PATENT SPECIFICATION

(11) **1 553 958**

1553958

(21) Application No. 16498/78 (22) Filed 26 April 1978
(31) Convention Application No. 7 704 656
(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 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 now been found that the conversion that can be reached at a given temperature, pressure and space velocity by contacting the low-hydrogen gas mixtures with a catalyst (X) which meets certain minimum requirements with regard to its behaviour in the Fischer-Tropsch reaction, can be considerably increased by using this catalyst in a physical mixture with a catalyst (Y) which meets certain minimum requirements with regard to its behaviour in the well-known CO-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$).

For one catalyst (X) of the physical mixture it holds that it must be capable, at the given temperature, pressure and space velocity, of converting at least 30%m of the low-hydrogen gas mixture with a selectivity of at least 70%w.

For the other catalyst (y) of the physical mixture it holds that it must be capable, at the given temperature and pressure and at a space velocity of 1000 $Nl.l^{-1}.h^{-1}$, of converting at least 80%m of the water present in a mixture of carbon monoxide and water with a CO/H_2O molar ratio of 10.0 into hydrogen.

As far as the mixing ratio of the catalysts is concerned, at least 10%v of each of the catalysts (X) and (Y) should be present in the catalyst physical mixture.

In the above formulation it has been taken for granted that the catalysts (X) of the physical mixture which meets the criterion in respect of the Fischer-Tropsch reaction, does not meet the criterion in respect of the CO-shift reaction and conversely. This is in conformity with actual practice, where catalysts that are recommended for the Fischer-Tropsch reaction show, as a rule, no or only little activity for the CO-shift reaction and conversely.

In the investigation concerning this subject the Applicants have realized that the principle on which the present invention is based, namely that for the preparation of hydrocarbons from low-hydrogen gas mixtures very suitable catalysts can be obtained by physically mixing a catalyst (X) having Fischer Tropsch activity with a catalyst (Y) having CO-shift activity, can also be used in another way, namely by using one catalyst which combines those two functions. Such a catalyst may for instance be prepared by emplacing on an inert carrier, by impregnation, both one or more metals having Fischer-Tropsch activity and one or more metals having CO-shift activity. Such catalysts fall outside the scope of the present patent application. The use of a number of catalysts belonging to this type for the preparation of hydrocarbons from low-hydrogen gas mixtures is the subject of the co-pending British patent application No. 16499/78 (Serial No. 1553959) in the name of the Applicant.

The present patent application therefore relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, 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 physical mixture of two catalysts of which one catalyst (X) is capable, at the temperature, pressure and space velocity at which the above-mentioned process is carried out, of converting at least 30%m of the H_2/CO mixture with a selectivity of at least 70%w, and of which the other catalyst (Y) is capable, at the temperature and pressure at which the above-mentioned process is carried out and at a space velocity of 1000 $Nl.l^{-1}.h^{-1}$, of converting at least 80%m of the water present in a mixture of carbon monoxide and water having a CO/H_2O molar ratio of 10.0 into hydrogen, and in which process at least 10%v of each of the catalysts (x) and (y) is present in the catalyst physical mixture.

In the process according to the invention a physical mixture of two catalysts is used, which, for convenience, will be designated catalysts X and Y. The two catalysts may be present as a mixture, in which, in principle, each particle of catalyst X is surrounded by a number of particles of catalyst Y and conversely. If the process is carried out with use of a fixed catalyst bed, this bed may be built up of alternate layers of particles of catalyst X and catalyst Y. If the two catalysts are used as a mixture, this mixture may be a macromixture or a micromixture. In the first case the physical mixture consists of two kinds of macroparticles of which one kind is completely made up of catalyst X and the other one completely of catalyst Y. In the second case the physical mixture consists of one kind of macroparticles, each macroparticle being made up of a large number of microparticles of both catalyst X and catalyst Y.

Catalyst physical mixtures according to the invention in the form of micromixtures may be prepared, for instance, by thoroughly mixing a fine powder of catalyst X with a fine powder of catalyst Y and shaping the mixture to larger particles, for instance, by extruding or pelletizing. In the process according to the invention it is preferred to use catalyst physical mixtures in the form of micromixtures.

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 one of the catalysts of the physical mixture should be capable, at the temperature, pressure and space velocity at which the process is carried out, of converting at least 30%m of the H_2/CO mixture with a selectivity of at least 70%w. Catalysts (X) having this quality are known and are among the group of catalysts referred to in the literature as Fischer-Tropsch catalysts. Such catalysts often comprise one or more metals from the iron group of ruthenium together with one or more promoters for increasing the activity and/or selectivity, and sometimes a carrier material such as kieselguhr. They can be prepared by precipitation, by melting or by impregnation. Preparation of catalysts comprising one or more metals from the iron group by impregnation is effected by impregnating a porous carrier with one or more aqueous solutions of salts of metals of the iron group and, if necessary, promoters, followed by drying and calcining of the composition. In the process according to the invention it is preferred to use a catalyst physical mixture of which the catalyst (X) having the required Fischer-Tropsch activity is an iron or a cobalt catalyst, and in particular such a catalyst (X) which has been prepared by impregnation. Very suitable Fischer-Tropsch catalysts (X) for use in the catalyst physical mixtures according to the invention are the catalysts prepared by impregnation according to the co-pending United Kingdom patent application No. 46427/77 (Serial No. 1548468). The catalysts comprise per 100 pbw carrier, 10—75 pbw of one or more metals from the iron group together with one or more promoters in a quantity of 1—50% of the quantity of metals from the iron group present on the catalyst (X), which catalysts (X) have such a specific average pore diameter (p) of at most 10,000 nm and such a specific average particle diameter (d) of at most 5 mm, that the quotient p/d is more than 2 (p in nm and d in mm).

If it is intended in the process according to the invention to use a catalyst physical mixture of which the catalyst (X) having the Fischer-Tropsch activity is an iron catalyst, preference is given to an iron catalyst which contains a promoter combination consisting of an alkali metal, a metal that is easy to reduce, such as copper or silver and optionally a metal that is difficult to reduce, such as aluminium or zinc. A very suitable iron catalyst for the present purpose is a catalyst prepared by impregnation, containing iron, potassium and copper on silica as the carrier. When use is made of an iron catalyst in the catalyst physical mixture as the catalyst (X) having the required Fischer-Tropsch activity, the process according to the invention is preferably carried out at a temperature of from 250 to 325°C and a pressure of from 20 to 50 bar.

If it is intended in the process according to the invention to use a catalyst physical mixture of which the catalyst (X) having the required Fischer-Tropsch activity is a cobalt catalyst, preference is given to a cobalt catalyst which contains a promoter combination consisting of an alkaline-earth metal and thorium, uranium or cerium.

A very suitable cobalt catalyst for the present purpose is a catalyst prepared by impregnation containing cobalt, magnesium and thorium on silica as the carrier. Other very suitable cobalt catalysts prepared by impregnation are catalysts containing, in addition to cobalt, one of the elements chromium, titanium, zirconium and zinc on silica as the carrier. When use is made of a cobalt catalyst in the catalyst mixture as a catalyst (X) having the required Fischer-Tropsch activity, 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 one of the catalysts of the physical mixture should be capable, at the temperature and pressure at which the process is carried out and at a space velocity of 1000 $\text{Nl.l}^{-1}.\text{h}^{-1}$, of converting at least 80%m of the water present in a mixture of carbon monoxide and water with a CO/H_2O molar ratio of 10.0 into hydrogen. Catalysts (Y) having this quality are known and are among the group of catalysts referred to in the literature as CO-shift catalysts. Such catalysts often comprise one or more metals selected from the group composed of iron, chromium, copper, zinc, cobalt, nickel and molybdenum as the catalytically active component, either per se or in the form of their oxides or sulphides. Examples of suitable CO-shift catalysts are the mixed sulphidic catalysts according to the United Kingdom patent specification No. 1472595 and the spinel catalysts according to the co-pending United Kingdom patent application No. 46426/77 (Serial No. 1536052). In the process according to the invention use is preferably made of a catalyst physical mixture of which the catalyst (Y) having the required CO-shift activity is a catalyst containing both copper and zinc, in particular a catalyst in which the Cu/Zn atom ratio lies between 0.25 and 4.0.

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 material containing carbon and hydrogen, in particular a material with a low hydrogen content. Examples of these materials are brown coal, anthracite and coke. During the partial combustion the feed, in finely divided form, is converted with oxygen or air, if desired enriched with oxygen, into a gas mixture containing, among other substances, 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 purification of the crude gas mixture, in 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. If a gas mixture is available of which the H_2/CO molar ratio lies between 0.8 and 1.0, it is preferred in the process according to the invention to use a catalyst combination of which the catalyst having the required Fischer-Tropsch activity is a cobalt catalyst.

In the process according to the invention at least 10%v of each of the catalysts (X) and (Y) should be present in the catalyst physical mixture. The ratio in which the two catalysts (X) and (Y) should be present in the catalyst physical mixture 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 two catalysts (X) and (Y) in the physical mixture. Thus, a decrease in the conversion, which occurs if under certain reaction conditions the H_2/CO molar ratio of the feed gas is reduced, may be compensated for by using a catalyst (Y) with a higher CO-shift activity in the physical mixture. An increase in selectivity can be reached by using a more selective Fischer-Tropsch catalyst (X) in the physical mixture (e.g. a catalyst with a higher content of selectivity promoters). An increase in conversion can be reached by using more active Fischer-Tropsch and CO-shift catalysts in the physical mixture (e.g. catalysts with a higher content of catalytically active metals).

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 physical mixture 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 physical mixture 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 physical mixture, which results in a decrease in activity. This deactivation may effectively be counteracted by washing the catalyst physical mixture 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 physical mixture 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.

Six catalyst physical mixtures (I—VI) were prepared according to the invention. Catalyst physical mixtures I—IV were obtained by mixing a Fischer-Tropsch catalyst selected from catalysts 1—4 with a CO-shift catalyst selected from catalysts A—C in a volume ratio 1:1. Catalyst physical mixture VI was obtained by grinding both Fischer-Tropsch catalyst 5 and CO-shift catalyst A to powders with a particle size diameter smaller than 44 microns, mixing the powders in a volume ratio of 1:1 and pelletizing the mixture into large particles, which were subsequently converted — by crushing and sieving — into granules having a diameter of from 1.7 to 2.8 mm. In order to be able to obtain a proper judgement of the behaviour of catalyst physical mixture VI in the hydrocarbon synthesis according to Fischer-Tropsch, a sixth Fischer-Tropsch catalyst was included in the investigation (catalyst 6).

Catalysts 1—6 and A—C were composed as follows:

Catalyst 1.

$Fe/Cu/K/SIO_2$ catalyst which comprised 25 pbw iron, 1.25 pbw copper and 1 pbw potassium per 100 pbw silica. Particle diameter: 1.0—2.4 mm.

Catalyst 2.

$Fe/Cu/K/SiO_2$ catalyst which comprised 25 pbw iron, 1.25 pbw copper and 2 pbw potassium per 100 pbw silica. Particle diameter: 1.7—2.8 mm.

Catalyst 3.

$Co/Th/Mg/SiO_2$ catalyst which comprised 25 pbw cobalt, 1.04 pbw thorium and 1.18 pbw magnesium per 100 pbw silica. Particle size: 1.7—2.8 mm.

Catalyst 4.

$Co/Cr/SiO_2$ catalyst which comprised 25 pbw cobalt and 1 pbw chromium per 100 pbw silica. Particle size: 1.7—2.8 mm.

Catalyst 5.

$Fe/K/SiO_2$ catalyst which comprised 25 pbw iron and 2 pbw potassium per 100 pbw silica. Particle size: 1.7—2.8 mm.

Catalyst 6.

$Fe/K/SiO_2$ catalyst which comprised 25 pbw iron and 2 pbw potassium per 200 pbw silica. Catalyst 6 had been obtained by grinding catalyst 5 and a silica to powders with a particle size smaller than 44 microns, mixing the powders in a volume ratio corresponding to the above-mentioned composition, pelletizing the mixture into large particles, which were subsequently converted — by crushing and sieving — into granules having a diameter of from 1.7 to 2.8 mm.

Catalyst A.

Cu/Zn/SiO_2 catalyst which comprised 15 pwb copper and 30 pbw zinc per 100 pbw silica. Particle size 1.0—3.4 mm.

Catalyst B.

Cu/Al/Zn catalyst which comprised 53.8 pbw copper and 18.1 pbw aluminium per 100 pbw zinc. Particle size: 1.7—2.8 mm.

Catalyst C.

Cu/Al/Zn catalyst which comprised 225 pbw copper and 105 pbw aluminium per 100 pbw zinc. Particle size: 1.7—2.8 mm.

Catalyst physical mixtures I—VI and catalysts 1—6 and A—C were tested for the hydrocarbon synthesis according to Fischer-Tropsch by contacting a mixture of carbon monoxide and hydrogen, whose H_2/CO molar ratio was 0.5, at 280°C and 30 bar with each of these catalyst physical mixtures and catalysts. In addition, the behaviour of catalysts 1—6 and A—C in respect of the CO-shift reaction was examined by contacting a mixture of carbon monoxide and water, whose CO/H_2O molar ratio was 10.0, at 280°C, 30 bar and a space velocity of 1000 $Nl.l^{-1}.h^{-1}$ with each of these catalysts. The results of these experiments and the space velocities used in the Fischer-Tropsch reaction are given in the table.

TABLE

Exp. No.	No. of cat. or cat. physical mixture used	Cat. from which the cat. physical mixture had been composed	Space velocity used in the Fischer-Tropsch reaction, $l.l^{-1}.h^{-1}$	Conversion in the Fischer-Tropsch reaction, %m	Selectivity in the Fischer-Tropsch reaction, %w	Conversion in the CO-shift reaction, %m
1	1	—	500	48	85	55
2	2	—	500	50	82	60
3	3	—	500	36	75	5
4	4	—	500	46	82	7
5	5	—	1000	47	86	52
6	6	—	1000	41	86	42
7	A	—	500	*)	—	83
8	B	—	500	*)	—	92
9	C	—	500	*)	—	90
10	I	1 and A	500	65	82	—
11	II	2 and B	500	63	75	—
12	III	2 and C	500	58	82	—
13	IV	3 and A	500	50	76	—
14	V	4 and B	500	84	78	—
15	VI	5 and A	1000	65	84	—

*) With catalysts A—C there is some conversion of the H_2/CO mixture into methanol, but not into hydrocarbons.

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 physical mixture of two catalysts of which one catalyst (X) is capable, at the temperature, pressure and space velocity at which the above-mentioned process is carired out, of converting at least 30%m of the H_2/CO mixture with a selectivity of at least 70%w for C_3^+ hydrocarbons and of which the other catalyst (Y) is capable, at the temperature and pressure at which the above-mentioned process is carried out and at a space velocity of 1000 $Nl.l^{-1}.h^{-1}$, of converting at least 80%m of the water present in a mixture of carbon monoxide and water having a CO/H_2O molar ratio of 10.0 into hydrogen, and in that at least 10%v of each of the catalysts (X) and (Y) is present in the catalyst physical mixture.

2. A process according to claim 1, characterized in that a catalyst physical mixture is used which consists of one kind of macroparticles, each macroparticle being made up of a large number of microparticles of each of the two catalysts.

3. A process according to claim 1 or 2, characterized in that it is carried out at a temperature of from 200—350°C, a pressure of from 10 to 70 bar and a space velocity of from 400 to 5000.

4. A process according to claim 1, characterized in that a catalyst physical mixture is used of which the catalyst (X) having the required Fischer-Tropsch activity is an iron or a cobalt catalyst.

5. A process according to claim 4, characterized in that the catalyst (X) concerned comprises per 100 pbw carrier, 10—75 pbw iron or cobalt together with one or more promoters in a quantity of 1—50% of the quantity of iron or cobalt present on the catalyst, which catalyst has such a specific average pore diameter (p) of at most 10,000 nm and such a specific average particle diameter (d) of at most 5 mm, that the quotient p/d is more than 2 (p in nm and d in mm).

6. A process according to claim 4 or 5, characterized in that the catalyst (X) concerned is an iron catalyst, which contains a promoter combination consisting of an alkali metal, a metal that is easy to reduce, such as copper or silver and optionally a metal that is difficult to reduce, such as aluminium or zinc.

7. A process according to any one of claims 4—6, characterized 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.

8. A process according to claim 4 or 5, characterized in that the catalyst (X) concerned is a cobalt catalyst which contains a promoter combination consisting of an alkaline-earth metal and thorium, uranium or cerium.

9. A process according to claim 4 or 5, characterized in that the catalyst X contains, in addition to cobalt, one of the elements chromium, titanium, zirconium and zinc on silica as the carrier.

10. A process according to any one of claims 4, 8 and 9, characterized in that the catalyst X is a cobalt catalyst 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.

11. A process according to any one of claims 4 and 8—10 characterized in that the catalyst X is a cobalt catalyst and in that the process is applied to a feed gas whose H_2/CO molar ratio lies between 0.8 and 1.0.

12. A process according to any one of claims 1—11, characterized in that a catalyst combination is used of which the catalyst (Y) having the required CO-shift activity is a catalyst containing both copper and zinc.

13. A process according to any one of claims 1—12, characterized in that the H_2/CO molar ratio of the feed gas is more than 0.4.

14. A process according to any one of claims 1—13, 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.

15. A process according to any one of claims 1—14, characterized in that it is carried out with use of a fixed catalyst bed and in that the catalyst physical mixture is continuously washed with a fraction of the product prepared in the process.

16. A process for the preparation of hydrocarbons, substantially as described hereinbefore and with reference to experiments 10—15 of the example.

17. Hydrocarbons which have been prepared by using a process as claimed in any one of claims 1—16.

ROY C. ROGERS,
Chartered Patent Agent,
Shell Centre, London, SE17NA.
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.