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(71) Applicants
**Shell Internationale Research Maatschappij BV
(Netherlands)
Carel Van Bylandtlaan 30, The Hague, Netherlands**

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(72) Inventors
**Dirk Bode
Swan Tjong Sie**

(74) Agent and/or Address for Service
K. R. I. Hunter, 4 York Road, London SE1 7NA

(54) Process for the preparation of hydrocarbons

(57) A process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen wherein the feed is contacted at elevated temperature and pressure with a catalyst comprising 3-60 pbw cobalt, 0.1-100 pbw zirconium, titanium, chromium and/or ruthenium per 100 pbw of a silica and/or alumina carrier, which catalyst is in the form of a fixed bed and has an external surface area S_E and wherein together with the feed a hydrocarbon-containing liquid boiling above 100°C is passed through the catalyst in a downward direction at such a superficial liquid flow velocity V_g at the inlet of the bed that the product $V_g \times S_E$ is larger than $(\ln 5^{-1})$.

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SPECIFICATION

Process for the preparation of hydrocarbons

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

The preparation of hydrocarbons from an H_2/CO mixture by contacting this mixture at elevated temperature and pressure with a catalyst is known in the literature as the Fischer-Tropsch hydrocarbon synthesis process. Catalysts frequently used for the purpose contain one or more metals of the iron group together with one or more promoters and a carrier material. Suitable techniques for the preparation of these catalysts are such known techniques as precipitation, impregnation, kneading and melting. The products that can be prepared by using these catalysts usually have a very wide range of molecular weight distribution and, in addition to branched and unbranched paraffins, often contain considerable amounts of olefins and oxygen-containing organic compounds. Usually only a minor portion of the products obtained is made up of middle distillates. Of these middle

20 distillates not only the yield but also the pour point is unsatisfactory. Therefore the direct conversion of H_2/CO mixtures according to Fischer-Tropsch is not a very attractive route for the production of middle distillates on a technical scale.

30 In this patent application by "middle distillates" are meant hydrocarbon mixtures whose boiling range corresponds substantially with that of the kerosene and gas oil fractions obtained in the conventional atmospheric distillation of crude mineral oil. The middle distillate range lies substantially between about 150 and 360°C.

Recently a class of Fischer-Tropsch catalysts was found which have the property of yielding a product in which only very minor amounts of olefins and

40 oxygen-containing organic compounds occur and which consists virtually completely of unbranched paraffins, a considerable portion of which paraffin boils above the middle distillate range. It has been found that the high-boiling part of this product can be converted in high yield into middle distillates by means of hydrocracking. As feedstock for the hydrocracking at least a part of the product is chosen whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product.

50 The hydrocracking, which typically proceeds at a very low hydrogen consumption, yields middle distillates with a considerably better pour point than those obtained in the direct conversion of an H_2/CO mixture according to Fischer-Tropsch.

55 The Fischer-Tropsch catalyst belonging to the above-mentioned class contain silica, alumina or silica-alumina as carrier material and, in specific quantities, cobalt together with zirconium, titanium, chromium and/or ruthenium as catalytically active metals. The catalysts are prepared by depositing the metals involved on the carrier material by kneading and/or impregnation. For further information on the preparation of these catalysts by kneading and/or impregnation reference may be made to Netherland

65 patent application No. 8301922.

Further investigation into the use of the above-mentioned cobalt catalysts in the form of a fixed bed has now shown that the C_{3+} selectivity of these catalysts is improved when during the process a liquid which boils above 100°C and consists substantially of one or more hydrocarbons is passed through the catalyst bed in a downward direction together with the feed gas, in particular when applying at the inlet of the catalyst bed a certain determined minimum superficial liquid flow velocity (V_s) which should be higher according as the external surface area (S_E) of the catalyst bed is smaller. The relation between V_s (in cm/s) and S_E (in cm²/ml) is rendered by $V_s \times S_E > 1$ (in sec⁻¹).

80 The invention therefore related to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide and hydrogen, in which a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst comprising 3-60 parts by weight of cobalt and 0.1-100 parts by weight of at least one other metal chosen from zirconium, titanium, chromium and ruthenium per 100 parts by weight of silica, alumina or silica-alumina, which catalyst has been prepared by kneading and/or impregnation, in which the catalyst is present in the form of a fixed bed having an external surface area S_E , and in which during the process a liquid which boils above 100°C and consists substantially of one or more hydrocarbons is passed through the catalyst bed in a downward direction together with the feed gas, at such a superficial liquid flow rate V_s at the inlet of the catalyst bed that $V_s \times S_E > 1$.

It is highly surprising that the favourable influence which is exercised on the catalyst selectivity by passing the liquid through the catalysts bed is not observed with iron catalysts prepared by impregnation and/or kneading, which catalysts are closely relate to the present cobalt catalysts. On the contrary, comparative experiments with iron catalysts have shown that the C_{3+} selectivity of these catalysts decreases when said liquid is passed through the catalyst bed.

Passing the liquid through the catalyst bed has the additional advantage of facilitating temperature control during the highly exothermal hydrocarbon synthesis.

The external surface area (S_E) of the catalyst bed can be found by taking a representative sample of a given volume expressed in ml and determining the external surface area expressed in cm² of each of the catalyst particles present therein, adding up the found external surface areas, and dividing the sum by the volume of the sample. For all practical purposes a maximum value for $V_s \times S_E$ of 200 is applicable.

120 For the liquid which is passed through the catalyst bed during the process according to the invention use may very suitably be made of a portion of a heavy fraction which has been separated by distillation from the product obtained in the hydrocarbon synthesis, and/or which has been separated from the product obtained in the hydrocracking if the hydrocarbon synthesis is followed by a hydrocracking treatment for the preparation of middle distillates. Said fraction which is partly used to be passed through the catalyst

130 bed, may be either a distillate or a residual fraction. For

instance, starting from the product obtained in the hydrocarbon synthesis or in the hydrocracking treatment, said product may be divided by distillation into a distillation fraction and a residual fraction boiling above 100°C, upon which a portion of the residual fraction is passed over the catalyst bed. Or, starting from the product obtained in the hydrocarbon synthesis or in the hydrocracking treatment, said product may be divided by distillation into a light distillation fraction, a middle distillation fraction boiling above 100°C and a residual fraction, upon which a portion of the middle distillation fraction is passed over the catalyst bed. Preference is given to the use of a portion of a heavy fraction which has been separated by distillation from the product obtained in the hydrocarbon synthesis and in particular a portion of a residual fraction which has been separated from this product.

In the process according to the invention it is preferred to use a catalyst bed of such an external surface area (S_E) between 5 and 70 cm²/ml and such an internal surface area (S_i) between 10 and 400 m²/ml as to satisfy the relation $10^6 > S_E^2 \times S_i > 2.5 \times 10^4$. The hydrocarbon synthesis using a catalyst bed which meets this requirement forms the subject matter of Netherlands patent application No. 8402149.

In the process according to the invention use is preferably made of the cobalt catalysts which form the subject matter of Netherlands patent application No. 8301922. These are catalysts which satisfy the relation

$(3 + 4R) > \frac{L}{S_i} > (0.3 + 0.4R)$, where
 L = the total quantity of cobalt present on the catalyst, expressed in mg of Co/ml,
 S_i = the internal surface area of the catalyst, expressed in m²/ml, and
 R = the weight ratio between the quantity of cobalt applied to the catalyst by kneading and the total quantity of cobalt present on the catalyst.

In the process according to the invention it is further preferred to use cobalt catalysts which have been prepared by any one of the following three procedures:

- a) cobalt is first applied by impregnation in one or more steps and subsequently the other metal is likewise applied by impregnation in one or more steps,
- b) the other metal is first applied by impregnation in one or more steps and subsequently cobalt is likewise applied by impregnation in one or more steps, and
- c) cobalt is first applied by kneading in one or more steps and subsequently the other metal is applied by impregnation in one or more steps.

In the process according to the invention it is further preferred to use cobalt catalysts comprising 10-50 parts by weight of cobalt per 100 parts by weight of carrier. The quantity of the other metal(s) preferably present in the cobalt catalyst depends on the manner in which the said metal(s) has/have been applied. In the case of catalysts where first the cobalt and then the other metal is applied to the carrier, preference is given to catalysts comprising 0.1-5 parts by weight of the other metal per 100 parts by weight of carrier. In the case of catalyst where first the other metal and then the cobalt is applied to the carrier, preference is

given to catalysts comprising 5-40 parts by weight of the other metal per 100 parts by weight of carrier. For the other metal it is preferred to use zirconium and for the carrier it is preferred to use silica.

70 Preparatory to becoming eligible for use in the preparation of hydrocarbons from an H₂/CO mixture, the cobalt catalysts should be activated. This activation may suitably be carried out by contacting the catalysts at a temperature between 200 and 350°C with hydrogen or a hydrogen-containing gas.

75 The conversion of the H₂/CO mixture into hydrocarbons according to the invention is preferably carried out at a temperature of 125-350°C and in particular of 175-275°C and a pressure of 0.5-10 MPa and in particular of 1-7.5 MPa.

80 The process according to the invention is suitably carried out in one of the reactors described hereinafter.

1. A reactor consisting of a pressure vessel in which are present vertical tubes containing the catalyst. In order to withdraw the reaction heat a coolant is passed along the exterior of the tubings.

2. A reactor substantially as that described hereinabove, but with the catalyst on the outside of the tubings and the coolant passing through the tubes. The tubes may be placed parallel to the flow direction of the synthesis gas as well as perpendicular to the flow direction, in the form of straight pipes or cooling spirals.

3. A reactor consisting of a pressure vessel containing the catalyst in a plurality of horizontal layers. After each transition of a catalyst layer the temperature of the reaction mixture, which has risen owing to the reaction heat, is cooled down, and subsequently the reaction mixture is passed through the following catalyst layer. Cooling can be achieved by means of heat exchangers or by admixture of cold synthesis gas and/or cold liquid.

H₂/CO mixtures which are suitable for conversion according to the invention into hydrocarbons can be very suitably obtained starting from light hydrocarbons such as methane by means of steam reforming or partial oxidation. Special preference is given to the use of natural gas as feedstock for the preparation of the H₂/CO mixture.

The H₂/CO mixture which is converted according to the invention into hydrocarbons preferably has an H₂/CO molar ratio higher than 1.5 and in particular an H₂/CO molar ratio between 1.75 and 2.25.

As has already been observed hereinbefore, when used for the conversion of an H₂/CO mixture the present cobalt catalysts yield a substantially paraffinic product whose high-boiling part can be converted in high yield into middle distillates by the use of a hydrocracking treatment. The feedstock chosen for the hydrocracking treatment is at least the part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product.

Although in the preparation of middle distillates from the product obtained over the cobalt catalyst the part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product will do as feed for the hydrocracking treatment, the total C₅⁺ fraction of the

product prepared over the cobalt catalyst may also be used for the purpose, if desired.

The hydrocracking treatment is carried out by contacting the fraction to be treated at elevated temperature and pressure and in the presence of hydrogen, with a catalyst containing one or more noble metals from Group VIII supported on a carrier. The hydrocracking catalyst used preferably is a catalyst comprising 0.2-1%w of platinum or palladium on silica-alumina as carrier. The hydrocracking treatment is preferably carried out at a temperature of 250-350°C and a pressure of 1-7.5 MPa.

The invention is now illustrated with the aid of the following example.

15 Example

Three catalysts (catalysts 1-3) were prepared by single or two-step impregnation of three spherical silica carriers (silicas A-C) with aqueous solutions of metal compounds. Silica A had a specific surface area of 260 m²/g and an internal surface area of 117 m²/ml, for silica B these values were 235 m²/g and 99 m²/ml and for silica C 250 m²/g and 112 m²/ml. At each impregnation step a quantity of solution was used of which the volume corresponded substantially with the pore volume of the carrier concerned. After each impregnation step the material was dried at 120°C and calcined at 500°C. After the final calcination step the compositions were activated in hydrogen: catalysts 1 and 2 at 250°C and catalyst 3 at 280°C. More details regarding catalysts 1-3 and their preparation follow here.

Catalyst 1

Single-step impregnation of silica A with a solution of cobalt nitrate in water, followed by single-step impregnation of the cobalt-loaded carrier with a solution of zirconium nitrate in water. Catalyst 1 comprised 25 parts by weight of cobalt and 0.9 parts by weight of zirconium per 100 parts by weight of silica and had an S_E of 24 cm²/ml.

40 Catalyst 2

This catalyst was prepared starting from silica B in the same manner as catalyst 1. Catalyst 2 comprised 25 parts by weight of cobalt and 0.9 parts by weight of zirconium per 100 parts by weight of silica and had an S_E of 40 cm²/ml.

Catalyst 3

Single-step impregnation of silica C with an aqueous solution comprising iron nitrate, copper nitrate and potassium nitrate. Catalyst 3 comprised 25 parts by weight of iron, 1.25 parts by weight of copper and 1 part by weight of potassium per 100 parts by weight of silica and had an S_E of 27 cm²/ml.

Catalysts 1-3 were applied in nine experiments in the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen. To this end the H₂/CO mixture was passed in downward direction through a vertically arranged reactor containing a fixed catalyst bed. In some of the experiments the reaction product was separated by means of distillation into a distillation fraction and a residual fraction having an initial boiling point of 150°C, and part of the residual fraction was recirculated over the catalyst bed. The conditions under which the experiments were carried out and their results are given in Tables I and II.

Of the experiments named in the tables only experiments 3, 6 and 7 are experiments according to the invention. In these experiments such a liquid recirculation was applied as to satisfy the requirement $V_s \times S_E > 1$, and a considerable increase in C₃⁺ selectively was obtained. Experiments 1, 2, 4, 5, 8 and 9 fall outside the scope of the invention. They have been included in the patent application for comparison. In experiments 1, 4 and 8 no liquid was passed over the catalyst bed. In experiments 2 and 5 liquid recirculation was applied, but without meeting the requirement $V_s \times S_E > 1$. In these experiments only a minor increase in C₃⁺ selectively was attained. In experiment 9, which was carried out using an iron catalyst, a liquid recirculation was applied which did meet the requirement $V_s \times S_E > 1$; nevertheless the C₃⁺ selectivity was seen to fail.

TABLE I

Experiment No.	1-3	4-7	8-9
Catalyst No.	1	2	3
H ₂ /CO molar ratio of the feed	2	1.85	2
Temperature, °C	190	221	220
Pressure, bar	25	20	30
Space velocity, h ⁻¹	850	650	1000

TABLE II

Experiment No.	V _s , cm/s	CO conversion, %	C ₃ ⁺ selectivity, V _s × S _E , %	Liquid space velocity, l/l.h
1	0	15	75	0
2	0.03	15	75.5	0.27
3	0.125	15	80	1.125
4	0	67	81	0
5	0.005	66	81.5	0.36
6	0.03	66	85	2.16
7	0.3	65	86	21.6
8	0	49	90	0
9	0.1	45	88	7.2

CLAIMS

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 is contacted at elevated temperature and pressure with a catalyst which comprises 3-60 parts by weight of cobalt and 0.1-100 parts by weight of at least one other metal chosen from zirconium, titanium, chromium and ruthenium per 100 parts by weight of silica, alumina or silica-alumina and which has been prepared by kneading and/or impregnation, that the catalyst is present in the form of a fixed bed having an external surface area S_E (in cm^2/ml), and that during the process a liquid which boils above 100°C and consists substantially of one or more hydrocarbons is passed through the catalyst bed in a downward direction together with the feed gas, at such a superficial liquid flow velocity V_s (in cm/s) at the inlet of the catalyst bed as to satisfy the relation $V_s \times S_E > 1$ (in s^{-1}).
2. A process as claimed in claim 1, characterized in that for the liquid which is passed through the catalyst bed during the process use is made of part of a heavy fraction which has been separated by distillation from the product obtained in the hydrocarbon synthesis, and/or which has been separated from the product obtained in the hydrocracking treatment if the hydrocarbon synthesis is followed by a hydrocracking treatment for the preparation of middle distillates.
3. A process as claimed in claim 2, characterized in that for the liquid which is passed through the catalyst bed during the process use is made of part of a residual fraction which has been separated from the product obtained in the hydrocarbon synthesis.
4. A process as claimed in any one of claims 1-3, characterized in that the catalyst bed has such an external surface area (S_E) between 5 and $70 \text{ cm}^2/\text{ml}$ and such an internal surface area (S_i) between 10 and $400 \text{ m}^2/\text{ml}$ as to satisfy the relation $10^6 > S_E^2 \times S_i > 2.5 \times 10^4$.
5. A process as claimed in any one of claims 1-4, characterized in that the catalyst satisfies the relation $(3 + 4R) > \frac{L}{S_i} > (0.3 + 0.4R)$, wherein
 L = the total quantity of cobalt present on the catalyst, expressed in mg of Co/ml ,
 S_i = the internal surface area of the catalyst, expressed in m^2/ml , and
 R = the weight ratio between the quantity of cobalt applied to the catalyst by kneading and the total quantity of cobalt present on the catalyst.
6. A process as claimed in any one of claims 1-5, characterized in that per 100 parts by weight of carrier the catalyst comprises 15-50 parts by weight of cobalt, and either 0.1-5 parts by weight of the other metal if during the preparation cobalt was applied first and the other metal next, or 5-40 parts by weight of the other metal if during the preparation the other metal was applied first and cobalt next.
7. A process as claimed in any one of claims 1-6, characterized in that the catalyst comprises zirconium as the other metal and silica as the carrier.
8. A process as claimed in any one of claims 1-7, characterized in that it is carried out at a temperature of $125-350^\circ\text{C}$ and a pressure of $0.5-10 \text{ MPa}$.
9. A process as claimed in claim 8, characterized in that it is carried out at a temperature of $175-275^\circ\text{C}$ and a pressure of $1-7.5 \text{ MPa}$.
10. A process as claimed in any one of claims 1-9, characterized in that the H_2/CO mixture has been obtained by steam reforming or partial oxidation starting from light hydrocarbons such as natural gas.
11. A process as claimed in any one of claims 1-10, characterized in that the H_2/CO mixture has an H_2/CO molar ratio higher than 1.5.
12. A process as claimed in claim 11, characterized in that the H_2/CO mixture has an H_2/CO molar ratio between 1.75 and 2.25.
13. A process as claimed in any one of claims 1-12, characterized in that in order to prepare middle distillates from the product prepared over the cobalt catalyst, at least the part whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product is subjected to a hydrocracking treatment by contacting it at elevated temperature and pressure with a catalyst comprising one or more noble metals from Group VIII supported on a carrier.
14. A process as claimed in claim 13, characterized in that in the hydrocracking treatment a catalyst is used which comprises 0.2-1%w of platinum of palladium on silica-alumina as carrier.
15. A process as claimed in claim 13 or 14, characterized in that the hydrocracking treatment is carried out at a temperature of $250-350^\circ\text{C}$ and a pressure of $1-7.5 \text{ MPa}$.
16. A process for the preparation of hydrocarbons according to claim 1, substantially as described hereinbefore and in particular with reference to the example.
17. Hydrocarbons whenever prepared according to a process as described in claim 16.