PATENT SPECIFICATION

(11) 1 553 959

1 553 959

(21) Application No. 16499/78 (22) Filed 26 April 1978
(31) Convention Application No. 7704658
(32) Filed 28 April 1977 in
(33) Netherlands (NL)
(44) Complete Specification published 17 Oct. 1979
(51) INT CL² C07C 1/04
(52) Index at acceptance
C5E 222 332 386 391 CF
(72) Inventors HENRICUS MICHAEL JOSEPH BIJWAARD and
SWAN TIONG SIE

(19) THE PATENT OFFICE LONDON

(54) PREPARING HYDROCARBONS BY THE FISCHER-TROPSCH SYNTHESIS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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:—

The invention relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen.

The preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen by contacting this mixture at elevated temperature and pressure with a catalyst is known in the literature as the hydrocarbon synthesis according to Fischer-Tropsch. The behaviour of a catalyst for the Fischer-Tropsch synthesis can be judged on the basis of the conversion and selectivity that can be reached with this catalyst in relation to the space velocity that is used therewith. The term conversion should be taken to mean in this connection the molar percentage of the gas mixture that is converted into hydrocarbons and the term selectivity the weight percentage of C_3^+ hydrocarbons produced, based on the total quantity of hydrocarbons produced. In general it may be stated that a good catalyst for the hydrocarbon synthesis according to Fischer-Tropsch should meet the requirements that at a space velocity of at least 400 Nl . l⁻¹ . h⁻¹ it must be capable of converting at least 50%m of a gas mixture with a selectivity of at least 70%w. A catalyst is judged to be better suited for the present purpose, according as higher conversions and selectivities can be reached with it and according as higher space velocities can be used. Among the catalysts that have been proposed in the literature for use in the hydrocarbon synthesis according to Fischer-Tropsch there are a number that meet the three above-mentioned requirements if they are applied to mixtures of carbon monoxide and hydrogen whose H_2/CO molar ratio is at least 1.0. In an investigation by the Applicant it has been found, however, that when these catalysts are applied to mixtures of carbon monoxide and hydrogen whose H_2/CO molar ratio is smaller than 1.0, it is in most cases impossible to meet the three above-mentioned minimum requirements all at the same time. As a rule, when the catalysts are applied to the low-hydrogen gas mixtures, two of the minimum requirements can readily be met, but the third parameter that is important in this connection then has an unacceptably low value.

It has been found by the Applicant that very suitable catalysts for the preparation of hydrocarbons from low-hydrogen gas mixtures can be obtained by combining two catalysts, of which one catalyst has Fischer-Tropsch activity and the other catalyst CO-shift activity. This finding is the subject of the co-pending United Kingdom Patent Application No. 16498/78, Serial No. 1,553,958. It has been stated in the said patent application that the principle on which the invention described therein is based can also be used in another way, namely by using one catalyst which combines both these functions. A group of such catalysts is the subject of the present patent application.

It has been found that the excellent behaviour of the catalyst combinations according to the afore-mentioned patent application, which are capable, at high space velocity, of converting a low-hydrogen gas mixture with a high conversion and selectivity into hydrocarbons, is also shown by single catalysts which contain both certain metals having Fischer-Tropsch activity and certain metals having CO-shift activity, provided that the quantities in which these metals are present in the catalyst as well as their relative proportions meet certain requirements. As metals having Fischer-Tropsch activity the catalysts should contain one or more metals from the iron group and/or ruthenium. The quantity of metals from the iron group which may be present in the catalysts is 5—50%w. The quantity of ruthenium may be 0.1—5%w. As metals having CO-shift activity the catalysts should contain copper and/or zinc. The quantity of copper and/or zinc which may be present in the catalysts is 5—50%w. Finally, the weight ratio of the total quantities of copper and zinc in respect of the total quantity of metals from the iron group, plus ten times the quantity of ruthenium, should be 0.5—5.

According to the present invention a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen is provided, in which process a mixture of carbon monoxide and hydrogen whose H_2/CO molar ratio is less than 1.0, is contacted at elevated temperature and pressure with a catalyst (a) containing 5—50%w of one or more metals from the iron group and/or 0.1—5%w ruthenium and (b) 5—50%w copper and/or zinc, the weight ratio of the total quantity of copper and zinc in respect of the total quantity of metals from the iron group, plus ten times the quantity of ruthenium being 0.5—5, which catalyst is prepared by impregnating an inert carrier with solutions of salts of one or more metals from the iron group and/or ruthenium and of copper and/or zinc.

The process according to the invention is preferably carried out at a temperature of from 200 to 350°C, a pressure of from 10 to 70 bar and a space velocity of from 400 to 5000 and in particular of from 400 to 2500 $Nl.l^{-1}.h^{-1}$.

In the process according to the invention a catalyst should be used which contains as metals having Fischer-Tropsch activity, one or more metals from the iron group and/or ruthenium. Preference is given to catalysts which contain as metals having Fischer-Tropsch activity iron or cobalt. If in the process according to the invention an iron-containing catalyst is used, the process is preferably carried out at a temperature of from 250 to 325°C and a pressure of from 20 to 50 bar. If use is made of a cobalt-containing catalyst, the process according to the invention is preferably carried out at a temperature of from 220 to 300°C and a pressure of from 10 to 35 bar.

In the process according to the invention a catalyst should be used which contains as metals having CO-shift activity copper and/or zinc. Preference is given to catalysts which contain as metals having CO-shift activity both copper and zinc, in particular catalysts in which the Cu/Zn atom ratio lies between 0.25 and 4.0.

The preparation of the catalysts according to the invention is effected by impregnating an inert carrier, such as silica or alumina, with solutions of salts of one or more metals from the iron group and/or of ruthenium and of copper and/or zinc.

In the process the starting materials should be mixtures of carbon monoxide and hydrogen of which the H_2/CO molar ratio is smaller than 1.0. Such mixtures can very suitably be prepared by partial combustion of a carbon- and a hydrogen-containing material; in particular a material having a low hydrogen content. Examples of these materials are brown coal, anthracite and coke. During the partial combustion the feed is converted in finely divided form which oxygen or air, if desired enriched with oxygen, into a gas mixture containing such substances as hydrogen, carbon monoxide, carbon dioxide, nitrogen and water. In the combustion steam is preferably used as the temperature moderator. The partial combustion is preferably carried out at a temperature between 900 and 1500°C and a pressure between 10 and 50 bar. By purifying the crude gas mixture, upon which, among other substances, ash, carbon-containing material, hydrogen sulphide and carbon dioxide are removed, a gas is obtained which consists substantially of a mixture of carbon monoxide and hydrogen.

In the process according to the invention the starting material is preferably a gas mixture whose H_2/CO molar ratio is higher than 0.4. If gas mixtures are available of which the H_2/CO molar ratio is less than 0.4 this molar ratio is preferably increased to a value between 0.4 and 1.0 before the process according to the invention is applied to these gas mixtures. Previous increase of the H_2/CO molar ratio of the gas mixtures can very suitably be effected by adding hydrogen or by subjecting the gas mixtures to the known CO-shift reaction. If the starting materials are gas mixtures whose H_2/CO molar ratio is less than 0.4, attractive results can also be obtained by applying the process according to the invention to such mixtures to which water has been added.

In the process according to the invention a catalyst should be used of which the weight ratio of the total quantity of copper and zinc in respect of the total quantity of metals from the iron group, plus ten times the quantity of ruthenium, is 0.5—5. The ratio in which the two types of metals should be present within these limits in the catalysts differs from case to case and depends among other factors on the conversion and selectivity envisaged, the composition of the gas mixture, the reaction conditions used and the activities of the metals of the two types. For instance, a decrease in the conversion, which occurs if under certain conditions the H_2/CO molar ratio of the feed gas is reduced, may be offset by increasing the activity of the CO-shift function of the catalyst. An increase in the selectivity can be reached in the process by increasing the selectivity of the Fischer-Tropsch function of the catalyst (e.g. by incorporating into the catalyst a higher content of selectivity promoters). An increase in the conversion can be reached by increasing the activities of the Fischer-Tropsch and CO-shift functions of the catalyst (e.g. by incorporating into the catalyst a higher content of metals having Fischer-Tropsch activity and CO-shift activity). Very satisfactory results can generally be obtained with the process according to the invention, if the said weight ratio of the two types of metals in the catalyst is more than 0.75 and in particular if this weight ratio lies between 1.0 and 3.0. A very suitable catalyst for carrying out the process according to the invention is a catalyst containing the metals iron, potassium, copper and zinc, applied or not to silica as the carrier.

The process according to the invention can very suitably be carried out by passing the feed in upward or in downward direction through a vertically disposed reactor in which a fixed or a moving bed of the catalyst is present. The process may be carried out, for instance, by passing the feed in upward direction through a vertically disposed catalyst bed, use being made of such a gas rate that the catalyst bed expands. If desired, the process may also be carried out by using a suspension of the catalyst in a hydrocarbon oil. Depending on whether the process is carried out with use of a fixed catalyst bed, an expanded catalyst bed or a catalyst suspension, catalyst particles having a diameter between 1 and 5 mm, 0.5 and 2.5 mm and 20 and 150 microns, respectively, are preferred.

If the process is carried out with use of a fixed catalyst bed, deposition of waxy hydrocarbons takes place on the catalyst, which results in a decrease in activity. This deactivation may effectively be counteracted by washing the catalyst continuously with a fraction of the product prepared in the process. For this purpose preference is given to a fraction that has an initial boiling point above 200°C and a final boiling point below 550°C. An additional advantage of the above-mentioned continuous washing of the catalyst is that temperature control of the process, which is highly exothermic, is simplified. In addition to hydrocarbons and oxygen-containing hydrocarbons whose molecular weight extends over a wide range, the reaction product that leaves the reactor in the process according to the invention contains, inter alia, water, nitrogen, carbon dioxide and non-converted carbon monoxide and hydrogen. If the process is carried out in once-through operation, the C_3^+-fraction is separated from the reaction product as the end product. If the process is carried out in recycle operation, the C_3^+-fraction is also separated from the reaction product as the end product, but now the remainder of the reaction product is recycled to the reactor, if necessary after reduction of the carbon dioxide content and with use of a bleed stream to avoid build-up of, inter alia, nitrogen.

The invention will now be further explained with the aid of the following example.

EXAMPLE

Five catalysts (I—V) according to the invention were prepared.

Catalysts I and II

$Fe/K/Cu/Zn/SiO_2$ catalysts which comprised 25 pbw iron, 5 pbw potassium, 10 pbw copper and 20 pbw zinc per 100 pbw silica. The preparation of these catalysts was started from four aqueous solutions containing 1533 g $Fe(NO_3)_3 . 9$ aq, 110 g KNO_3, 323 g $Cu(NO_3)_2 . 3$ aq and 773 g $Zn(NO_3)_2 . 6$ aq, respectively. The solutions were combined and water was added to the volume of the combined solution to 1600 ml. This 1600 ml solution was used in three portions of 800, 400 and 400 ml, respectively, for impregnating 850 g silica in three steps. In the first impregnation 800 ml of the solution was used. After drying at 120°C and calcining for 1 hour at 500°C the material was again impregnated, now with 400 ml of the solution. After drying once more at 120°C and calcining for 1 hour at 500°C the material was finally impregnated again with the remaining 400 ml of the solution. After drying at 120°C and calcining for two hours at 500°C part of the catalyst material was ground into particles of 1.7—2.8 mm in diameter (catalyst I) and the remainder into particles of 0.15—0.30 mm in diameter (catalyst II).

Catalysts III and IV

$Fe/K/Cu/Zn/SiO_2$ catalysts which comprised 25 pbw iron, 2 pbw potassium, 15 pbw copper and 30 pbw zinc per 100 pbw silica. The preparation of the catalysts was carried out in substantially the same way as that of catalysts I and II. Catalyst III had a particle diameter of 1.7—2.8 mm and catalyst IV had a particle diameter of 0.15—0.30 mm.

Catalyst V

Fe/K/Cu/Zn catalyst having a potassium content of 2%w. Catalyst V was prepared by impregnating a Fe/Cu/Zn catalyst which comprised 76.7 pbw iron and 49.7 pbw copper per 100 pbw zinc oxide with an aqueous solution of KNO_3 followed by drying at 120°C and calcining for 1 hour at 500°C.

Catalysts I—V were tested for the hydrocarbon synthesis according to Fischer-Tropsch by contacting a mixture of carbon monoxide and hydrogen of which the H_2/CO molar ratio was 0.5 with each of these catalysts at 280°C, 30 bar and a space velocity of 1000 $Nl\,.\,l^{-1}\,.\,h^{-1}$. The results of the experiments are given in the table.

TABLE

Exp. No.	No. of catalyst used	Conversion, %m	Selectivity, %w
1	I	60	87
2	II	77	82
3	III	67	82
4	IV	82	83
5	V	53	84

WHAT WE CLAIM IS:—

1. A process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, characterized in that a mixture of carbon monoxide and hydrogen, whose H_2/CO molar ratio is less than 1.0 is contacted at elevated temperature and pressure with a catalyst containing (a) 5—50%w of one or more metals from the iron group and/or 0.1—5%w ruthenium and (b) 5—50%w copper and/or zinc, the weight ratio of the total quantity of copper and zinc in respect of the total quantity of metals from the iron group plus ten times the quantity of ruthenium being 0.5—5, which catalyst is prepared by impregnating an inert carrier with solutions of salts of one or more metals from the iron group and/or ruthenium and of copper and/or zinc.

2. A process according to Claim 1, characterized in that it is carried out at a temperature of from 200 to 350°C, a pressure of from 10 to 70 bar and a space velocity of from 400 to 5000 and preferably of from 400 to 2500 $Nl\,.\,l^{-1}\,.\,h^{-1}$.

3. A process according to Claim 1 or 2, characterized in that a catalyst is used which contains iron or cobalt.

4. A process according to Claim 3, characterized in that a catalyst is used which contains iron and in that the process is carried out at a temperature of from 250 to 325°C and a pressure of from 20 to 50 bar.

5. A process according to Claim 3, characterized in that a catalyst is used which contains cobalt and in that the process is carried out at a temperature of from 220 to 300°C and a pressure of from 10 to 35 bar.

6. A process according to any one of Claims 1—5, characterized in that a catalyst is used which contains both copper and zinc.

7. A process according to any one of Claims 1—6, characterized in that a catalyst is used of which the weight ratio of the total quantity of copper and zinc in respect of the total quantity of metals from the iron group, plus ten times the quantity of ruthenium, is more than 0.75.

8. A process according to any one of Claims 1—4, 6 and 7, characterized in that a catalyst is used which contains the metals iron, potassium, copper and zinc, with silica as the carrier.

9. A process according to any one of Claims 1—8, characterized in that the H_2/CO molar ratio of the feed gas is more than 0.4.

10. A process according to any one of Claims 1—9, characterized in that it is carried out with use of a fixed catalyst bed, an expanded catalyst bed or a catalyst suspension and catalyst particles having a diameter between 1 and 5 mm, 0.5 and 2.5 mm and 20 and 150 microns, respectively.

11. A process according to any one of Claims 1—10, characterized in that it is carried out with use of a fixed catalyst bed and in that the catalyst is continuously washed with a fraction of the product prepared in the process.

12. A process for the preparation of hydrocarbons, substantially as described herein before and in particular with reference to experiments 1—5 from the example.

13. Hydrocarbons which have been prepared by using a process according to Claim 12.

R. C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London SE1 7NA.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.