(12) UK Patent Application (19) GB (11) 2 077 754 A

(21) Application No 8116650
(22) Date of filing 1 Jun 1981
(30) Priority data
(31) 8003215
(32) 3 Jun 1980
(33) Netherlands (NL)
(43) Application published
23 Dec 1981
(51) INT CL^3
C07C 1/04
(52) Domestic classification
C5E 332 386 CF
(56) Documents cited
None
(58) Field of search
C5E

(71) Applicant
Shell Internationale Research Maatschappij B.V.,
Carel Van Bylandtlaan 30,
The Hague, The Netherlands
(72) Inventors
Henricus Michael,
Michael Adriaan,
Lambert Schaper,
Joseph Bijwaard,
Maria Boersma
(74) Agent
R. C. Rogers,
4 York Road, London SE1 7NA

(54) A Process for the Preparation of Hydrocarbons

(57) Syngas with a H_2/CO molar ratio less than 1 is contacted in a first stage with a Fe-comprising catalyst having Fischer-Tropsch as well as CO-shift activity; a H_2/CO mixture optionally separated from the first stage product and having as such or after adjusting a H_2/CO molar ratio of at least 1.5 is contacted in a second stage with a Co- or Ru- comprising Fischer-Tropsch catalyst. In this way the stability of the process is improved.

ERRATUM

SPECIFICATION No. 2 077 754 A

Front page, Heading (72) Inventors, *delete* whole lines *insert* (72) Inventors Henricus Michael Joseph Bijwaard, Michael Adriaan Maria Boersma, Lambert Schaper.

THE PATENT OFFICE
13th August, 1982

GB 2 077 754 A

SEE ERRATA SLIP ATTACHED

(12) UK Patent Application (19) GB (11) 2 077 754 A

(21) Application No 8116650
(22) Date of filing 1 Jun 1981
(30) Priority data
(31) 8003215
(32) 3 Jun 1980
(33) Netherlands (NL)
(43) Application published
23 Dec 1981
(51) INT CL³
C07C 1/04
(52) Domestic classification
C5E 332 386 CF
(56) Documents cited
None
(58) Field of search
C5E

(71) Applicant
Shell Internationale
Research Maatschappij
B.V.,
Carel Van Bylandtlaan 30,
The Hague, The
Netherlands
(72) Inventors
Henricus Michael,
Michael Adriaan,
Lambert Schaper,
Joseph Bijwaard,
Maria Boersma
(74) Agent
R. C. Rogers,
4 York Road, London SE1
7NA

(54) A Process for the Preparation of Hydrocarbons

(57) Syngas with a H_2/CO molar ratio less than 1 is contacted in a first stage with a Fe-comprising catalyst having Fischer-Tropsch as well as CO-shift activity; a H_2/CO mixture optionally separated from the first stage product and having as such or after adjusting a H_2/CO molar ratio of at least 1.5 is contacted in a second stage with a Co- or Ru- comprising Fischer-Tropsch catalyst. In this way the stability of the process is improved.

SEE ERRATA SLIP ATTACHED

SPECIFICATION

A Process for the Preparation of Hydrocarbons

The invention relates to a process for the preparation of a hydrocarbon mixture from a mixture monoxide and hydrogen having an H_2/CO molar ratio of less than 1.0, with the use of an Fe-containing bifunctional catalyst or catalyst combination possessing, in addition to activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, activity for the conversion of an H_2/CO mixture into an H_2/CO_2 mixture.

In an investigation into said process by the Applicant it has been found that if the process is carried out at a certain high space velocity R, a certain high conversion C can be obtained, but that the stability of the bifunctional catalyst or catalyst combination is not entirely satisfactory. On further investigation into said process by the Applicant it has been found that this drawback can be eliminated by contacting carbon monoxide and hydrogen present in the reaction product, if desired together with other components of the reaction product, in a second stage with a cobalt- or ruthenium-containing monofunctional catalyst having activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, with the proviso that if the feed for the second stage has an H_2/CO molar ratio of less than 1.5, water is added to said feed and that in the second stage use is made of a cobalt- or ruthenium-containing bifunctional catalyst or catalyst combination having, in addition to activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, activity for the conversion of an H_2O/CO mixture into an H_2/CO_2 mixture. This process not only ensures that by the use of the above-mentioned high space velocity R (now based on the total catalyst system in the first and second stage) a high conversion can be obtained without stability problems becoming manifest, but that the conversion obtained moreover has a higher value than the above-mentioned conversion C.

The present patent application therefore relates to a process for the preparation of a hydrocarbon mixture, in which a mixture of carbon monoxide and hydrogen having an H_2/CO molar ratio of less than 1.0 is contacted in a first stage with an Fe-containing bifunctional catalyst or catalyst combination as defined above and which carbon monoxide and hydrogen present in the reaction product of the first stage, if desired together with other components of said reaction product, are contacted in a second stage with a cobalt- or ruthenium-containing monofunctional catalyst as defined above, with the proviso that if the feed for the second stage has an H_2/CO molar ratio of less than 1.5, water is added to said feed and that in the second stage use is made of a cobalt- or ruthenium-containing bifunctional catalyst or catalyst combination as defined above.

In the process according to the invention the starting material is an H_2/CO mixture having an H_2/CO molar ratio of less than 1.0. Such H_2/CO mixture can very suitably be prepared by steam gasification of a carbon-containing material. Examples of such materials are lignite, anthracite, coke, crude mineral oil and fractions thereof as well as oils produced from tarsand and bituminous shale. Steam gasification is preferably carried out at a temperature of 900—1500°C and a pressure of 10—100 bar. In the process according to the invention the starting H_2/CO mixture preferably has an H_2/CO molar ratio of more than 0.25.

The Fe-containing bifunctional catalysts or catalyst combinations that are suitable for use in the first stage of the process according to the invention, should possess, in addition to activity for the conversion of an H_2/CO mixture substantially hydrocarbons, activity for the conversion of an H_2/CO mixture into an H_2/CO_2 mixture. In the first stage of the process use is preferably made of a bifunctional catalyst prepared by impregnation and containing iron on a carrier. Examples of such catalysts are:

(a) catalysts containing 30—75 parts by weight of iron and 5—40 parts by weight of magnesium per 100 parts by weight of alumina and prepared by impregnating an alumina carrier with one or more aqueous solutions of salts of iron and magnesium and subsequently drying the composition, calcining it at a temperature of 700—1200°C and reducing it. Special preference is given to such catalysts containing, in addition to 40—60 parts by weight of iron and 7.5—30 parts by weight of magnesium, 0.5—5 parts by weight of copper as reduction promoter and 1—5 parts by weight of potassium as selectivity promoter per 100 parts by weight of alumina and calcined at 750—850°C and reduced at 250—350°C.

b) catalysts containing 10—40 parts by weight of iron and 0.25—10 parts by weight of chromium per 100 parts by weight of silica and prepared by impregnating a silica carrier with one or more aqueous solutions of salts of iron and of chromium followed by drying the composition, calcining it and reducing it at a temperature of 350—750°C. Special preference is given to such catalysts containing, in addition to 20—35 parts by weight of iron and 0.5—5 parts by weight of chromium, 1—5 parts by weight of potassium as selectivity promoter per 100 parts by weight of silica and calcined at 250—700°C and reduced at 350—500°C.

The first stage of the process according to the invention can very suitably be carried out by passing the feed in upward or downward direction through a vertically arranged reactor containing a fixed or moving bed of the Fe-containing bifunctional catalyst combination. The first stage can, for example, be carried out in fixed-bed operation, bunker-flow operation, ebullated-bed operation or fluidized-bed operation. The first stage of the operation is preferably carried out under the following conditions: a temperature of 200—350°C and in particular of 250—350°C, a pressure of 10—70 bar and in particular of 20—50 bar and a space velocity of 500—5000 and in particular of 500—2500 Nl of gas/l of catalyst/h.

In the process according to the invention carbon monoxide and hydrogen present in the reaction product of the first stage are used as feed for the second stage. In addition to carbon monoxide and hydrogen, the feed for the second stage may contain other components of the reaction product of the first stage. For example, it is possible to use as feed for the second stage the C_2^- fraction or C_4^- fraction of the reaction product of the first stage and even the entire reaction product of the first stage. In the second stage of the process according to the invention the aim is that the largest possible quantity of the carbon monoxide present in the feed for the second stage is converted into substantially hydrocarbons over a monofunctional cobalt- or ruthenium-containing catalyst having activity for this reaction. To this end the H_2/CO molar ratio in the feed for the second stage must be at least 1.5 and preferably 1.75—2.25. If an H_2/CO mixture with a high H_2/CO molar ratio is used as feed for the first stage, it is possible in the process according to the invention to obtain a reaction product from the first stage having an H_2/CO molar ratio of at least 1.5, which is suitable as such to be converted in the second stage over said catalyst.

If in the process according to the invention a reaction product having an H_2/CO molar ratio of less than 1.5 is obtained from the first stage, water should be added to the feed for the second stage and a cobalt- or ruthenium-containing bifunctional catalyst or catalyst combination should be used in the second stage that has, in addition to activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, activity for the conversion of an H_2O/CO mixture into an H_2/CO_2 mixture.

If in the process according to the invention the feed for the second stage has an H_2/CO molar ratio of less than 1.5 a bifunctional catalyst combination consisting of two separate catalysts is preferably used in the second stage, which catalysts will for convenience be indicated as catalysts A and B. Catalyst A is the cobalt- or ruthenium-containing catalyst having activity for the conversion of an H_2/CO mixture into substantially hydrocarbons and catalyst B is the catalyst with activity for the conversion of an H_2O/CO mixture into an H_2/CO_2 mixture. Both in the use of a monofunctional catalyst and in the use of a bifunctional catalyst combination in the second stage of the process according to the invention, as catalyst A preference is given to a cobalt catalyst and in particular to a catalyst prepared by impregnation and containing cobalt on a carrier. Very suitable for the present object are catalysts containing 10—40 parts by weight of cobalt and 0.25—5 parts by weight of zirconium, titanium or chromium and prepared by impregnating a silica carrier with one or more aqueous solutions of salts of cobalt and zirconium, titanium or chromium, followed by drying the composition, calcining it at 350—700°C and reducing it at 200—350°C. Catalysts containing copper and zinc and in which the Cu/Zn atomic ratio lies between 0.25 and 4.0 are especially eligible as catalysts B. In the cobalt or ruthenium-containing bifunctional catalyst combinations the catalyst A and B can be present as a physical mixture. When the second stage of the process is carried out with the use of a fixed catalyst bed, the bed is preferably built up of two or more alternating layers of particle of catalyst B and catalyst A, respectively. In the process according to the invention water can be added to the feed for the second stage and a bifunctional catalyst combination may be used in the second stage both in cases where the reaction product of the first stage has an H_2/CO molar ratio of less than 1.5, and in cases where the reaction product of the first stage already has an H_2/CO molar ratio of at least 1.5, it being desirable, however, that the feed which is contacted with catalyst A in the second stage has a higher H_2/CO molar ratio. If in the process according to the invention an embodiment is chosen in which water is added to the feed for the second stage and a bifunctional catalyst combination is used in the second stage, the quantity of water required is mainly determined by the H_2/CO molar ratio of the feed for the second stage, the activity of the catalyst combination for the conversion of an H_2O/CO mixture into an H_2/CO_2 mixture and the desirable H_2/CO molar ratio of the product that is contacted with catalyst A.

The second stage of the process according to the invention can very suitably be carried out by passing the feed in upward or downward direction through a vertically arranged reactor containing a fixed bed of the monofunctional catalyst or of the bifunctional catalyst or catalyst combination. The second stage of the process can also be carried out using a suspension of the catalyst or catalyst combination in a hydrocarbon oil.

The second stage of the process is preferably carried out under the following conditions: a temperature of 125—350°C, in particular of 175—275°C and a pressure of 1—150 bar, in particular of 5—100 bar.

The invention will now be illustrated with reference to the following example.

Example

The following catalysts were used during the investigation:

Catalyst 1

$Co/Zr/SiO_2$ catalyst containing 25 parts by weight of cobalt and 1.8 parts by weight of zirconium per 100 parts by weight of silica and prepared by impregnating a silica carrier with an aqueous solution containing a cobalt and a zirconium salt, followed by drying the composition, calcining it at 500°C and reducing it at 280°C.

Catalyst 2

Fe/Mg/Cu/KAl_2O_3 catalyst containing 50 parts by weight of iron, 20 parts by weight of magnesium, 2.5 parts by weight of copper and 4 parts by weight of potassium per 100 parts by weight of alumina and prepared by impregnating an alumina carrier with an aqueous solution containing an iron, magnesium, copper and a potassium salt, followed by drying the composition, calcining it at 800°C and reducing it at 325°C.

Catalyst 3

Cu/Zn/Al_2O_3 catalyst with a Cu/Zn atomic ratio of 0.55.

Catalyst Mixture I

Catalyst mixture I consisted of a layer of catalyst 3 and a layer of catalyst 1 in a volume ratio of 1:2. The catalyst 1 and 2 and the catalyst mixture I were tested for the preparation in one or two stages of a hydrocarbon mixture from an H_2/CO mixture. The test was carried out in one or two reactors of 50 ml each containing a fixed catalyst bed. Five experiments were carried out. Experiments 1 and 3 were carried out in one stage; the other experiments in two stages. In all experiments a temperature of 280°C was used in the first stage. In all experiments that were carried out in two stages the temperature was 230°C in the second stage. In all experiments the pressure was 30 bar and the space velocity based on the total catalyst system was 1000 Nl.l^{-1}.h^{-1}. In the experiments 2 and 5 the total reaction product from the first stage was used as feed for the second stage. In experiment 4 the C_4^- fraction of the product from the first stage was used as feed for the second stage. The results of the experiments are stated in the Table.

Table

Experiment No.	1	2	3	4	5
Catalyst No. in first stage	2	2	2	2	2
Quantity of catalyst in first stage, ml	10	5	10	5	7
H_2/CO molar ratio of feed for first stage	0.5	0.5	0.8	0.8	0.8
H_2/CO molar ratio of product from first stage					
after 250 run hours	0.06	0.41	9	1.3	2.2
after 3,000 run hours	0.32	0.44	1.75	1.11	1.73
Number of catalyst or catalyst mixture in second stage	—	I	—	I	1
Quantity of catalyst in second stage, ml	—	5	—	5	3
Quantity of water added to feed for second stage, ml (l of catalyst)$^{-1}$.h^{-1}					
after 250 run hours	—	241	—	66	—
after 3,000 run hours	—	244	—	114	—
Conversion of the synthesis gas, %					
after 250 run hours	90	96	85	96	97
after 3,000 run hours	75	93	70	92	95

Of the experiments stated in the table only the two-stage experiments 2, 4 and 5 are in accordance with the invention. The one-stage experiments 1 and 3 fall outside the scope of the invention. For comparison they have been included in the patent application.

The advantages of the two-stage process according to the invention in respect of conversion of the H_2/CO mixture and stability of the Fe-containing bifunctional catalyst are evident on comparing the results of: experiment 2 with that of experiment 1, and experiments 4 and 5 with that of experiment 3.

Claims

1. A process for the preparation of a hydrocarbon mixture, characterized in that a mixture of carbon monoxide and hydrogen having an H_2/CO molar ratio of less than 1.0 is contacted in a first stage with an Fe-containing bifunctional catalyst or catalyst combination having, in addition to activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, activity for the conversion of an H_2O/CO mixture into an H_2/CO_2 mixture and that carbon monoxide and hydrogen present in the reaction product of first stage, if desired together with other components of said reaction product, are contacted in a second stage with a cobalt or ruthenium-containing monofunctional catalyst having activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, with the proviso that if the feed for the second stage has an H_2/CO molar ratio of less than 1.5, water is added to said feed and that in the second stage use is made of a cobalt- or ruthenium-containing bifunctional catalyst or catalyst combination having, in addition to activity for the conversion of an H_2/CO mixture into substantially hydrocarbons, activity for the conversion of an H_2O/CO mixture in an H_2/CO_2 mixture.

2. A process as claimed in claim 1, characterized in that the H_2/CO mixture used as feed for the first stage has an H_2/CO molar ratio of more than 0.25.

3. A process as claimed in claim 1 or 2, characterized in that a catalyst is used containing 30—75 parts by weight of iron and 5—40 parts by weight of magnesium per 100 parts by weight of alumina and prepared by impregnating an alumina carrier with one or more aqueous solutions of salts of iron and magnesium followed by drying the composition, calcining it at a temperature of 700—1200°C and reducing it.

4. A process as claimed in claim 3, characterized in that a catalyst is used containing, in addition to 40—60 parts by weight of iron and 7.5—30 parts by weight of magnesium, 0.5—5 parts by weight of copper as reduction promoter and 1—5 parts by weight of potassium as selectivity promoter per 100 parts by weight of alumina and calcined at 750—850°C and reduced at 250—350°C.

5. A process as claimed in claim 1 or 2, characterized in that a catalyst is used containing 10—40 parts by weight of iron and 0.25—10 parts by weight of chromium per 100 parts by weight of silica and prepared by impregnating a silica carrier with one or more aqueous solutions of salts of iron and chromium followed by drying the composition, calcining it and reducing it at a temperature of 350—750°C.

6. A process as claimed in claim 5, characterized in that a catalyst is used containing in addition to 20—35 parts by weight of iron and 0.5—5 parts by weight of chromium, 1—5 parts by weight of potassium as selectivity promoter per 100 parts by weight of silica and calcined at 350—700°C and reduced at 350—500°C.

7. A process as claimed in any one of claims 1—6, characterized in that as catalyst with activity for the conversion of an H_2/CO mixture into substantially hydrocarbons that is used in the second stage of the process, use is made of a catalyst prepared by impregnation and containing cobalt on a carrier.

8. A process as claimed in claim 7, characterized in that a catalyst is used containing 10—40 parts by weight of cobalt and 0.25—5 parts by weight of zirconium, titanium or chromium per 100 parts by weight of silica and prepared by impregnating a silica carrier with one or more aqueous solutions of salts of cobalt and/or zirconium, titanium or chromium, followed by drying the composition, calcining it at 350—700°C and reducing it at 200—350°C.

9. A process as claimed in any one of claims 1—8, characterized in that water is added to the feed for the second stage and that in the second stage of bifunctional catalyst combination is used consisting of two separate catalysts A and B, catalyst A having activity for the conversion of an H_2/CO mixture into substantially hydrocarbons and catalyst B having activity for the conversion of an H_2O/CO mixture into an H_2/CO mixture.

10. A process as claimed in claim 9, characterized in that the second stage is carried out with the use of a fixed catalyst bed consisting of two or more alternating layers of particles of catalyst B and catalyst A respectively.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office,
25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.