PATENT SPECIFICATION

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COMPLETE SPECIFICATION

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

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of 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 copending Application No. 10728/50 (Serial No. 707,972) there is described a process for the production of hydrocarbons and oxygen-containing organic compounds from a mixture of carbon monoxide and water vapour containing at least two volumes of carbon monoxide for each volume of water vapour, by contacting the mixture at temperatures of from 150° to 350° C. and at normal or elevated pressure up to 100 atmospheres gauge with a catalyst the main metallic constitutent 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).

It has been found that the space velocity of the carbon monoxide/water vapour mixture to be reacted can be considerably increased when the operating pressure is increased at the same time. According to past experience, for example in the hydrogenation of carbon monoxide with hydrogen according to the Fischer-Tropsch process in the presence of fixed-bed catalyst, it was by no means to be foreseen that the reaction performance of the catalyst would be dependent on the pressure employed; rather was it to be assumed in the light of past experience and from the literature on the subject, that the performance of the catalyst with regard to the hydrogenation of carbon monoxide would not be affected by the pressure. Not only is the present invention contrary to past experience, but there is also the surprising factor that there is even a certain regularity in the relation between the operating pressure used and the maximum possible space velocity with the same conversion of carbon monoxide.

It has been found that the space velocity (expressed in volume of gas per hour relatively to unit volume of catalyst) of the carbon monoxide/water vapour mixture may exceed nine times the numerical value of the operating pressure (expressed in atmospheres) without the conversion of carbon monoxide with water vapour falling to below 90%.

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 which contains 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 a metal of the 8th group of the periodic system, 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, the carbon monoxide/water vapour mixture in the synthesis being contacted with the catalyst at a space velocity which is not less than nine times the numerical value of the synthesis pressure in atmospheres. The catalyst is preferably activated at a temperature within the range 230°—300° C. and the synthesis is preferably carried out at a temperature within the range 180°—280° C.

It is preferred to maintain the space velocity between nine and fourteen times the numerical value of the synthesis pressure in atmospheres.

When operating with a space velocity which is less than nine times the operating pressure, the catalyst, or the catalyst space, is utilised to a very incomplete extent, and, due to the very short contacting time, there is the danger of the carbon monoxide being decomposed to carbon. Under these operating conditions, the catalyst is moreover liable to form methane. If the space velocity used relatively to the pressure is excessive, the conversions of the carbon monoxide with water vapour are unsatisfactory.

By so adapting the space velocity to the working pressure, an optimum utilization of the catalyst space is rendered possible with optimum gas throughout and a very good conversion of carbon monoxide, so that optimum results are obtained in respect of the space-time yield and economy.

The carbon monoxide/water vapour ratio in the synthesis is at least 2 and is advantageously not greater than 3. If it is desired to produce predominantly hydrocarbons, it is advantageous for the carbon monoxide/water vapour ratio of the reactants to be about 3. If it is desired that the synthesis product should contain an appreciable amount of alcohols, then the carbon monoxide/water vapour ratio in the synthesis feed mixture is less than 3; in addition, the use of pressures exceeding 20 atmospheres is advantageous.

Water which, in its vapour form, constitutes one reactant in the process according to the invention, may be introduced into the reaction zone in the liquid state instead of in the vapour state. The injection of this reactant into the reaction zone in the liquid state affords the great advantage that a large part of the heat evolved during the reaction between the carbon monoxide and the water vapour is dissipated in converting the water from the liquid state into the vapour state, that is to say, a large part of the reaction heat is dissipated in the form of the latent heat of vaporisation of water.

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 utilization 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 process of the invention may be carried out with the catalyst in a fixed-bed, with the catalyst suspended in a suitable liquid medium, for example, an oil, or with the catalyst in a finely divided condition suspended in the synthesis gas stream (fluidised catalyst). 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 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 those given in 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 by the following example.

A mixture of carbon monoxide and water vapour in the ratio 3:1.25 was passed at 230° C. over an Fe-Mg-Kieselguhr catalyst which had been reduced for 72 hours at temperature of 200°—260° C. with a gas mixture consisting of one volume of carbon monoxide and two volumes of hydrogen. The operating pressure was increased, in steps of 10 atmospheres, from 10 to 70 atmospheres, and the space velocity was adjusted to nine times, advantageously to nine to fourteen times the operating pressure. As shown in the following table, the carbon monoxide conversion did not fall below 90%, in spite of increasing the space velocity from 175 at 10 atmospheres to 800 at 70 atmospheres.

Pressure in atmospheres	10	20	30	40	50	60	70
Space velocity units by volume of gas per hour relatively to unit volume of catalyst	175	240	350	420	610	720	800
Space velocity:—pressure	17.5	12.0	11.7	10.5	12.2	12.0	11.4
Carbon monoxide conversion, % by volume	90.5	90.8	91.5	92.3	90.6	92.4	91.3

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 containing at least two volumes of carbon monoxide per volume of water vapour with a catalyst the main metallic constituent of which is a metal of the 8th group of the periodic system, which catalyst has been previously 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, the contacting of the carbon monoxide and water vapour with the catalyst being carried out at a temperature between 150° C. and 350° C. and at a pressure from normal atmospheric pressure to about 100 atmospheres gauge and at a space velocity which is not less than nine times the numerical value of the synthesis pressure in atmospheres.

2. A process according to Claim 1, in which the space velocity is not greater than fourteen times the numerical value of the synthesis pressure in atmospheres.

3. A process according to either of the preceding claims, in which the carbon monoxide/water vapour ratio is not greater than 3.

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 10, 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 com-

pounds, 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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