(12) UK Patent Application (19) GB (11) 2 103 647 A

(21) Application No 8220554
(22) Date of filing **15 Jul 1982**
(30) Priority data
(31) **8103397**
(32) **17 Jul 1981**
(33) **Netherlands (NL)**
(43) Application published
23 Feb 1983
(51) **INT CL^3**
C07C 1/04
(52) Domestic classification
C5E 222 332 391 CF
C2C 20Y 229 30Y 360 361
364 36Y 408 509 50Y 566
623 624 65Y 771 JM YD
YK
(56) Documents cited
None
(58) Field of search
C5E

(71) Applicants
Shell Internationale
Research Maatschappij
BV,
(Netherlands),
Carel van Bylandtlaan 30,
The Hague,
The Netherlands.
(72) Inventors
Sikko Jan Alje Boelema,
Swan Tiong Sie,
Martin Franciscus Maria
Post.
(74) Agents
R.C. Rogers,
Shell Internationale
Petroleum Co.,
4 York Road,
London SE1 7NA.

(54) Process for the preparation of organic compounds

(57) A two-stage process for the conversion of H_2-poor syngas into hydrocarbons and oxygenates. Unconverted syngas from the first stage product is converted in a second stage into paraffins over a Ni, Co or Ru catalyst. The H_2/CO molar ratio of the feed for the second stage is adjusted to the required value of 1.75-2.25 by blending this feed with a H_2-rich syngas with a H_2/CO molar ratio of at least 1.75. The latter gas has been obtained by subjecting a small portion of the feed for the first stage to a high temperature (above 325°C) CO-shift.

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presents difficulties. When the process is used for the conversion of H_2/CO mixtures having a H_2/CO molar ratio below 1.0, the stability of the bifunctional catalyst or catalyst combination leaves to be desired. When the process is used for the conversion of H_2/CO mixtures having a H_2/CO molar ratio between 1.0 and 2.0, the conversion attained is low.

Oxygen-containing organic compounds may be prepared, for instance, by contacting a H_2/CO mixture having a H_2/CO molar ratio below 2.0, with a catalyst containing one or more metal components with catalytic activity for the conversion of a H_2/CO mixture into oxygen-containing organic compounds. A drawback to these reactions is the fact that they are highly limited thermodynamially, so that a considerable proportion of the H_2/CO mixture is not converted. According as higher space velocities are used, the conversion obtained is lower.

An investigation carried out by the Applicant has shown that the above-mentioned drawbacks attending the preparation of paraffinic hydrocarbons and oxygen-containing organic compounds starting from H_2/CO mixtures having a H_2/CO molar ratio below 2.0, as well as those attending the preparation of aromatic hydrocarbons from such a feed, can be overcome by contacting hydrogen and carbon monoxide present in the reaction product of the process, optionally together with other components from this reaction product, with a catalyst containing one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into paraffinic hydrocarbons, which components originate from the group formed by cobalt, nickel and ruthenium, provided that care is taken that the feed for the second step has a H_2/CO molar ratio of 1.75-2.25. As with the preparation of aromatic hydrocarbons, the preparation of paraffinic hydrocarbons and oxygen-containing organic compounds from H_2/CO mixtures having a H_2/CO molar ratio below 2.0, will often result in a product from the first step having a molar ratio lower than 1.75. In these cases, too, in order to raise the H_2/CO molar ratio of the feed for the second step, a hydrogen-rich H_2/CO mixture can very suitably be used as mixing component, the H_2/CO mixture having been prepared by subjecting a low-hydrogen H_2/CO mixture, separated from the feed for the first step of the two-step process, to a CO-shift at a temperature above 325°C.

The measure according to the invention may be used both in cases where the reaction product from the first step has a H_2/CO molar ratio below 1.75 and in cases where the reaction product from the first step already has a H_2/CO molar ratio of at least 1.75 (e.g. 1.8), but where it is desirable for the feed for the second step to have a higher H_2/CO molar ratio (e.g. 2.1).

The present patent application therefore relates to a process for the preparation, in two steps, of organic compounds from a mixture of carbon monoxide and hydrogen, in which a H_2/CO mixture having a H_2/CO molar ratio below 2.0 is divided into two portions, A and B, having the same composition, in which in the first step portion A, through contact with a catalyst comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into hydrocarbons and/or oxygen-containing organic compounds, is converted into a reaction mixture containing hydrogen and carbon monoxide, the H_2/CO molar ratio (R_1) of which is lower than 2.25, in which the H_2/CO molar ratio of portion B is raised to a value R_2 which is higher than R_1 and also higher than 1.75, by contacting portion B, together with water, at a temperature above 325°C, with a catalyst having CO-shift activity, in which hydrogen and carbon monoxide present in the reaction product prepared from portion A, together with other components from this reaction product, if desired, are mixed with the reaction product prepared from portion B to form a mixture having a H_2/CO molar ratio of 1.75-2.25, and in which the mixture thus obtained is contacted in the second step with a catalyst comprising one or more metal components with activity for the conversion of a H_2/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by cobalt, nickel and ruthenium.

In the process according to the invention organic compounds are prepared starting from a H_2/CO mixture having a H_2/CO molar ratio lower than 2.0. Such H_2/CO mixtures may very suitably be obtained by steam gasification of a carbonaceous material. Examples of such materials are brown coal, anthracite, coke, crude mineral oil and fractions thereof, as well as oils produced from tar sand and bituminous shale. The steam gasification is preferably carried out at a temperature of from 900-1500°C and a pressure of from 10-100 bar. In the process according to the invention the starting material is preferably a H_2/CO mixture having a H_2/CO molar ration above 0.25.

If the process according to the invention is intended for the preparation of aromatic hydrocarbons, the catalyst used in the first step is a bi- or trifunctional catalyst which, in addition to the metal components having catalytic activity, comprises a crystalline metal silicate which is capable of catalyzing the conversion of acyclic hydrocarbons and acyclic oxygen-containing organic compounds into aromatic hydrocarbons. The said cystalline metal silicates are characterized in that, after one hour's calcination in air at 500°C, they have the following properties:

a) thermally stable up to a temperature of at least 600°C,

b) an X-ray powder diffraction pattern in which the four lines listed in Tabel A are the strongest lines.

TABLE A

d(Å)	Relative intensity
11.1 ± 0.2	VS
10.0 ± 0.2	VS
3.84 ± 0.07	S
3.72 ± 0.06	S

in which the letters used have the following meanings:
VS = very strong; S = strong, and

c) in the formula which represents the composition of the silicate expressed in moles of the oxides, and which, in addition to oxides of hydrogen, alkali metal and/or alkaline-earth metal and silicon, comprises one or more oxides of a trivalent metal A chosen from the group formed by aluminium, iron, gallium, rhodium, chromium and scandium, the SiO_2/A_2O_3 molar ratio (for the sake of brevity hereinafter referred to as m) is higher than 10.

The expression "thermally stable up to a temperature of at least t°C", used in this patent application, means that, upon heating of the silicate to a temperature of t°C, the X-ray powder diffraction pattern of the silicate remains substantially unchanged.

Although, basically, the crystalline silicates may contain more than one metal A, for the process according to the invention it is preferred to use catalysts in which the silicate contains only one metal A and in particular silicates containing aluminium, iron or gallium as the metal. The crystalline silicates used in the bi- and trifunctional catalyst combinations should have a value of m that is higher than 10. Preferably crystalline silicates are used in which m is lower than 10. The crystalline silicate used in the bi- and trifunctional catalyst combinations is defined, among other things, with the aid of the X-ray powder diffraction pattern. In this pattern the strongest lines should be the four lines listed in Table A. The complete X-ray powder diffraction pattern of a typical example of a silicate applicable in the process according to the invention is given in Table B.

TABLE B

d(Å)	Rel. int.	d(Å)	Rel. int.
11.1	100	3.84 (D)	57
10.0 (D)	70	3.70 (D)	31
8.93	1	3.63	16
7.99	1	3.47	1
7.42	2	3.43	5
6.68	7	3.34	2
6.35	11	3.30	5
5.97	17	3.25	1
5.70	7	3.05	8
5.56	10	2.98	11
5.35	2	2.96	3
4.98 (D)	6	2.86	2
4.60	4	2.73	2
4.35	5	2.60	2
4.25	7	2.48	3
4.07	2	2.40	2
4.00	4		

(D) = doublet

The crystalline silicates may be prepared starting from an aqueous mixture comprising the following compounds:
one or more compounds of an alkali metal or alkaline-earth metal (M), one or more compounds containing an organic cation (R) or from which such a cation is formed during the preparation of the silicate, one or more silicon compounds and one or more compounds comprising a trivalent metal A. The preparation is carried out by maintaining the mixture at an elevated temperature until the silicate has formed and subsequently separating the silicate crystals from the mother liquor and calcining them. In the aqueous mixture from which the silicates are prepared, the various compounds should be present in the following ratios, expressed in moles of the oxides:

$M_{2/n}O : R_2O = 0.1\text{-}20,$
$R_2O : SiO_2 = 0.01\text{-}0.5,$
$SiO_2 : A_2O_3 > 10$ and
$H_2O : SiO_2 = 5\text{-}50;$ (n = the valency of M).

In the preparation of the silicates the base material preferred is a starting mixture in which M is present in an alkali metal compound and R in a tetra-alkylammonium compound, and in particular a starting mixture in which M is present in a sodium compound and R in a tetrapropylammonium compound. The crystalline silicates prepared in the way described hereinabove contain alkali metal and/or alkaline-earth metal ions. By suitable exchange methods these may be replaced by other cations, such as hydrogen ions or ammonium ions. The crystalline silicates used in the bi- and trifunctional catalyst combinations preferably have an alkali metal content below 0.1%w and in particular below 0.05%w. Although the trifunctional catalyst combinations are described in the present patent application as catalyst combinations comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixtures into acyclic hydrocarbons and/or acyclic oxygen-containing organic compounds, and one or more metal components having CO-shift activity, this certainly does not mean that the trifunctional catalyst combination should invariably comprise individual metal components, each having one of the two catalytic functions. For, it has been found that metal components and combinations of metal components with catalytic activity for the conversion of a H_2/CO mixture into substantially acyclic oxygen-containing organic compounds, often also have sufficient CO-shift activity, so that in such cases it is, usually, sufficient for one metal component or a combination of metal components to be incorporated into the trifunctional catalyst combinations. Metal components and combinations of metal components having catalytic activity for the conversion of a H_2/CO mixture into substantially acyclic hydrocarbons, often have insufficient or no CO-shift activity at all. Therefore, when such metal components or combinations of metal components are used in the trifunctional catalyst combinations, in most cases one or more separate metal components having CO-shift activity should be incorporated.

The bi- and trifunctional catalyst combinations used in the first step of the process according to the invention for the preparation of aromatic hydrocarbons are preferably composed of two or three separate catalysts, which, for convenience, will be referred to as catalysts X, Y and Z. Catalyst X is the catalyst comprising the metal components having catalytic activity for the conversion of a H_2/CO mixture into acyclic hydrocarbons and/or acyclic oxygen-containing compounds. Catalyst Y is the crystalline silicate. Catalyst Z is the catalyst comprising the metal components having CO-shift activity. As has been explained hereinbefore, in the trifunctional catalyst combinations the use of catalyst Z may in a number of cases be omitted.

Catalysts X which are capable of converting a H_2/CO mixture into substantially acyclic hydrocarbons are known in the literature as Fischer-Tropsch catalysts. Such catalysts comprise one or more metals from the iron group or ruthenium together with one or more promoters for increasing the activity and/or the selectivity and, sometimes, a carrier material such as kieselguhr. If in the first step of the process according to the invention a bi- or trifunctional catalyst combination is used having a Fischer-Tropsch catalyst as the catalyst A, an iron catalyst or a cobalt catalyst is preferably chosen for the purpose, in particular such a catalyst prepared by impregnation. Very suitable catalysts for the purpose are:

a) Catalysts comprising 30-75 pbw of iron and 5-40 pbw of magnesium per 100 pbw of alumina and prepared by impregnation of an alumina carrier with one or more aqueous solutions of salts of iron and of magnesium, followed by drying of the composition, calcination at a temperature of 700-1200°C and reduction. Special preference is given to catalysts of this type which, in addition to 40-60 pbw of iron and 7.5-30 pbw of magnesium, comprise 0.5-5 pbw of copper as a reduction promoter and 1-5 pbw of potassium as a selectivity promoter per 100 pbw of alumina and which have been calcined at 750-800°C and reduced at 250-350°C.

b) Catalysts comprising 10-40 pbw of iron and 0.25-10 pbw of chromium per 100 pbw of silica and prepared by impregnation of a silica carrier with one or more aqueous solutions of salts of iron and of chromium followed by drying of the composition, calcination and reduction at a temperature of from 350-750°C. Special preference is given to catalysts of this type which, in addition to 20-35 pbw of iron and 0.5-5 pbw of chromium, comprise 1-5 pbw of potassium as a selectivity promoter and which have been calcined at 350-750°C and reduced at 350-500°C.

c) Catalysts comprising 10-40 pbw of cobalt and 0.25-5 pbw of zirconium, titanium or chromium per 100 pbw of silica and prepared by impregnation of a silica carrier with one or more aqueous solutions of salts of cobalt and zirconium, titanium or chromium, followed by drying of the composition, calcination at 350-750°C and reduction at 200-350°C.

When the iron catalysts mentioned under a) and b) are used as catalysts X, the use of a catalyst Z in the trifunctional catalyst combinations may be omitted. When the cobalt catalysts mentioned under c) are used as catalysts X, a catalyst Z should also be incorporated into the trifunctional catalyst combinations. If in the first step of the process according to the invention a bi- or trifunctional catalyst combination is used in which catalyst X is a Fischer-Tropsch catalyst, an iron catalyst as described under a) and b) is preferably used for the purpose. The first step of the process according to the invention for the preparation of aromatic hydrocarbons is preferably carried out at a temperature of from 200-500°C and in particular of from 250-450°C, a pressure of from 1-150 bar and in particular of from 5-100 bar and a space velocity of from 50-5000 and in particular of from 300-3000 N1 gas/1 catalyst/hour.

If the process according to the invention is to be used for the preparation of paraffinic hydrocarbons, then in the first step an iron-containing bi-functional catalyst or catalyst combination is used which, in addition to activity for the conversion of a H_2/CO mixture into substantially paraffinic hydrocarbons, has CO-shift activity. Preferably, in the first step of the process use is made of a bi-functional catalyst comprising iron on a carrier, which has been prepared by impregnation. Examples of such catalysts are the Fe/Mg and Fe/Cr catalysts mentioned hereinabove under a) and b). The first step of the process according to the invention for the preparation of paraffinic hydrocarbons is preferably carried out at a temperature of from 200-350°C and in particular of from 250-350°C, a pressure of from 10-70 bar and in particular of from 20-50 bar and a space velocity of from 500-5000 and in particular of from 500-2500 Nl gas/l catalyst/hour.

If the process according to the invention is to be used for the preparation of oxygen-containing organic compounds, then in the first step a catalyst is used which contains one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into oxygen-containing organic compounds. Preferably, in the first step a catalyst is used which is capable of converting a H_2/CO mixture into substantially methanol and dimethylether. Examples of suitable catalysts capable of converting a H_2/CO mixture into substantially methanol are catalysts comprising:

1) zinc oxide and chromium oxide,
2) copper, zinc oxide and chromium oxide,
3) copper, zinc oxide and aluminium oxide, and
4) copper, zinc oxide and oxides of rare earths.

Examples of suitable catalysts capable of converting a H_2/CO mixture into substantially dimethyl ether are catalysts containing any one of the methanol sythesis functions mentioned under 1)-4) and, in addition, an acid function, such as a physical mixture of α-alumina and a composition comprising copper, zinc oxide and chromium oxide. Preferably, the first step of the process according to the invention for the preparation of oxygen-containing organic compounds is carried out at a temperature of from 175-325°C, a pressure of from 30-300 bar and in particular of from 50-150 bar.

The oxygen-containing organic compounds which can be prepared in the first step of the two-step process according to the invention can very suitably be used as the starting material for the catalytic conversion into lower olefins and/or aromatic hydrocarbons. Catalysts very suitable for the purpose are the crystalline metal silicates described hereinbefore.

In the process according to the invention hydrogen and carbon monoxide present in the reaction product from the first step are used, together with other components of this reaction product, if desired, as feed for the second step. Optionally, the complete reaction product from the first step may be used as the feed for the second step. Before this feed is contacted with the catalyst in the second step, its H_2/CO molar (ratio (R_1), which is below 2.25, is raised to a value lying between 1.75 and 2.25 by mixing the feed with a H_2/CO mixture having a H_2/CO molar ratio (R_2) which is higher than 1.75, the latter H_2/Co mixture having been obtained by separating a portion from the low-hydrogen H_2/CO mixture available as feed for the first step of the process, mixing this portion with water and containing the mixture, at a temperature above 325°C, with a catalyst having CO-shift activity. The percentage of low-hydrogen H_2/CO mixture to be separated from the feed for the first step of the process and to be subjected to the high-temperature CO-shift, is dependent on the H_2/CO molar ratio of that mixture, the percentage of H_2/CO mixture present in the reaction product from the first step and its H_2/CO molar ratio, the desired H_2/CO molar ratio of the feed for the second step and the conversion attained in the high-temperature CO-shift. If all the other parameters are considered to be constant, the proportion of low-hydrogen H_2/CO mixture to be separated from the feed for the first step of the process will be smaller according as the conversion attained in the high-temperature CO-shift is higher. In view of the desirability for the largest possible part of the available low-hydrogen H_2/CO mixture to be used as feed for the first step of the process, and therefore for the smallest possible part to be subjected to CO-shift, it is advisable to aim at the highest possible conversion in the CO-shift reaction. By preference the CO-shift is carried out in such a way that it yields a product having a H_2/CO molar ratio higher than 3 and in particular higher than 4. Suitable conditions for carrying out the CO-shift reaction are a temperature of from 325-540°C and in particular of from 325-400°C, a pressure of from 5-100 bar and in particular of from 10-75 bar and a space velocity of from 1000-50000 Nl. $l^{-1}.h^{-1}$ and in particular of from 200-10000 Nl. $l^{-1}.h^{-1}$. The high-temperature CO-shift catalyst used by preference is a chromium-containing catalyst. Particular preferece is given to catalysts which, in addition to chromium, comprise either iron or zinc.

In the second step of the process according to the invention the feed which has been mixed with the hydrogen-rich H_2/CO mixture to raise its H_2/CO molar ratio to a value of from 1.75-2.25, is contacted with a catalyst comprising one or more metal components with activity for the conversion of a H_2/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by cobalt, nickel and ruthenium. Preference is given to a cobalt catalyst and in particular a catalyst which comprises cobalt on a carrier and has been prepared by impregnation. Very suitable catalysts for the present purpose are the zirconium-, titanium- or chromium-promoted cobalt impregnation catalysts described hereinabove under c). The second step of the process according to the invention is preferably carried out at a temperature of from 125-325°C and in particular of from 175-275°C and a pressure of from 1-150 bar and in particular of from 5-100 bar.

The Applicant has found that the use in the second step of the process of the zirconium-, titanium- or chromium-promoted cobalt impregnation catalysts mentioned hereinbefore yields a mixture of heavy paraffinic hydrocarbons eminently suitable for conversion, by hydrocracking, into a middle distillate in high yields. The hydrocracking operation is characterized by very low gas production and hydrogen consumption.

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

Example

In the investigation the following catalysts were used:

Catalyst 1

ZnO-Cr_2O_3 catalyst in which the atomic percentage of zinc, calculated on the sum of zinc and chromium, was 70%.

Catalyst 2

Crystalline aluminium silicate catalyst prepared as follows. A mixure of NaOH, amorphous silica, $NaAlO_2$ and $(C_3H_7)_4NOH$ in water having the following molar composition $25\ SiO_2 . 0.04\ Al_2O_3 . 3\ Na_2O . 4.5\ [(C_3H_7)_4N]_2O . 450\ H_2O$ was heated in an autoclave under autogenous pressure for 24 hours at 150°C. After cooling of the reaction mixture, the silicate formed was filtered off, washed with water until the pH of the wash water was about 8, dried at 120°C and calcined for one hour in air at 500°C. The silicate has the following properties:

a) thermally stable up to a temperature of at least 800°C,

b) an X-ray powder diffraction pattern substantially corresponding with that given in Table B,

c) a SiO_2/Al_2O_3 molar ratio (m) of 225, and

d) a crystallite size of 1250 nm.

This silicate was converted into the H-form by boiling with a 1.0 molar NH_4NO_3 solution, washing with water, boiling again with a 1.0 molar NH_4NO_3 solution and washing, drying and calcination.

Catalyst 3

Fe_2O_3-Cr_2O_3 catalyst comprising 10%w Cr_2O_3.

Catalyst 4

$Co/Zr/SiO_2$ catalyst comprising 25 pbw cobalt and 1.8 pbw zirconium per 100 pbw silica and prepared by impregnation of a silica carrier with an aqueous solution comprising a cobalt salt and a zirconium salt, followed by drying of the composition, calcination at 500°C and reduction at 280°C.

Catalyst 5

$Fe/Mg/Cu/K/Al_2O_3$ catalyst comprising 50 pbw iron, 20 pbw magnesium, 2.5 pbw copper and 4 pbw potassium per 100 pbw alumina and prepared by impregnation of an alumina carrier with an aqueous solution comprising an iron salt, a magnesium salt, a copper salt and a potassium salt, followed by drying of the composition, calcination at 800°C and reduction at 325°C.

Catalyst mixture I

Physical mixture of catalyst 1 and catalyst 2 in a 5:1 weight ratio.

Catalysts 4 and 5 and catalyst mixture I were tested in the preparation, in two steps, of hydrocarbons from a H_2/CO mixture having a H_2/CO molar ratio of 0.5. The test was carried out in two reactors of 50 ml each, containing a fixed catalyst bed. Three experiments were carried out. In Experiments 2 and 3, part of the available H_2/CO mixture with a H_2/CO molar ratio of 0.5 was converted in a separate 50 ml reactor containing a fixed catalyst bed consisting of catalyst 3, into a reaction product with a H_2/CO molar ratio of 5.7, which reaction product was mixed with the total reaction product from the first step. The mixtures thus obtained were used as feed for the second step. In Experiment 1, carried out without using a separate CO-shift, the total reaction product from the first step was used as feed for the second step. Experiment 1 falls outside the scope of the invention. It has been included in the patent application for comparison.

The results of the three experiments are stated in Table C.

TABLE C

Experiment No.	1	2	3
First step			
Catalyst No.	I	1	5
Quantity of catalyst, ml	12	10	6
Feed, N1. hour^{-1}	15.5	10	10
H_2/CO molar ratio of feed	0.5	0.5	0.5
Temperature, °C	375	375	280
Pressure, bar	60	60	30
Conversion of H_2/CO mixture, %v	58	70	75
H_2/CO molar ratio of product	0.5	0.5	0.32
CO-shift reaction			
Catalyst No.	-	3	3
Quantity of catalyst, ml	-	2	2
Feed, N1. hour^{-1}	-	5.5	5.7
H_2/CO molar ratio of feed	-	0.5	0.5
Quantity of water added, ml.h^{-1}	-	3.0	3.1
Temperature, °C	-	350	350
Pressure, bar	-	60	60
H_2/CO molar ratio of product	-	5.7	5.7
Second step			
Catalyst No.	4	4	4
Quantity of catalyst, ml	10	10	10
H_2/CO molar ratio of feed	0.5	2	2
Temperature, °C	230	230	230
Pressure, bar	60	60	60
Total conversion of the H_2/CO mixture (1st + 2nd step), %v	78	94	95

CLAIMS

1. A process for the preparation, in two steps, of organic compounds from a mixture of hydrogen and carbon monoxide, characterized in that a H_2/CO mixture having a H_2/CO molar ratio below 2.0 is devided into two portions, A and B, of the same composition, that in the first step portion A, through contact with a catalyst comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into hydrocarbons and/or oxygen-containing organic compounds, is converted into a reaction mixture containing hydrogen and carbon monoxide in which the H_2/CO molar ratio (R_1) is lower than 2.25, that the H_2/CO molar ratio of portion B is raised to a value R_2 which is higher than R_1 and also higher than 1.75, by contacting portion B, together with water, at a temperature above 325°C, with a catalyst having CO-shift activity, that hydrogen and carbon monoxide present in the reaction product prepared from portion A, together with other components from this reaction product, if desired, are mixed with the reaction product prepared from portion B to form a mixture having a H_2/CO molar ratio of from 1.75-2.25, and that the mixture thus obtained is contacted in the second step with a catalyst comprising one or more metal components having activity for the conversion of a H_2/CO mixture into paraffinic hydrocarbons, which metal components have been chosen from the group formed by colbalt, nickel and ruthenium.

2. A process according to claim 1, characterized in that for the preparation of aromatic hydrocarbons the

first step is carried out using a bifunctional catalyst combination comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into acyclic hydrocarbons and/or acyclic oxygen-containing organic compounds and a crystalline metal silicate which, after one hour's calcination in air at 500°C has the following properties:

a) thermally stable up to a temperature of at least 600°C,
b) an X-ray powder diffraction pattern in which the four lines listed in Table A are the strongest lines.

TABLE A

(d(Å)	Relative intensity
11.1 ± 0.2	VS
10.0 ± 0.2	VS
3.84 ± 0.07	S
3.72 ± 0.06	S

in which the letters used have the following meanings:
VS = very strong; S = strong, and

c) in the formula which represents the composition, expressed in moles of the oxides, and which, in addition to hydrogen, alkali metal and/or alkaline-earth metal and silicon, comprises one or more oxides of a trivalent metal A chosen from the group formed by aluminium, iron, gallium, rhodium, chromium and scandium, the SiO_2/A_2O_3 molar ratio (m) is higher than 10,

with the understanding that if the H_2/CO mixture has a H_2/CO molar ratio lower than 1.5, the first step is carried out using a trifunctional catalyst combination comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into acyclic hydrocarbons and/or acyclic oxygen-containing organic compounds, one or more metal components with CO-shift activity and the crystalline metal silicate mentioned hereinbefore.

3. A process according to claim 2, characterized in that the crystalline metal silicate comprises only one metal A chosen from the group formed by aluminium, iron and gallium and that m has a value lower than 1000.

4. A process according to claim 2 or 3, characterized in that the first step is carried out using a catalyst combination comprising a mixture of the crystalline metal silicate and a catalyst chosen from the group formed by

a) catalysts which are capable of converting a H_2/CO mixture into substantially methanol and/or dimethyl ether,
b) catalysts comprising 30-75 pbw iron and 5-40 pbw magnesium per 100 pbw alumina carrier with one or more aqueous solutions of salts of iron and of magnesium, followed by drying of the composition, calcination at a temperature of from 700-1200°C, and reduction, and
c) catalysts comprising 10-40 pbw iron and 0.25-10 pbw chromium per 100 pbw silica and prepared by impregnation of a silica carrier with one or more aqueous solutions of salts of iron and of chromium, followed by drying of the composition, calcination and reduction at a temperature of from 350-750°C.

5. A process according to claim 1, characterized in that for the preparation of paraffinic hydrocarbons, the first step is carried out using an iron-containing bifunctional catalyst or catalyst combination which, in addition to activity for the conversion of a H_2/CO mixture into substantially paraffinic hydrocarbons, has CO-shift activity.

6. A process according to claim 1, characterized in that for the preparation of oxygen-containing organic compounds, the first step is carried out using a catalyst comprising one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into oxygen-containing organic compounds.

7. A process according to claim 6, characterized in that the first step is carried out using a catalyst which has the property of converting a H_2/CO mixture into substantially methanol and/or dimethyl ether.

8. A process according to claim 6 or 7, characterized in that the oxygen-containing organic compounds prepared in the first step are converted in an additional step into lower olefins and/or aromatic hydrocarbons.

9. A process according to any one of claims 1-8, characterized in that portion B of the H_2/CO mixture is contacted with a catalyst comprising chromium and, in addition, iron or zinc with the object of preparing a reaction mixture having a H_2/CO molar ratio higher than 3.

10. A process according to any one of claims 1-9, characterized in that the second step is carried out using a catalyst comprising 10-40 pbw cobalt and 0.25-5 pbw zirconium, titanium or chromium per 100 pbw silica and prepared by impregnation of a silica carrier with one or more aqueous solutions of salts of cobalt and zirconium, titanium or chromium, followed by drying of the composition, calcination at 350-700°C and reduction at 200-350°C.

11. A process for the preparation of organic compounds, as claimed in claim 1, substantially as described hereinbefore, and in particular with reference to Experiments 2 and 3 of the Example.

12. Organic compounds prepared according to a process as claimed in any one of claims 1-11.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1983.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.