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(54) Process for the preparation of hydrocarbons

(57) Syngas with a H_2/CO mol.ratio between 0.25 and 1.0 is converted into hydrocarbons by contacting it with a mixture of a cobalt-containing Fischer-Tropsch catalyst and a Cu- and Zn-containing CO-shift catalyst. In this mixture the two catalysts are present in such amounts that the following relation is met:

$$0.5 \times \frac{2-F}{1+F} < M < 5 \times \frac{2-F}{1+F},$$

M being the (Cu + Zn)/Co atomic ratio in the catalyst mixture and F being the H_2/CO mol.ratio in the syngas. The Co-containing catalyst comprises 3-60 pbw Co and 0.1-100 pbw Zr, Ti and/or Cr per 100 pbw silica and/or alumina.

SPECIFICATION

Process for the preparation of hydrocarbons

The invention relates to a process for the preparation of hydrocarbons by catalytic conversion of a mixture of carbon monoxide and hydrogen.

The preparation of hydrocarbons from a 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. Catalysts often used for the purpose comprise one or more metals from the iron group, together with one or more promotors, and a carrier material. These catalysts can suitably be prepared by the known techniques, such as precipitation, impregnation, kneading and melting. The products which can be prepared by using these catalysts generally have a very wide molecular weight distribution range and, in addition to branched and unbranched paraffins, they 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 distillates not only the yield but also the pour point is unsatisfactory. Therefore the direct conversion of H_2/CO mixtures according to Fischer-Tropch is not a very attractive route for the preparation of middle distillates on a technical scale.

In this patent application "middle distillates" should be taken to be hydrocarbon mixtures whose boiling range corresponds substantially with that of the kerosine 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 there was found a class of Fischer-Tropsch catalysts having the property of yielding a product in which only very minor amounts of olefins and oxygen-containing compounds occur which consists virtually completely of unbranched paraffins, a considerable portion of which paraffins boils above the middle distillate range. It has been found that by hydrocracking the high-boiling part of this product can be converted in high yield into middle distillates. As feed for the hydrocracking at least the 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. The hydrocracking, which is characterized by a very low hydrogen consumption, leads to middle distillates which have a considerably better pour point than those obtained in the direct conversion of a H_2/CO mixture according to Fischer-Tropsch.

The Fischer-Tropsch catalysts belonging to the above-mentioned class contain silica, alumina or silica-alumina as carrier material and cobalt together with zirconium, titanium and/or chromium as catalytically active metals, in such quantities that per 100 pbw of carrier material, the catalysts comprise 3-60 pbw of cobalt and 0.1-100 pbw of zirconium, titanium or chromium. 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 Netherlands Patent Application No. 8301922 recently filed in the name of the Applicant.

When the present cobalt catalysts are used for the Fischer-Tropsch hydrocarbon synthesis starting from H_2/CO mixtures having a H_2/CO molar ratio of about 2, very high H_2+CO conversions can be achieved. However, when feeds with lower H_2/CO molar ratios are used, the H_2+CO conversion is insufficient. The H_2+CO conversion is seen to be lower according as the feed has a lower H_2/CO molar ratio.

Since nature provides large amounts of material with a relatively low H/C ratio such as coal, which when converted into H_2/CO mixtures yields products having H_2/CO molar ratios lower than 2, it would naturally be very welcome if a way could be found to solve the afore-mentioned problem of low H_2+CO conversions.

During an investigation into this subject two measures were found which have made it possible to realise high H_2+CO conversions in the hydrocarbon synthesis starting from H_2/CO mixtures having H_2/CO molar ratios between 0.25 and 1.75 and by using the present cobalt catalysts. In addition the application of these measures leads to a high C_5^+ selectivity. By the first measure the H_2/CO mixture is converted over a mixture of two catalysts, one of which is the cobalt catalyst and the other a copper- and zinc-containing composition. By the second measure the H_2/CO mixture is first partly converted over the cobalt catalyst, and subsequently the unconverted H_2 and CO is converted over a bifunctional catalyst or catalyst combination which, in addition to activity for the conversion of a H_2/CO mixture into hydrocarbons, has activity for the conversion of a mixture of H_2O and CO into a mixture of H_2 and CO_2.

Conditional upon the H_2/CO molar ratio of the feed to be converted it is either exclusively measure 1, or exclusively measure 2, or either one of the two measures that is eligible for use. For feeds with a H_2/CO molar ratio between 0.25 and 0.75 only measure 1 is applicable. If the feed has a H_2/CO molar ratio between 1.0 and 1.75, it is only measure 2 that is eligible. For feeds with a H_2/CO molar ratio between 0.75 and 1.0 either measure 1 or measure 2 can be used at choice.

The present patent application relates to the use of measure 1 for feeds with a H_2/CO molar ratio between 0.25 and 1.0. The use of measure 2 for feeds having a H_2/CO molar ratio between 0.75 and 1.75 forms the subject matter of Netherlands Patent Application (K 5733).

In the catalyst mixture which according to measure 1 is used for the conversion of the H_2/CO mixture the copper- and zinc-containing composition should have a Cu/Zn atomic ratio in the range between 0.1 and 10. In addition the ratio in which the two catalysts are present in the catalyst mixture should be such as to satisfy the relation

$$0,5 \times \frac{2-F}{1+F} < M < 5 \times \frac{2-F}{1+F},$$

wherein F represents the H_2/CO molar ratio of the feed and M the (Cu+Zn)/Co atomic ratio in the catalyst mixture.

The present patent application therefore relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, in which a H_2-and CO-containing feed having a H_2/CO molar ratio (F) in the range between 0.25 and 1.0 is contacted at elevated temperature and pressure with a mixture of two catalysts, the one being a catalyst which comprises 3-60 pbw of cobalt and 0.1-100 pbw of at least one other metal chosen from the group formed by zirconium, titanium and chromium per 100 pbw of silica, alumina or silica-alumina and which has been prepared by kneading and/or impregnation, and the other catalyst being a copper- and zinc-containing composition having a Cu/Zn atomic ratio in the range between 0.1 and 10, and in which the two catalysts are present in the catalyst mixture in such a ratio as to satisfy the relation

$$0,5 \times \frac{2-F}{1+F} < M < 5 \times \frac{2-F}{1+F},$$

wherein M represents the (Cu+Zn)/Co atomic ratio in the catalyst mixture.

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

$$(3 + 4\,R) > \frac{L}{S} > (0.3 + 0.4\,R), \text{ wherein}$$

L = the total quantity of cobalt present on the catalyst, expressed as mg Co/ml catalyst,
S = the surface area of the catalyst, expressed as m^2/ml catalyst, and
R = the weight ratio of the quantity of cobalt deposited on the catalyst by kneading, to the total quantity of cobalt present on the catalyst.

The preparation of the cobalt catalysts which are used according to the invention is preferably carried out according to one of the three procedures mentioned hereinafter:

a) first cobalt is deposited in one or more steps by impregnation and subsequently the other metal is deposited in one or more steps, also by impregnation,

b) first the other metal is deposited in one or more steps by impregnation and subsequently the cobalt is deposited in one or more steps, also by impregnation, and

c) first cobalt is deposited in one or more steps by kneading and subsequently the other metal is deposited in one or more steps by impregnation.

In the process according to the invention preference is given to the use of cobalt catalysts containing 15-50 pbw of cobalt per 100 pbw of carrier. The preferred quantity of other metal present in the cobalt catalysts depends on the way in which this metal has been deposited. In the case of catalysts where first cobalt has been deposited on the carrier, followed by the other metal, preference is given to catalysts containing 0.1-5 pbw of the other metal per 100 pbw of carrier. In the case of catalysts where first the other metal has been deposited on the carrier, followed by the cobalt, preference is given to catalysts containing 5-40 pbw of the other metal per 100 pbw of carrier. Preference is given to zirconium as other metal and to silica as carrier material.

The copper- and zinc-containing composition which in the process according to the invention is used as a component of the catalyst mixture preferably has a Cu/Zn atomic ratio in the range between 0.25 and 4. Preparatory to being suitable for use the catalyst mixtures should be activated. This activation can suitably be carried out by contacting the catalyst mixture with hydrogen or a hydrogen-containing gas, first at a temperature between 150 and 250°C and subsequently at a higher temperature, between 200 and 350°C.

The process according to the invention is preferably carried out at a temperature of 125-350°C and a pressure of 5-100 bar. Special preference is given to a temperature of 175-275°C and a pressure of 10-75 bar.

As explained hereinbefore, the present cobalt catalysts when used for the conversion of a H_2-and Co-containing feed yield a product which is substantially waxy and whose high-boiling part can be converted in high yield into middle distilates by using a hydrocracking treatment. This is also true when, instead of the cobalt catalysts alone, the catalyst mixtures proposed here are used.

Although in the preparation of middle distillates from the product obtained over the catalyst mixture 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, it is preferred to use for this purpose the total C_5^+ fraction of the product prepared over the catalyst mixture, since it has been found that the catalytic hydrotreatment leads to enhanced quality of the gasoline, kerosine and gas oil fractions present therein.

The hydrocracking is carried out by contacting the fraction to be treated at elevated temperature and pressure and in the presenceof hydrogen with a catalyst containing one or more noble metals from Group VIII supported on a carrier. The hydrocracking catalyst used by preference is a catalyst containing 0.1-2 %w and in particular 0.2-1 %w of one or more noble metals from Group VIII supported on a carrier. Preference is given to catalysts comprising platinum or palladium as Group VIII noble metal and silica-alumina as carrier. The hydrocracking is preferably carried out at a temperature of 200-400°C and in particular of 250-350°C and a pressure of 5-100 bar and in particular of 10-75 bar.

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

Example

Starting from three catalysts (1-3) five catalyst mixtures (I-V) were composed by mixing.

Catalyst 1

$Co/Zr/SiO_2$ catalyst which comprised 25 pbw of cobalt and 0.9 pbw of zirconium per 100 pbw of silica and had been prepared by single-step impregnation of a silica carrier 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. The catalyst had a value for L of 98 mg/ml and for S of 96 m^2/ml and therefore for L/S of 1.02 mg/m^2.

Catalyst 2

$Co/Zr/SiO_2$ catalyst which comprised 25 pbw of cobalt and 12 pbw of zirconium per 100 pbw of silica and had been prepared by threestep impregnation of a silica carrier with a solution of zirconiumtetra n-propoxide in a mixture of n-propanol and benzene, followed by impregnation of the zirconium-loaded carrier with a solution of cobalt nitrate in water. The catalyst had a value for L of 97 mg/ml and for S of 100 m^2/ml and therefore for L/S of 0.97 mg/m^2.

In the preparation of Catalysts 1 and 2 a quantity of solution was used in each impregnation step which corresponded substantially with the pore volume of the carrier and the material was dried after each impregnation step and then calcined at 500°C.

Catalyst 3

$Cu/Zn/Al_2O_3$ catalyst which comprised 24.3 %w of copper and 38.0 %w of zinc and therefore had a Cu/Zn atomic ratio of 0.66.

Catalyst 3 was mixed with Catalyst 1 or Catalyst 2 to prepare the catalyst mixtures I-V having (Cu+Zn)/Co atomic ratios (M) ranging from 0.19 to 21.8. The mixing components of which each catalyst mixture was composed as well as the value for M of each catalyst mixture are given in Table I.

Catalyst testing

Catalyst mixtures I-V were used in eight experiments (1-8) in the preparation of hydrocarbons from mixtures of carbon monoxide and hydrogen. The experiments were carried out at a temperature of 250°C, a pressure of 20 bar and a space velocity of 400 Nl gas/l catalyst mixture/h in a reactor containing a fixed catalyst bed. Before they were subjected to the testing the catalyst mixtures were activated by contacting them with a hydrogen-containing gas, first at 200°C and then at 250°C. The results of the experiments and the H_2/CO molar ratios (F) of the feeds used in each one of the experiments are given in Table II.

The parameters H_2+CO conversion and C_5^+ selectivity mentioned in Table II are defined as follows:

$$H_2+CO \text{ conversion} = \frac{\text{mol } H_2+CO \text{ in feed} - \text{mol } H_2+CO \text{ in product}}{\text{mol } H_2+CO \text{ in feed}} \times 100,$$

$$C_5^+ \text{ selectivity} = \frac{\text{pbw } C_5^+ \text{ hydrocarbons in product}}{\text{pbw hydrocarbons in product}} \times 100.$$

Of the experiments mentioned in Table II Experiments 3, 5 and 6 are experiments according to the invention. These experiments, in which the relation according to the invention of M of the catalyst mixture to F of the feed was satisfied,yielded both high conversions and high C_5^+ selectivites. Experiments 1, 2, 4, 7 and 8 falls outside the scope of the invention. They have been included in the patent application for comparison. These experiments, in which the relation according to the invention of M of the catalyst mixture and F of the feed was not satisfied, yielded too low conversions and/or too low C_5^+ selectivities.

TABLE I

Catalyst mixture	*Catalyst mixing components*	*M*
I	1 + 3	21,8
II	1 + 3	3,75
III	2 + 3	1,41
IV	1 + 3	0,85
V	1 + 3	0,19

TABLE II

Experiment No.	*Catalyst* mixture No.	*F*	*H_2+CO* conversion, %mol	*C_5^+* selectivity, %w
1	I	0,55	45	75
2	I	0,90	65	68
3	II	0,55	84	85
4	II	0,90	82	70
5	III	0,55	91	86
6	IV	0,90	91	77
7	V	0,55	54	87
8	V	0,90	74	86

CLAIMS

1. A process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, characterized in that a H_2– and CO-containing feed with a H_2/CO molar ratio (F) in the range between 0.25 and 1.0 is contacted at elevated temperature and pressure with a mixture of two catalysts, the one catalyst being a catalyst which comprises 3-60 pbw of cobalt and 0.1-100 pbw of at least one other metal chosen from the group formed by zirconium, titanium and chromium per 100 pbw of silica, alumina or silica-alumina and which has been prepared by kneading and/or impregnation, and the other catalyst being a copper- and zinc-containing composition having a Cu/Zn atomic ratio in the range between 0.1 and 10, and that the two catalysts are present in the catalyst mixture in such a ratio as to satisfy the relation

$$0.5 \times \frac{2-F}{1+F} < M < 5 \times \frac{2-F}{1+F} ,$$

wherein M represents the (Cu +Zn)/Co atomic ratio in the catalyst mixture.

2. A process as claimed in claim 1, characterized in that the cobalt catalyst satisfies the relation

$$(3 + 4\,R) > \frac{L}{S} > (0.3 + 0.4\,R), \text{ wherein}$$

L = the total quantity of cobalt present on the catalyst, expressed as mg Co/ml catalyst,
S = the surface area of the catalyst, expressed as m^2/ml catalyst, and
R = the weight ratio of the quantity of cobalt deposited on the carrier by kneading to the total quantity of cobalt present on the catalyst.

3. A process as claimed in claim 1 or 2, characterized in that per 100 pbw of carrier the cobalt catalyst comprises 15-50 pbw of cobalt and either 0.1-5 pbw of the other metal if during the preparation cobalt was deposited first and the other metal next, or 5-40 pbw of the other metal if during the preparation the other metal was deposited first and cobalt next.

4. A process as claimed in any one of claims 1-3, characterized in that the cobalt catalyst contains zirconium as other metal and silica as carrier.

5. A process as claimed in any one of claims 1-4, characterized in that the copper- and zinc-containing composition has a Cu/Zn atomic ratio in the range between 0.25 and 4.

6. A process as claimed in any one of claims 1-5, characterized in that it is carried out at a temperature of 125-350°C and a pressure of 5-100 bar.

7. A process as claimed in claim 6, characterized in that it is carried out at a temperature of 175-275°C and a pressure of 10-75 bar.

8. A process as claimed in any one of claims 1-7, characterized in that in order to prepare middle distillates from the product obtained over the catalyst mixture, 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 hydrocracking by contacting it at elevated temperature and pressure with a catalyst comprising one or more noble metals from Group VIII supported on a carrier.

9. A process for the preparation of hydrocarbons as claimed in claim 1, substantially as described hereinbefore and in particular with reference to the example.

10. Hydrocarbons whenever prepared according to a process as described in claims 1-9.

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