# PATENT SPECIFICATION

# 728,602

*Date of Application and filing Complete Specification: July 21, 1952.*
*No. 18432/52.*
*Application made in Germany on July 21, 1951.*
*Application made in Germany on Sept. 27, 1951.*
*Complete Specification Published: April 20, 1955.*

**Index at acceptance:—Classes 1(1),** F3B1; **and 2(3),** B1(G: X), C3A13A3(A1C: B1: J2: M).

COMPLETE SPECIFICATION

## A process for the Synthesis of Hydrocarbons and Oxygen-Containing Organic Compounds

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FÜR BERGBAU UND CHEMIE, Homberg/Niederrhein, 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:—

This invention relates to a process for the synthesis of hydrocarbons and oxygen-containing organic compounds.

In Patent Application No. 10728/50 (Serial No. 707,972) there is described a process for the production of hydrocarbons and oxygen-containing organic compounds from carbon monoxide and water vapour by passing a mixture of carbon monoxide and water vapour containing at least two volumes of carbon monoxide for each volume of water vapour, at temperatures of from 150° to 350° C. and at normal or elevated pressure up to 100 atmospheres over a catalyst of which the main metallic constituent is a metal of the eighth group of the periodic system previously activated by treatment with carbon monoxide and then with hydrogen, or with a mixture of carbon monoxide and hydrogen, at a temperature of from 150° to 350° C.

It has now been found that the synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and water vapour may be effected with particular advantage with the use of a catalyst containing iron, cobalt, nickel or ruthenium, in which the metal is present to a large extent in the form of a nitride or nitrides.

According to the invention, a process for the synthesis of hydrocarbons and oxygen-containing organic compounds comprises contacting a mixture of carbon monoxide and water vapour containing at least 2 volumes of carbon monoxide per volume of water vapour, at a temperature between 150° C. and 350° C. and at a pressure from normal atmospheric pressure to about 100 atmospheres gauge, with a catalyst, the main metallic constituent of which is iron, cobalt, nickel or ruthenium, which metal is present in the form of a nitride to the extent of about 50% or more. The temperature at which the mixture of carbon monoxide and water vapour is contacted with the catalyst, is preferably within the range 180° — 280° C. The preferred, main metallic constituent of the catalyst is iron.

When the catalyst is prepared from material in which the iron, cobalt, nickel or ruthenium is in oxidic form, the material is reduced prior to conversion of the iron, cobalt, nickel or ruthenium into nitride. The reduction is preferably effected by means of hydrogen or a hydrogen-containing gas.

The metal may be converted into a nitride in known manner, for example, by reaction with ammonia. When reduction of the metal has to be effected, the reduction and conversion into nitride may be carried out simultaneously by the use of a gas mixture containing hydrogen and ammonia. Where such a gas mixture is used, it is advantageous that it should not contain such a proportion of carbon monoxide as to result in the formation of ammonium carbamate in any appreciable quantity, since the ammonium carbamate would be deposited in the cooler parts of the apparatus and would lead to the plugging of the lines.

As compared with the catalysts hitherto used, the catalysts used in the process according to the invention give the great advantage of reducing the undesirable separation of elementary carbon through which the activity of the catalyst is prematurely reduced or destroyed. The particularly advantageous behaviour of the nitrides in the process according to the invention was in no way to be foreseen; rather was it to be assumed that the nitrides, for example the nitride of iron, would be largely hydrolysed by the water vapour or steam under the synthesis reaction conditions.

The catalyst may contain one or more promoters, selected from those given in the following groups:—

(a) oxides, hydroxides and salts of alkali-metals and of alkaline earth metals including magnesium;
(b) oxides which are difficult to reduce, such as thorium oxide and cerium oxide;
(c) aluminium oxide and chromium oxide;
(d) compounds of manganese, vanadium and boron; and
(e) compounds of copper, nickel, silver and gold.

The catalyst may also contain a carrier such as kieselguhr, talc, dolomite, limestone, activated carbon and pumice.

It is preferred that the $CO/H_2O$ ratio in the synthesis gas should be between 2 and 3 by volume.

The space velocity (expressed in volume of gas per hour relative to unit volume of catalyst) of the carbon monoxide/water vapour mixture may with advantage be at least nine times the numerical value of the operating or synthesis pressure expressed in atmospheres. Particularly advantageous results are obtained when the space velocity is maintained between nine and fourteen times the numerical value of the synthesis pressure.

The quantity of water required for the reaction with carbon monoxide can be injected into the reaction space in the liquid state. This method affords the great advantage that the greater part of the reaction heat evolved during the reaction between carbon monoxide and water vapour is consumed in the conversion of the water from the liquid state into the vapour state, that is to say, may be dissipated from the system in the form of heat of vaporisation.

Though it is known from the literature to use liquid water for the dissipation of the reaction heat in various other synthesis, this water does not participate in any way in the synthesis, and in many cases constitutes a hindrance to the desired reaction. In the process according to the invention, the utilisation of the heat of vaporisation of a reaction component for the dissipation of the reaction heat is absolutely new and was not to be foreseen in any way. A considerable technical advantage is obtained in that the cooling devices required for the dissipation of heat are wholly or partly dispensed with.

The invention is not limited to one determined manner of carryng out the synthesis from water vapour and carbon monoxide. It may be used both with fixed-bed catalysts and also in the liquid phase, that is to say, when the catalyst is a fine suspension in oil, and also in the so-called "fluid-bed" catalysis in which the catalyst is maintained in suspension in the gas-stream. It is particularly advantageous, however, to carry out the synthesis according to the invention in liquid phase operation.

The injection into the reaction space of the amount of liquid water required for the reaction with carbon monoxide, may be effected in one operation or in determined amounts at different positions of the reaction space. It is determined by the operating conditions provided at the time.

The synthesis may be carried out in two or more stages; the exit gases may also be recycled. The carbon dioxide formed in the synthesis is advantageously separated from the products and reduced to carbon monoxide, and the carbon monoxide so obtained may then be fed to the synthesis.

Hydrogen may also be added to the mixture of carbon monoxide and water vapour which is contacted with the catalyst. In such case, synthesis products are produced by the reaction of carbon monoxide and hydrogen simultaneously with those produced by the reaction of carbon monoxide and water vapour.

The invention is illustrated by the following example.

EXAMPLE.

Electrolytic hydrogen was passed first for three hours at 400° C. at a space velocity of 1000 over an alkalised Fe-Cu catalyst. The catalyst was then treated for three hours with ammonia at 300° C. and at a space velocity of 1000. In this way, a catalyst was obtained which consisted of 50% nitride of the empirical formula $Fe_{1.8}N$. When this catalyst was treated at 10 atmospheres gauge pressure with a $CO/H_2O$ vapour mixture in the ratio 8:1.25 there was obtained over an operating period of 300 hours at 230° C. a constant CO conversion of 95%, and at the end of this period the catalyst had a carbon content of 6.5%.

When, in a comparative run, under otherwise the same conditions, the catalyst was not converted into nitride, but was pre-treated with CO and then with $H_2$, the temperature had to be increased from

230° C. to 240° C. in order to maintain a constant CO conversion of 95% for 300 hours. In addition, the catalyst had at the end of this period a carbon content of 15.2%.

What we claim is:—

1. A process for the synthesis of hydrocarbons and oxygen - containing organic compounds, which comprise contacting a mixture of carbon monoxide and water vapour containing at least 2 volumes of carbon monoxide per volume of water vapour, at a temperature between 150° C. and 350° C. and at a pressure from normal atmospheric pressure to about 100 atmospheres, with a catalyst the main metallic constituent of which is iron, cobalt, nickel or ruthenium, which metal is present in the form of a nitride to the extent of about 50% or more.

2. A process according to claim 1, in which the carbon monoxide/water vapour ratio is not greater than 3.

3. A process according to claim 1 or claim 2, in which the carbon monoxide/water vapour mixture is contacted with the catalyst at a space velocity which is not less than nine times the numerical value of the synthesis pressure expressed in atmospheres.

4. A process according to claim 3, in which the space velocity is not greater than fourteen times the numerical value of the synthesis pressure expressed in atmospheres.

5. A process according to any one of the preceding claims, in which the water is introduced into the reaction space in the liquid state.

6. A process according to claim 5, in which the water is fed into the reaction space at more than one position.

7. A process according to any one of the preceding claims in which the mixture of carbon monoxide and water vapour is contacted with the catalyst at a temperature within the range of 180°—280° C.

8. A process according to any one of the preceding claims, in which the catalyst contains one or more promoters selected from the following groups:—

(a) oxides, hydroxides and salts of alkali-metals and of alkaline earth metals including magnesium;
(b) oxides which are difficult to reduce, such as thorium oxide and cerium oxide;
(c) aluminium oxide and chromium oxide;
(d) compounds of manganese, vanadium and boron; and
(e) compounds of copper, nickel, silver and gold.

9. A process according to any one of the preceding claims, in which a carrier such as kieselguhr, dolomite, talc, limestone, activated carbon and pumice, is incorporated with the catalyst.

10. A process according to any one of the preceding claims, in which the synthesis is carried out in two or more stages.

11. A process according to any one of claims 1 to 9, in which exit gases are recycled to the synthesis.

12. A process according to any one of the preceding claims, in which the synthesis is carried out with the catalyst suspended in a suitable liquid medium.

13. A process according to any one of claims 1 to 11, in which the synthesis is carried out with the catalyst in a finely divided condition suspended in the synthesis gas.

14. A process according to any one of the preceding claims, in which carbon dioxide formed in the synthesis is separated from the products and is reduced to carbon monoxide, the carbon monoxide so obtained being fed to the synthesis.

15. A process according to any one of the preceding claims, in which the main metallic constituent is iron.

16. A process according to any one of the preceding claims, in which hydrogen is added to the mixture of carbon monoxide and water vapour whereby synthesis products are produced by the reaction of carbon monoxide and hydrogen simultaneously with those produced by the reaction of carbon monoxide and water vapour.

17. A process for the synthesis of hydrocarbons and oxygen - containing organic compounds, substantially as hereinbefore described in the Example.

18. Hydrocarbons and oxygen-containing organic compounds whenever produced by the process of any preceding claim.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.