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PATENT SPECIFICATION

Application Date: Nov. 6, 1939. No. 29430/39.

Complete Specification Left: Nov. 5, 1940.

Complete Specification Accepted: July 25, 1941.

538,225

1660

PROVISIONAL SPECIFICATION

Process for the 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, to be as follows:—

It is already known in the conversion of carbon monoxide with hydrogen into liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule, to use catalysts which consist of or contain iron. Several methods have already been proposed for the preparation of these catalysts, for example, iron hydroxide has been precipitated from solutions of iron salts and subsequently been reduced by a treatment with reducing gases, such as hydrogen, at such high temperatures above 500° Centigrade that a sintering occurred, or iron powder obtained by decomposition of iron carbonyl, has been converted into a solid porous mass by sintering. The said catalysts have further been prepared by combustion of iron in a stream of oxygen and subsequent reduction of the molten iron oxide thus obtained.

In the following the expression " compact iron " will be used and this means non-porous iron in the form of pieces of which two dimensions are at least 2 and 1 millimetre respectively.

My foreign correspondents have now found that the aforesaid conversion of carbon monoxide with hydrogen may be carried out with particular advantage in the presence of iron catalysts, prepared by treating compact iron with oxidising gases at such high temperatures that iron oxide is obtained without melting of the iron or of the iron oxide formed and subsequently reducing the said iron oxide to metal by treatment with reducing gases.

According to the process of the present invention catalysts are prepared from very cheap and readily available iron materials, as any suitable compact iron may be employed. Compact iron having two dimensions of more than about 5 millimetres and a third one of more than 0.1 millimetre is a preferred initial material. Advantageously sheet iron, for example, in the form of Raschig rings or other hollow objects, is used. The compact iron treated may already be in part present in the form of oxides.

The said treatment with oxidising gases, for example, air may be carried out within a wide range of temperatures below the melting point of iron, preferably from 700° to 800° Centigrade and is continued until the iron is substantially converted into iron oxide.

The said treatment with reducing gases may be carried out at any temperature, suitable for the reduction of iron oxide. Preferably a temperature of about 500° Centigrade or more is used. In order to increase the mechanical strength of the catalyst, the said treatment with reducing gases may after the reduction of the iron oxide still be continued at the same or at higher temperatures below the melting point of iron, for example, from 600° to about 1000° Centigrade, or the said reduction may also be carried out at the said higher temperatures.

During the said treatments with oxidising gases and reducing gases the original shape of the compact iron objects remains substantially unchanged.

The catalysts according to the present process, in particular those prepared from compact iron consisting of hollow objects as stated above, are very suitable if high rates of flow of the gases are employed in the said conversion of carbon monoxide with hydrogen, as they cause only a slight resistance to the flow of the gases, so that no undesired difference in pressure at the inlet and outlet of the catalyst space occurs. Therefore, the said catalysts may, for example, advantageously be employed when converting carbon monoxide with hydrogen according to the process described in the specification 24,683/38.

The activity of the said catalysts may be increased by additions of alkali metal compounds, for example, halides, phos-

[*Price* 1/-]

Price 4s 6d.

phates or borates of potassium, sodium, lithium or caesium, for example, in amounts of about 0.1 to 10 per cent. by weight or more. The said compounds may be added to the catalysts in a dry state during or after the said treatment with reducing gases or as aqueous solutions before or after the said treatment. The activity of the catalysts may further be increased by the addition of other substances beside the said alkali metal compounds, for example aluminium oxide, aluminium hydroxide, silicon dioxide, kieselguhr and the like, and/or compounds of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, zirconium or other rare earths.

As initial materials for the said conversion of carbon monoxide with hydrogen gas mixtures may be employed, which contain the said gases in approximately equal volumetric amounts. However, as is known the said mixtures may also contain considerably larger proportions of carbon monoxide or of hydrogen. Furthermore the said gas mixtures may contain diluent gases, such as nitrogen, carbon dioxide, methane and the like. If desired additional amounts of carbon monoxide and/or hydrogen may be added during the said conversion.

The said conversion of carbon monoxide with hydrogen may be carried out in the gaseous phase or in the liquid phase. When working in the gaseous phase the said conversion is preferably carried out with circulating gases, for example as described in the said specification 24,683/38. When carrying out the said conversion in the liquid phase, suitable liquid or fusible hydrocarbons are employed as the liquid medium, such as for example mineral oils or fractions thereof, tar oils, paraffin wax, products obtained by destructive hydrogenation of carbonaceous materials, and the like. Advantageously oils obtained by the conversion of carbon monoxide with hydrogen are employed as a liquid medium, suitably oils obtained in a previous conversion under substantially the same conditions are used.

The said conversion of carbon monoxide with hydrogen may be carried out at any suitable temperature, preferably a temperature within the range of about 180° to about 450° Centigrade, and under reduced pressure, atmospheric pressure or higher pressures, for example of 5, 10, 20, 50, 100 atmospheres or more.

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

EXAMPLE.

Raschig rings with a diameter of 10 millimetres, made of sheet iron of a thickness of 1.5 millimetres, are treated with air at 700° Centigrade, until the said iron is completely oxidised. Thereupon the rings are reduced by means of hydrogen at 600° Centigrade and subsequently treated with a solution of borax in such a manner that the prepared catalyst contains 1 per cent. by weight of borax. Water gas containing carbon monoxide and hydrogen in volumetric proportions of 4:5, is passed over this catalyst at a temperature of 320° Centigrade and under a pressure of 20 atmospheres, in a circulation process as described in the said specification 24,683/38, whereby 80 per cent. by volume of the water gas is converted into hydrocarbons substantially boiling within the boiling range of benzine.

Dated this 4th day of November, 1939.

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

COMPLETE SPECIFICATION

Process for the 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 already known in the conversion of carbon monoxide with hydrogen into liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule, to use catalysts which consist of or contain iron. Several methods have already been proposed for the preparation of these catalysts, for example, iron hydroxide has been precipitated from solutions of iron salts and subsequently been reduced by a treatment with reducing gases, such as hydrogen, at such high temperatures above 500° Centigrade and for such a long time that a sintering occurred, or iron powder obtained by decomposition of iron carbonyl, has been converted into a solid porous mass by sintering. The said catalysts have further been prepared by combustion of iron in a stream of oxygen and subsequent reduction of the molten ferroso-ferric oxide thus obtained.

In the following specification and claims the expression "compact iron" will be used and this means non-porous iron in the form of pieces of which two dimensions are at least 2 and 1 millimetre respectively.

My foreign correspondents have now found that the aforesaid conversion of carbon monoxide with hydrogen may be carried out with particular advantage in the presence of iron catalysts, prepared by treating compact iron with oxidizing gases at such high temperatures and for such a long time that the iron is substantially completely converted into iron oxide, but without melting of the iron or of the iron oxide formed and subsequently reducing the said iron oxide to metal by treatment with reducing gases.

According to the process of the present invention catalysts are prepared from very cheap and readily available iron materials, as any suitable compact iron may be employed. Compact iron having two dimensions of more than about 5 millimetres and a third one of more than 0.1 millimetre is a preferred initial material. Advantageously sheet iron, for example, in the form of Raschig rings or other hollow objects, is used. The compact iron treated may already be in part present in the form of oxides.

The said treatment with oxidising gases, for example, air may be carried out within a wide range of temperatures below the melting point of iron from 400° to 1200° C. preferably from 700° to 900° C. and is continued until the iron is substantially completely converted into iron oxide.

The said treatment with reducing gases may be carried out at any temperature, suitable for the reduction of iron oxide. Preferably a temperature of about 500° C. or more is used. In order to increase the mechanical strength of the catalyst, the said treatment with reducing gases may after the reduction of the iron oxide still be continued until sintering sets in at the same or at higher temperatures below the melting point of iron, for example, from 600° to about 1000° C. or the said reduction may also be carried out at the said higher temperatures.

During the said treatments with oxidising gases and reducing gases the original shape of the compact iron objects remains substantially unchanged.

The catalysts according to the present process, in particular to those prepared from compact iron consisting of hollow objects as stated above or those which during their preparation have been brought into such a form, are very suitable if high rates of flow of the gases are employed in the said conversion of carbon monoxide with hydrogen, as they cause only a slight resistance to the flow of the gases, so that no undesired high difference in pressure at the inlet and outlet of the catalyst space occurs. Therefore the said catalysts may, for example, advantageously be employed when converting carbon monoxide with hydrogen according to the process described in the specification No. 518,372.

The activity of the said catalysts may be increased by additions of alkali metal compounds, for example, halides, phosphates or borates of potassium, sodium, lithium or caesium, for example, in amounts of about 0.1 to 10 per cent. by weight or more. The said compounds may be added to the catalysts in a dry state during or after the said treatment with reducing gases or as aqueous solutions before or after the said treatment. The activity of the catalysts may further be increased by the addition of other substances beside the said alkali metal compounds, for example aluminium oxide, aluminium hydroxide, silicon dioxide, and the like, and/or compounds for example oxides, hydroxides, carbonates, or halogenides of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, zirconium or other rare earths, which compounds may be added to the catalysts in amounts of a few per cent. by weight or less, for example, less than 1 per cent. by weight.

As initial materials for the said conversion of carbon monoxide with hydrogen, gas mixtures may be employed, which contain the said gases in approximately equal volumetric amounts. However, as is known the said mixtures may also contain considerably larger proportions of carbon monoxide or of hydrogen. Furthermore the said gas mixtures may contain diluent gases, such as nitrogen, carbon dioxide, methane and the like. If desired additional amounts of carbon monoxide and/or hydrogen may be added during the said conversion.

The said conversion of carbon monoxide with hydrogen may be carried out in the gaseous phase or in the liquid phase. When working in the gaseous phase the said conversion is preferably carried out with circulating gases, for example as described in the said specification No. 518,372. When carrying out the said conversion in the liquid phase, suitable liquid or fusible hydrocarbons are employed as the liquid medium, such as for example mineral oils or fractions thereof, tar oils, paraffin wax, products obtained by destructive hydrogenation of carbonaceous materials, and the like. Advantageously oils obtained by the conversion of carbon monoxide with hydrogen are employed as a liquid medium, suitably oils obtained in a previous conversion under substantially the same conditions are used.

The said conversion of carbon monoxide with hydrogen may be carried out at any suitable temperature, preferably a temperature within the range of about 180° to about 450° C. and under reduced pressure, atmospheric pressure or higher pressures, for example of 5, 10, 20, 50, 100 atmospheres.

The catalysts prepared as above described may also be used in other catalytic reduction processes, particularly the high pressure hydrogenation of heavy oils in the liquid phase, and also for de-sulphurization.

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

EXAMPLE.

Raschig rings with a diameter of 10 millimetres, made of sheet iron of a thickness of 1.5 millimetres, are treated with air at 700° C. until the said iron is completely oxidized. Thereupon the rings are reduced by means of hydrogen at 600° C. and subsequently treated with a solution of borax in such a manner that the prepared catalyst contains 1 per cent. by weight of borax. Water gas containing carbon monoxide and hydrogen in volumetric proportions of 4:5, is passed over this catalyst at a temperature of 320° C. and under a pressure of 20 atmospheres, in a circulation process as described in the said specification No. 518372, whereby 80 per cent. by volume of the water gas is converted into hydrocarbons substantially boiling within the boiling range of benzine.

Having now particularly described and ascertained the nature of our 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. Process for preparing an iron catalyst for example for preparing hydrocarbons from carbon monoxide and hydrogen or the high pressure hydrogenation of oils in the liquid phase which consists in treating compact iron with oxidising gases at a high temperature and for such a long time that the iron is substantially completely converted into iron oxide without melting of the iron or of the iron oxide formed, and subsequently reducing the said iron oxide to metal by treatment with reducing gases.

2. A process for the conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule in the presence of iron catalysts which comprises employing catalysts prepared as in claim 1.

3. Process for the high pressure hydrogenation of heavy oils in the liquid phase using catalyst prepared as in claim 1.

4. Process as claimed in claims 2 and 3 in which the catalyst is prepared from compact iron which has two dimensions of more than 5 mm. and a third one of more than 0.1 mm. and is in the form of sheet iron.

5. Process as claimed in claims 2 and 3 in which the catalyst is prepared from sheet iron used in the form of hollow bodies, for example Raschig rings.

6. Process as claimed in claims 2 and 3 in which alkali metal compounds are added to increase the activity of the catalysts.

7. Process as claimed in claim 6 in which the metal compounds are added to the iron oxide during or after the reduction treatment.

8. In the process as claimed in any of claims 2—7 the employment of a catalyst in which the treatment with oxidising gases has been effected at temperatures from 700—900° C.

9. In a process as claimed in any of claims 2—7 the employment of a catalyst in the preparation of which the treatment with reducing gases has been carried out at a temperature of 500° or above.

10. In a process as claimed in any of claims 2—9 the employment of a catalyst in the preparation of which the treatment with reducing gases is continued after the reduction of the iron oxide, at the same or at higher temperatures below the melting point of iron until sintering sets in.

11. A process as claimed in any of claims 2—10 in which the reaction gases are circulated as described in patent specification No. 518,732.

12. A catalyst for example for the preparation of hydrocarbons from carbon

monoxide and hydrogen whenever prepared according to the process of claim 1.

13. A process for the conversion of carbon monoxide with hydrogen into hydrocarbons as particularly described with reference to the above example.

14. Hydrocarbons whenever obtained by the process as claimed in any of the preceding claims.

Dated this 4th day of November, 1940.
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12, Church Street, Liverpool, 1,
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Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1941.