PATENT SPECIFICATION

762,705

Date of Application and filing Complete Specification: July 21, 1952.
No. 17322/54.
Application made in Germany on Sept. 4, 1951.
Application made in Germany on Sept. 27, 1951.
(Divided out of No. 728,602).
(Patent of Addition to No. 707,972, dated May 1, 1950).
Complete Specification Published: Dec. 5, 1956.

Index at acceptance:—**Class 2(3),** B1(G:X), C3A13A3(A1C:B1:J2).

COMPLETE SPECIFICATION

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

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER 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 the co-pending 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 gauge over a catalyst the main metallic constituent of which is a metal of the eighth group of the periodic system, the catalyst having been 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.

The present invention is an improvement in or modification of the process claimed in the co-pending Application No. 10728/50 (Serial No. 707,972).

As stated in the specification of Application No. 10728/50 (Serial No. 707,972), there is a relatively rapid fall in the activity of the catalyst when the molar ratio of carbon monoxide to water vapour in the feed gas is below 2.

It has now been found, that for high, overall yields of hydrocarbons and alcohols, the molar ratio of carbon monoxide to water vapour in the feed gas should not exceed 3. The molar ratio of carbon monoxide to water vapour in the feed gas is thus to be maintained in the narrow range of from 2 to 3.

According to the present invention therefore, a process for the synthesis of hydrocarbons and oxygen-containing organic compounds comprises contacting a mixture of carbon monoxide and water vapour in which the molar ratio CO/H_2O is within the limits 2:1 and 3:1, with a catalyst the main metallic constituent of which is a metal of the 8th group of the periodic system at a temperature within the range 150°—350°C. and at a pressure from normal atmospheric pressure to about 100 atmospheres gauge, the catalyst having previously been activated at a temperature in the range 150°—350°C. by treatment with carbon monoxide and subsequently with hydrogen or by treatment with a CO/H_2 mixture.

If it is desired to produce predominantly hydrocarbons, it is advantageous to select the upper limit, that it to say, a carbon monoxide/water vapour ratio of 3:1. However, if it is desired to produce predominantly alcohols, it is necessary to use a synthesis mixture, the carbon monoxide/water vapour ratio of which is less than 3:1. In addition it is then advisable to employ pressures exceeding 20 atmospheres.

If the ratio of the carbon monoxide/water vapour mixtures used is less than 2:1, that is to say, is outside the stated limits, for example 1:1, the yield will be considerably reduced even with a high CO-conversion and even when the CO/H_2O mixture is completely converted.

It has also been found that, to obtain maximum yields, not only is it necessary to keep within the stated limits of the CO/H_2O ratio of the starting gas, but beyond this, it is only within this range that the catalyst can operate reliably. If the CO/H_2O ratio used is more than 3, that is to say, outside the limit, CO being thus present in excess of the limit, the result after prolonged operation will be the separation of carbon and the obstruction and deactivation of the catalyst. If the CO/H_2O ratio is less than 2, that is to say, if on the other hand the ratio is less than the lower limit according to the invention, water vapour being thus present in excess of the limit, the catalyst is destroyed or deactivated by oxidation by water vapour. It is thus necessary to adjust the CO/H_2O ratio in the synthesis mixture in such manner that the reduction value of the catalyst, or its contents of metal and compounds of metallic character—which is of decisive importance for its activity—is not made less and that a determined carbon content of the catalyst is not exceeded. This is attained by adjusting the synthesis mixture within the stated limits.

The effect of the proportion of water vapour present in the carbon monoxide/water vapour mixture on the oxidation effect thereof, has been examined in the presence of a carrier-free, reduced Fe-Cu-alkali catalyst. The Fe-Cu-catalyst used was free from carrier materials and contained 0.1 parts by weight of copper and 0.25 parts by weight of potassium carbonate for every 100 parts by weight of iron. It was produced by precipitating an aqueous solution of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ containing 5% by weight of Fe, at the boil with the stoichiometrical amount of sodium carbonate in aqueous solution. The precipitated mixture was brought to the boil for a short time (a few minutes), filtered and the precipitate washed with 70 to 90 times the amount of boiling water (relatively to the amount of iron). The residue was then made into a paste with a little water, thoroughly mixed with an aqueous solution of potassium carbonate (0.25 parts by weight of K_2CO_3 for 100 parts by weight of Fe) and dried at 110°C.

For converting the catalyst into the active state, CO was passed over the catalyst at 270°C. for 24 hours at a space velocity of 100, and then, also for 24 hours, hydrogen at the same temperature, at normal pressure and normal space velocity. The reduction value of the catalyst, that is to say, its content of metallic iron relatively to its total content of iron, in its dependence on the carbon monoxide/water vapour ratio in the starting mixture was determined each time after an operating period of 70 hours at 235°C. and a space velocity of 100. The reduction value of the catalyst was taken as a measure of its activity. When the reduction value falls, this indicates an oxidation of the catalyst which goes hand in hand with a reduction of its activity, as, in that case, the carbon monoxide activation takes place only with compounds having a metallic character. In these experiments, the reduction value of the catalyst fell to 8% from an original value of 73%, when the carbon monoxide/water vapour ratio was 3:3. Even at a CO/H_2O ratio 3:1.75, a considerable oxidation was noticeable, the reduction value dropping to 64%. It is only when starting from proportions of water vapour of from 1.5 per 3 parts by volume of carbon monoxide that the reduction value was not reduced and oxidation does not occur to any substantial extent.

It has also been found that the quantity of water required for the reaction with carbon monoxide can be injected into the reaction space in the liquid state. This process according to the invention 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 syntheses, 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. According to the invention, a considerable technical advantage is obtained in that the cooling devices required for the dissipation of heat are wholly or partly dispensed with.

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 invention is not limited to one determined manner of carrying 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 a suitable liquid medium, such as a hydrocarbon 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 synthesis may be effected in one or more stages; exit gases may also be recycled where necessary or desired. Carbon dioxide present in the exit gases from the reaction zone may be separated from such gases and be reduced to carbon monoxide, and the carbon monoxide so obtained may be used as part of the gas fed to the synthesis.

Hydrogen may also be introduced into the reaction space in addition to the CO and H_2O, whereby synthesis products are produced by the reaction of carbon monoxide with hydrogen simultaneously with those produced by the reaction of carbon monoxide with the water vapour.

The metal of the 8th group in the catalyst is preferably iron. It may, however, be another of such metals, for example cobalt, nickel or ruthenium, which are known to be effective in the Fischer-Tropsch synthesis. The catalyst may contain one or more promoters selected from the following groups (a) to (e):—

(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 sesquioxide;

(d) compounds of manganese, vanadium and boron; and

(e) compounds of copper, nickel, silver and gold.

The catalyst may also be supported on a carrier such as Kieselguhr, dolomite, talc, limestone, activated carbon and pumice.

The invention is illustrated in the two following examples. Both examples illustrate the formation of hydrocarbons; in Example 1 the catalyst is used in a fixed-bed and the H_2O is fed into the reaction space in the vapour state, whilst in Example 2 the catalyst is suspended in a liquid phase and the H_2O is injected in the liquid state at two different positions into the catalyst suspension.

EXAMPLE 1

The catalyst used was an Fe-Cu-Keiselguhr catalyst, alkalised with potassium carbonate and containing 10 parts of magnesium, 10 parts of copper, 60 parts of Kieselguhr and 2 parts of K_2CO_3 for 100 parts by weight of iron. It was produced from an aqueous solution of $Fe(NO_3)_3$, $Mg(NO_3)_2$ and $Cu(NO_3)_2$ containing 5% by weight of iron, after the addition of 60 parts of Kieselguhr, by precipitation at boiling temperature with the stoichiometrical quantity of sodium carbonate in aqueous solution. The precipitated mixture was quickly brought to the boil, filtered, and the precipitate washed with 70 to 90 times the quantity of boiling water relatively to the amount of iron. The residue was immediately afterwards made into a paste with a little water, thoroughly mixed with an aqueous solution of potassium carbonate (2 parts by weight of K_2CO_3 for 100 parts by weight of Fe) and dried at 110°C.

The catalyst must be activated before being used. For this purpose, a CO/H_2 mixture containing two volumes of hydrogen for each volume of carbon monoxide was passed over the catalyst for 24 hours at a temperature of 270°C. at normal pressure and at a space velocity of 100, that is to say, 100 normal cubic metres of CO/H_2 mixture per cubic metre of catalyst space per hour.

A carbon monoxide/water vapour mixture in which the molar ratio CO/H_2O was 3:1, and thereafter a similar mixture in which the molar ratio was 1.15:1 was passed at a pressure of 10 atmospheres over the catalyst so pre-treated. The temperature was 230°C. and the space velocity was 100, that is to say, 100 cubic metres of $CO—H_2O$ mixture per cubic metre of catalyst volume per hour.

The results of the two runs are compared in the following Table:—

Dependence of the hydrocarbon yield in the synthesis from water vapour and carbon monoxide on the CO/H_2O ratio in the starting mixture:

CO/H_2O in the synthesis mixture	CO-conversion % by volume	CO/H_2O consumption	Yield of hydrocarbons, grams per normal cubic metre CO
3:1	94.5	3:1	185.3
1.15:1	93.5	1.15:1	95.1

When the CO conversion is about the same and the $CO—H_2O$ mixture is completely worked up, the hydrocarbon yield is reduced from 185 grams to 95 grams, if the CO/H_2O ratio of the starting mixture is decreased from 3:1 to 1.15:1.

EXAMPLE 2

Approximately 600 grams of a carrier-free Fe-Cu-alkali catalyst, the composition and preparation of which have been hereinbefore described in connection with the examination of the influence of the proportion of water present in the CO/water vapour mixture on its oxidation effect, were ground in a ball-mill into fine dust and suspended in approximately 4 kg. of Fischer-Tropsch oil boiling in the range 300°—340°C. For the activation of the catalyst, 400 litres of CO were passed per hour at 4 atmospheres and 270°C. for approximately 20 hours through this catalyst-oil suspension, which was contained in a vertical reaction tube of about 4 metres in length, after which 800 litres of hydrogen were passed through the suspension for the same period under the same conditions of temperature and pressure. The temperature of the suspension was then lowered to 240°C., and CO was passed through the suspension at the rate of 1000 litres per hour under a pressure of 11 atmospheres, liquid water at a temperature of 30°C. being simultaneously injected into the reaction space at the rate of 18 grams of water for every three mols of carbon monoxide. Two-thirds of the water was injected at the bottom and one-third in the middle part of the reaction space. 94% of the carbon monoxide reacted with the water thus forming 189 grams of hydrocarbons per normal cubic metre of carbon monoxide.

What we claim is:—

1. A process for the synthesis of hydrocarbons and oxygen-containing organic compounds, which comprises contacting a mixture of carbon monoxide and water vapour in which the molar ratio CO/H_2O is within the limits 2:1 and 3:1, with a catalyst the main metallic constituent of which is a metal of the 8th group of the periodic system at a temperature within the range 150°—350°C. and at a pressure from normal atmospheric pressure to about 100 atmospheres gauge, the catalyst having previously been activated at a temperature in the range 150°—350°C. by treatment with carbon monoxide and subsequently with hydrogen or by treatment with a CO/H_2 mixture.

2. A process according to claim 1, in which the molar ratio CO/H_2O in the feed is approximately 3:1 to give a synthesis product rich in hydrocarbons.

3. A process according to claim 1, in which the feed contains less than three volumes of carbon monoxide per volume of water vapour and the synthesis pressure exceeds 20 atmospheres, whereby a product rich in alcohols is obtained.

4. A process according to any one of the preceding claims, in which the water vapour reacted with the carbon monoxide is introduced into the reaction space in the liquid state.

5. A process according to claim 4 in which the water is fed into the reaction space at more than one position.

6. 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 180°—280°C.

7. A process according to any one of the preceding claims, in which the catalyst is activated at a temperature within the range 230°—300°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 sesquioxide;

(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 8, in which exit gases are recycled to the reaction space.

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 metal of the 8th group in the catalyst 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 Example 1 or Example 2.

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

EDWARD EVANS & CO.,
14—18, High Holborn, London, W.C.1,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1956.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.