvements in Carrying Out the Reaction of Carbon Monoxide with Hydrogen.

I, George William Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

For the production of gaseous, liquid and/or solid hydrocarbons (the gaseous hydrocarbons containing more than one carbon atom in the molecule) or their derivatives containing oxygen by the reaction of carbon monoxide with hydrogen it has been proposed to use catalysts comprising more than one substance, the main constituent being metals of the 8th group of the periodic system. Such catalysts have usually been prepared by bringing soluble compounds containing the single components into solution together and then subjecting them in this solution to a common further treatment, for example by precipitating the components together from the solution, drying and reducing, or evaporating the solution and then subjecting the residue to a decomposing thermal treatment. The reducing treatment has usually been carried out at temperatures of the order of about 400° Centigrade which are sufficient for the conversion of the compounds of the metals of the 8th group into the free metals.

My foreign correspondents have now found that when employing, for the said conversion, catalysts which are prepared by heating in the presence of reducing gases to such a high temperature above 500° Centigrade and for such a long time that a partial sintering takes place, (which treatment has the effect of increasing the catalytic activity towards the formation of hydrocarbons containing more than 1 carbon atom in the molecule and of imparting to the catalysts at the same time a higher mechanical strength), it is of particular advantage to precipitate, before the said heating, the metals of the iron group alone from the solutions or dispersions of their compounds in the form of their difficultly soluble or insoluble compounds and thereupon to add the further components to the precipitated compounds. By this procedure the mechanical strength of the catalysts, as compared with that obtained by simultaneous precipitation of the iron compounds and the additional compounds, and also the catalytic activity is increased. The procedure may also be that to the precipitated compound of a metal of the iron group there is added the solution of a compound of another metal the latter then being precipitated in the presence of the first compound. This modification of the preparation of catalysts according to the present invention is particularly advantageous as well as that in which the compound of another metal is added to the precipitated compound of the metal of the iron group in the form of a fresh voluminous precipitate which is another form of a dispersion of the added metal compound with water. The good effect is probably due to the fine distribution of the added metal compound on the surface of the iron metal which is attained by the addition of the said metal compound while being dispersed with water.

Of the metals of the iron group, iron itself is of special advantage, but nickel and cobalt may also be employed. It is precipitated, similarly to the other iron metals, in the form of a compound which is reducible to metal with hydrogen, as for example as the hydroxide, carbonate, basic acetate or oxalate.

As further components to be added to the aforesaid compounds of the iron group metals may be mentioned for example compounds of aluminium, beryllium, manganese, zinc, thorium, cerium, zirconium and other earth metals, the oxides of which metals are not reducible to metal with hydrogen at temperatures up to 900° Centigrade and they are preferably employed in the form of compounds which by heating are decomposed with the formation of the oxide, for example the nitrates, carbonates, hydroxides or salts with organic acids. These further compounds may be added in such amounts that the metals building them up are present in the mixture in amounts up to 30 parts by weight, preferably from 0.1 part or still less up to 15 or 20 parts, for each 100 parts of the metal from the iron group.

Compounds of the said metals obtained by precipitation methods, in particular the hydroxides, as for example aluminium hydroxide, may, however, be used with equally good results. The salts with organic acids, as for example aluminium acetate, aluminium oxalate and the like have also proved to be suitable additions. Two or more of the said components may also be added to the catalyst. Thus for example good yields are obtained with catalysts which have been prepared by the addition of aluminium hydroxide and manganese hydroxide to precipitated ferric hydroxide.

As the third or further component there may also be used a compound of a metal which forms a readily reducible oxide. Thus for example catalysts which contain not only aluminium nitrate, but also copper nitrate as a second additional substance to precipitated iron hydroxide, also give good yields.

The catalysts provided with the additions are then subjected in the presence of reducing gases, as for example hydrogen, gases containing hydrogen or carbon monoxide, to the said thermal treatment at a temperature ranging between 500° and 1100° Centigrade, as for example at 800° Centigrade, in such a manner that a partial sintering of the catalyst takes place. The thermal treatment may also be carried out in two or more stages, for example by first heating the catalysts in the presence of non-reducing gases, as for example nitrogen or air, and then with reducing gases.

The thermal treatment in one or more stages may take place at atmospheric pressure or at pressures of any value, as for example at 2, 5, 10, 50, 100 atmospheres or more. In some cases, when working in two or more stages, it is also advantageous to use different pressures in the single stages.

The reaction of carbon monoxide with hydrogen is carried out at temperatures above 150°, preferably between 200° and

450° Centigrade. The proportions of carbon monoxide and hydrogen may be for example 1:1 (calculated by volume), but this ratio may also be varied in favour of hydrogen or carbon monoxide. The hydrocarbon synthesis for which the catalysts prepared according to this invention are of particular advantage may be carried out at any desired pressure. It is preferable, however, to use increased pressure, as for example 5, 10, 20, 50, 100 atmospheres or more.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

Ferric hydroxide is precipitated and filtered off. A suspension of precipitated aluminium hydroxide is added to the still moist ferric hydroxide, the amounts being such that there are 5 per cent. of aluminium oxide with respect to metallic iron. The mixture of the hydroxides is then intimately stirred and dried in a drying cabinet and reduced in a stream of hydrogen at 850° Centigrade.

If a mixture of equal parts of carbon monoxide and hydrogen be led over the said catalyst at a pressure of 15 atmospheres and at a temperature of 300° Centigrade, there are formed in addition to small amounts of products containing oxygen, mainly liquid hydrocarbons and small amounts of gaseous and solid hydrocarbons. The amount of liquid and solid products obtained per day is equal to the volume of the catalyst used.

If on the other hand the ferric hydroxide be precipitated together with the aluminium hydroxide, filtered off and reduced, the yield of liquid and solid products under the same reaction conditions is considerably less. It amounts to only about one quarter of the volume of the catalyst used per day.

EXAMPLE 2.

Precipitated ferric hydroxide is made into a paste with an aqueous solution of aluminium nitrate. The aluminium nitrate is added in such an amount that there are 10 per cent. of aluminium oxide with respect to metallic iron. The paste is dried in a drying cabinet and treated at 800° Centigrade with hydrogen.

If a mixture of carbon monoxide and hydrogen be led over the catalyst thus prepared under the reaction conditions specified in Example 1, there are obtained in the course of a day about one and a half times the catalyst volume of liquid and solid products.

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

1. A process for the thermal conversion of carbon monoxide with hydrogen into liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule and/or their oxygen-containing derivatives which comprises heating the said carbon monoxide and hydrogen in the presence of a catalyst which has been prepared by precipitating from a solution of a compound of a metal of the iron group such difficultly soluble or insoluble compound of the said metal as is easily reducible to the metal by heating in the presence of hydrogen, adding to the precipitated compound such compound of another metal as by heating yields an oxide not reducible to metal by hydrogen below 900° Centigrade, and subsequently heating the resulting mixture in the presence of a gas having a reducing action to such a high temperature above 500° Centigrade and for such a long time that a partial sintering of the catalyst takes place.

2. In the process as claimed in claim 1, adding a compound of aluminium to the precipitated compound of a metal of the iron group.

3. In the process as claimed in claim 1 or 2, adding to the precipitated compound of a metal of the iron group the other compound in the form of a dispersion or solution with water.

4. In the process as claimed in any of claims 1 to 3, adding a compound of the earth metals to a precipitated compound of iron which is easily reducible by hydrogen.

5. In the process as claimed in any of claims 1 to 4, adding precipitated aluminium hydroxide to a precipitated compound of iron which is easily reducible by hydrogen.

6. In the process as claimed in any of claims 1 to 4, operating in the presence of a catalyst prepared by adding a solution of aluminium nitrate to a precipitated compound of iron which is easily reducible by hydrogen, drying the resulting mass and subsequently heating it in the presence of a gas having a reducing action to such a high temperature and for such a long time that partial sintering of the catalyst takes place.

7. In the process as claimed in any of claims 1 to 4, operating in the presence of a catalyst prepared by adding a solution of aluminium nitrate to a precipitated compound of iron which is easily reducible by hydrogen, precipitating

aluminium hydroxide from the said solution and subsequently heating the mixture of precipitates in the presence of a gas having a reducing action to such a high temperature and for such a long time that partial sintering of the catalyst takes place.

8. In the process as claimed in any of claims 1 to 7, adding, in addition to the metal compound which yields an oxide not reducible to metal by hydrogen below 900° Centigrade, a third metal compound.

9. The process for the thermal conversion of carbon monoxide with hydrogen into liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule and/or their oxygen-containing derivatives substantially as described in each of the foregoing Examples.

10. Liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule and/or their oxygen-containing derivatives when obtained by the process as particularly described and ascertained.

Dated this 8th day of March, 1937.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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