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(54) Process for the preparation of hydrocarbons

(57) C_4^- hydrocarbons are converted into syngas with a H_2/CO mol.ratio between 0.25 and 2.25 by reforming at a pressure above 10 bar in the presence of specified amounts of carbon dioxide and steam followed by conversion of the syngas at the same pressure into C_5^+ hydrocarbons over a cobalt-containing catalyst together with at least one other metal chosen from zirconium, titanium and chromium and also silica, alumina or silica-alumina and having CO-shift activity.

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SPECIFICATION

Process for the preparation of hydrocarbons

The invention relates to a process for the preparation of hydrocarbons having at least five carbon atoms per molecule.

Hydrocarbons with at least five carbon atoms per molecule (hereinafter referred to as "C_5^+ hydrocarbons") can be prepared from hydrocarbons having at most four carbon atoms per molecule (hereinafter referred to as "C_4^- hydrocarbons") by a two-step process in which the C_4^- hydrocarbons are converted in the first step by steam reforming into a mixture of carbon monoxide and hydrogen, which mixture is subsequently converted in the second step into a mixture of hydrocarbons consisting substantially of C_5^+ hydrocarbons by contacting it at elevated temperature and pressure with a catalyst. The reaction which takes place in the second step of the process 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 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 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.

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 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 oxygen-containing organic compounds occur and which consits virtually completely of unbranched paraffins, a considerable portion of which paraffins 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 hydrocracking. 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 with 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 the catalysts comprise 3-60 pbw of cobalt and 0.1-100 pbw of zirconium, titanium and/or chromium per 100 pbw of carrier material. 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.

Although the use of the afore-defined cobalt catalysts for the conversion of H_2/CO mixtures yields a product whose high-boiling part can be converted in a simple manner and in high yield into middle distillates, the use of these catalysts in the second step of the two-step process described hereinabove is attended with a number of drawbacks. As described hereinbefore the conversion of the C_4^- hydrocarbons in the first step can be carried out by steam reforming. With a view to the reactions which occur during the conversion of the C_4^- hydrocarbons and in order to minimize carbonization of the catalyst used, this conversion should be carried out by using a steam/hydrocarbon ratio higher than 1 g mol/g at C. The drawbacks attached to the use of the present cobalt catalysts in the second step combined with a conversion of the C_4^- hydrocarbons by steam reforming in the first step are connected with the fact that this conversion of the C_4^- hydrocarbons yields a H_2/CO mixture having a H_2/CO molar ratio which is considerably higher than 2. This can be suitably demonstrated with the aid of the development of the reaction when methane is used as feed. In the steam reforming of methane two reactions occur, viz. a main reaction $CH_4 + H_2O \rightarrow CO + 3H_2$ and a side reaction $CO + H_2O \rightarrow CO_2 + H_2$. This reaction development, when H_2O/CH_4 molar ratios between 2 and 3 which are generally used in practice are applied, leads to H_2/CO mixtures having H_2/CO molar ratios between 3.8 and 4.5. It should be noted here that with the present cobalt catalysts the $H_2 + CO$ conversion is smaller according as the $H_2 + CO$ molar ratio of the H_2/CO mixture supplied varies more from 2, and that in addition their C_5^+ selectivity is lower according as the H_2/CO mixture supplied has a higher H_2/CO molar ratio. Consequently, when the present cobalt catalysts are used for the conversion of a H_2/CO mixture prepared by steam reforming, this leads to both a low $H_2 + CO$ conversion and a low C_5^+ selectivity. Therefore, in view of the high H_2/CO molar ratio of the H_2/CO mixture formed therein, steam reforming is not very suitable to be used for the preparation of the feed for the present cobalt catalyst.

H_2/CO mixtures having considerably lower H_2/CO molar ratios than when steam reforming is used can be prepared by starting from C_4^- hydrocarbons and carrying out the conversion in the presence of carbon dioxide. This so-called carbon dioxide reforming, which, for the same reasons as given for the steam reforming, should be carried out by using a carbon dioxide/hydrocarbon ratio higher than 1 g mol/g atom C, yields a H_2/CO mixture having a H_2/CO molar ratio which is considerably lower than 2. As in the case with the steam reforming, this can suitably be demonstrated with the aid of the development of the reaction when methane is used as feed. In the carbon dioxide reforming of methane two reactions occur, viz. a main reaction $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ and a side reaction $H_2 + CO_2 \rightarrow H_2O + CO$. This reaction development, when CO_2/CH_4 molar ratios between 1.5 and 2 which are generally used in practice are applied, leads to H_2/CO mixtures having H_2/CO molar ratios between 0.70 and 0.64. Although replacing steam reforming with carbon dioxide reforming in the first step of the two-step process wherein the present cobalt catalysts are used in the second step offers a solution to the low C_5^+ selectivity problem (since the cobalt catalysts show a higher C_5^+ selectivity according as the H_2/CO molar ratio of the feed is lower), said replacement has no influence in the low H_2+ CO conversion problem (caused by a H_2/CO molar ratio of the fed which varies considerably from 2) and gives rise to another problem. To solve these two problems a solution has now been found. High conversions of low-hydrogen H_2/CO mixtures using the present cobalt catalysts can be achieved by using these catalysts in a catalyst combination which has CO-shift activity. The fresh problem mentioned above is connected with the need of carrying out the two steps of the two-step process at substantially the same pressure in obviate compression of large gas volumes. Since the hydrocarbon synthesis over the cobalt catalyst of the second step requires a pressure higher than 10 bar, a corresponding high pressure must also be used in the first step. However, a drawback of the carbon dioxide reforming carried out a high pressure is its low conversion. For instance, the carbon dioxide reforming of methane at a pressure of 20 bar and a CO_2/CH_4 molar ratio of 2 yields a H_2/CO mixture having a H_2/CO molar ratio of 0.64 at a methane conversion of not more than 50%. This drawback can be taken away by carrying out the reforming in the presence of both carbon dioxide and steam. For instance, the above-described reforming of methane in the presence of carbon dioxide at a pressure of 20 bar and a CO_2/CH_4 molar ratio of 2 in the presence of a quantity of steam corresponding with a H_2O/CO molar ratio of 0.25 leads to an increase in methane conversion of from 50 to 91%, whilst the H_2/CO molar ratio of the H_2/CO mixture produced only increases from 0.64 to 0.66. More generally, it has been found that H_2/CO mixtures whose H_2/CO molar ratios may lie between 0.25 and 2.25 at choice can be prepared in high yield by reforming C_4^- hydrocarbons at a pressure higher than 10 bar in the presence of carbon dioxide and steam, provided that the following requirements are met

1) the carbon dioxide/hydrocarbon ratio (a) should be higher than 0.1 but lower than 10 g mol CO_2/g atom C,
2) the steam/hydrogen ratio (b) should be higher than 0.1 but lower than 1 g mol H_2O/g atom C, and
3) the carbon dioxide/steam ratio should be chosen such as to meet the requirement $(2 \times a + 3 \times b) \geq 3$.

By using the afore-described reforming as the first step of the two-step process for the preparation of C_5^+ hydrocarbons from C_4^- hydrocarbons while using the present cobalt catalysts in the second step and at a pressure which corresponds substantially with that used in the first step, C_5^+ hydrocarbons can be prepared according to this two-step treatment in high yield and with high selectivity, provided that if the H_2/CO mixture prepared in the first step has a H_2/CO molar ratio lower than 1.5, the cobalt catalyst should be used in a catalyst combination which has CO-shift activity.

The present patent application therefore relates to a process for the preparation of C_5^+ hydrocarbons from C_4^- hydrocarbons, in which C_4^- hydrocarbons are converted at a pressure higher than 10 bar by reforming in the presence of carbon dioxide and steam into a mixture of carbon monoxide and hydrogen having a H_2/CO molar ratio between 0.25 and 2.25 by using a carbon dioxide/hydrocarbon ratio (a) higher than 0.1 but lower than 10 g mol CO_2/g atom C, a steam/hydrocarbon ratio (b) higher than 0.1 but lower than 1 g mol H_2O/g atom C and such a carbon dioxide/steam ratio that $(2 \times a + 3 \times b) \geq 3$, in which the mixture of carbon monoxide and hydrogen thus prepared is converted into a mixture of hydrocarbons substantially consisting of C_5^+ hydrocarbons by contacting it at an elevated temperature and a pressure substantially corresponding with that used in the reforming with a cobalt catalyst comprising 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, which catalyst has been prepared by kneading and/or impregnation, and in which the cobalt catalyst is used in a catalyst combination which has CO-shift activity if the H_2/CO mixture has a H_2/CO molar ratio lower than 1.5.

In the process according to the invention the starting material may be a feed which consists substantially of one or more C_4^- hydrocarbons or a feed which, in addition to C_4^- hydrocarbons, comprises carbon dioxide. It should be noted in this connection that natural gas, which where hydrocarbons are concerned consists mainly of methane, can contain up to 75% vol. of carbon dioxide. Examples of C_4^- hydrocarbons which alone or in admixture can be present in the feed are methane, ethane, propane, butane and iso-butane. Preferably, the process is applied to a feed in which the C_4^- hydrocarbons consist substantially of methane. Special preference is given to natural gas as feed and more particular to carbon dioxide-contaminated natural gas.

The reforming according to the invention can be carried out by contacting the hydrocarbons to be converted together with carbon dioxide and steam at a temperature of 500-1200°C and a pressure of 10-100 bar with a catalyst comprising one or more metals from the iron group supported on a carrier. The reforming is preferably carried out at a temperature of 700-1000°C, a pressure of 10-75 bar and by using a nickel-containing catalyst. In order to prevent the formation of carbon deposits on the catalyst and to remove deposits already formed from the catalyst by conversion into CO, it is preferred to use a catalyst comprising an alkali metal, in particular potassium. In order to prevent the catalyst from sintering it is moreover preferred to use a catalyst comprising an alkaline earth metal, in particular calcium. If the C_4^- hydrocarbons in the feed consist largely or wholly of hydrocarbons containing two or more carbon atoms per molecule, it is preferred to use a catalyst having cracking activity. Cracking activity may be imparted to the catalyst by the use of a silica-alumina as carrier material.

The reforming according to the invention is carried out in the presence of both carbon dioxide and steam, which can be fed to the process from external sources. As described hereinbefore, the process according to the invention can very suitably be applied to a feed which by its nature contains carbon dioxide, so that at least part of the carbon dioxide requirement of the reforming is met. Use can further be made of carbon dioxide and steam which are found in the reaction products of the process according to the invention. Carbon dioxide and steam find their way into the reaction product of the reforming as a result of the fact that the reforming is not a complete reaction, so that even when a stoichiometric quantity is used, a minor portion of the quantity used will be found in the reaction product in the original state. Since in the reforming the total quantity of carbon dioxide and steam used is larger than the stoichiometrically required quantity, the amount used in excess will also be found in the reaction product. It is true that in the reforming there is a minor occurrence of side reactions by which some carbon dioxide and steam is withdrawn from the reaction with the hydrocarbon feed, but these side reactions in themselves yield steam or carbon dioxide as reaction product. Carbon dioxide and steam occur in the reaction product of the hydrocarbon synthesis as well. For in the hydrocarbon synthesis according to the equation $CO + 2H_2 \rightarrow -(CH_2)- + H_2O$ a considerably amount of steam is formed as byproduct. And minor quantities of carbon dioxide can find their way into the reaction product of the hydrocarbon synthesis by the occurence of side reactions. If the process according to the invention preference is given to at least part of the steam and/or carbon dioxide present in the reaction products being separated therefrom and being recycled to the reforming.

The reforming is preferably carried out by using a carbon dioxide/hydrocarbon ratio (a) higher than 0.3 and lower than 4 g mol CO_2/g atom C and a steam/hydrocarbon ratio (b) higher than 0.2 and lower than 0.8 g mol H_2O/g atom C.

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

$$(3 + 4\,R) > L/S > (0.3 + 0.4\,R),$$

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 in the hydrocarbon synthesis is preferably carried out by 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 use is preferably made 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 the other metal and to silica as carrier material. Preparatory to being suitable for use the cobalt catalysts should be activated. This activation can suitably be carried out by contacting the catalyst at a temperature between 200 and 350°C with hydrogen or a hydrogen-containing gas.

In the process of the invention the hydrocarbon synthesis is preferably carried out at a temperature of 125-350°C and in particular of 175-275°C and a pressure of 10-100 bar and in particular of 10-75 bar.

In the process of the invention the reforming yields a H_2/CO mixture whose H_2/CO molar ratio may vary between 0.25 and 2.25. If the H_2/CO molar ratio of the H_2/CO mixture is lower than 1.5, the cobalt catalyst should be used in a catalyst combination which has CO-shift activity. Although for the conversion of H_2/CO mixtures with a H_2/CO molar ratio between 1.5 and 2.25 the use of the cobalt catalyst per se will do, it is preferred even for the conversion of H_2/CO mixtures with a H_2/CO molar ratio between 1.5 and 1.75 to use the afore-mentioned catalyst combination. The catalyst combinations used in the process according to the invention should have higher CO-shift activities according as the H_2/CO mixtures to be converted have lower H_2/CO molar ratios.

If in the process of the invention the reforming has yielded a H_2/CO mixture with a H_2/CO molar ratio (F) between 0.25 and 1.0, then the conversion of this H_2/CO mixture is preferably carried out by using a mixture of two catalysts one of which is the cobalt catalyst and the other a copper and zinc containing composition having a Cu/Zn atomic ratio between 0.1 and 10, in which catalyst mixture the two catalysts are present in such a ratio as to satisfy the relation

$$0.5 \times 2-F/1+F < M < 5 \times 2-F/1+F,$$

wherein M represents the (Cu+Zn)/Co atomic ratio in the catalyst mixture. By preference the copper and zinc containing composition has a Cu/Zn atomic ratio 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 next at a higher temperature, between 200 and 350°C.

If in the process of the invention the reforming has yielded a H_2/CO mixture with a H_2/CO molar ratio (F) between 0.75 and 1.75, then the conversion of this H_2/CO mixture is preferably carried out in two steps, in which in the first step the H_2/CO mixture is partly converted over the cobalt catalyst under such conditions as to satisfy the relation

$$150 \times F-0.5/F + 1 < C < 250 \times F-0.5/F + 1,$$

wherein C represents the H_2 + CO conversion as %mol, and in which of the product from the first step, after the water formed has been removed, at least the H_2 and CO which has remained unconverted is contacted in a second step with a catalyst or catalyst combination which, in addition to activity for the conversion of a H_2/CO mixture into hydrocarbons, has CO-shift activity. In the second step preference is given to the use of a mixture of two catalysts, one catalyst being a cobalt catalyst belonging to the same class as the class from which the cobalt catalyst used in the first step was chosen, and the other catalyst being a copper and zinc containing composition having a Cu/Zn ratio between 0.1 and 10. Special preference is given to such catalyst mixtures wherein the two catalysts are present in such a ratio that the (Cu+Zn)/Co atomic ratio of the catalyst mixture lies between 0.5 and 5. The copper and zinc containing composition present in the catalyst mixture preferably has a Cu/Zn atomic ratio between 0.25 and 4. Preparatory to being suitable for use the catalyst mixtures should be activated in the way described hereinbefore.

As already observed hereinbefore, the present cobalt catalysts when used for the conversion of a H_2/CO mixture yield a substantially waxy product the high-boiling part of which can be converted in high yield into middle distillates by the use of hydrocracking. This also holds when not the cobalt catalysts alone are used, but the above-described catalyst combination which comprise such a cobalt catalyst. Although in the preparation of middle distillates from the products obtained over the cobalt catalyst the part of these products 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 these products, since it has been found that the catalytic hydro-treatment 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 presence of hydrogen with a catalyst comprising 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.

Feed 1: A natural gas substantially consisting of methane.

Feed 2: A natural gas substantially consisting of a mixture of methane and carbon dioxide in a 1:3 volume ratio.

Feed 3: A natural gas substantially consisting of a mixture of methane and carbon dioxide in a 4:3 volume ratio.

Feed 4: A natural gas substantially consisting of a mixture of methane and carbon dioxide in a 10:3.5 volume ratio.

Feed 5: A natural gas substantially consisting of a mixture of methane and carbon dioxide in a 1:1.2 volume ratio.

Catalyst 1: $Ni/Ca/K/Al_2O_3$ catalyst comprising 13 pbw of nickel, 12 pbw of calcium and 0.2 pbw of potassium per 100 pbw of alumina.

Catalyst 2: $Co/Zr/SiO_2$ catalyst which comprised 25 pbw of cobalt and 18 pbw of zirconium per 100 pbw of silica and has been prepared by three-step impregnation of a silica carrier with a solution of zirconium tetra n-propoxide in a mixture of n-propanol and benzene, followed by single-step 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 consequently for L/S of 0.97 mg/m^2.

Catalyst 3: 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 consequently for L/S of 1.02 mg/m^2.

Catalyst 4: 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 three-step impregnation of a silica carrier with a solution of zirconium tetra 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 subsequently for L/S of 0.97 mg/m^2.

In the preparation of Catalysts 2-4 a quantity of solution was used in each impregnation step which substantially corresponded with the pore volume of the carrier, and after each impregnation step the material was dried and then calcined at 500°C.

Catalyst 5: Cu/Zn/Al_2O_3 catalyst which comprised 24.3 %w of copper and 38.0 %w of zinc and consequently had a Cu/Zn atomic ratio of 0.66.

Catalyst Mixture I: Catalysts 4 and 5 were mixed in such a ratio as to yield a Catalyst Mixture I whose (Cu+Zn)/Co atomic ratio (M) was 1.41.

Six experiments (1-6) were carried out starting from Feeds 1-5. In each of the experiments a feed was converted into a H_2 and CO containing reaction product by contacting it, whether or not together with steam, at a temperature of 950°C and a pressure of 21 bar with Catalyst 1. In Experiments 1 and 4-6 the reaction product was freed from water by cooling and subsequently converted into a mixture of hydrocarbons by contacting it with either one of Catalysts 2 and 3, and/or with Catalyst Mixture I. Preparatory to being used for the hydrocarbon synthesis Catalysts 2 and 3 and Catalyst Mixture I were activated by contacting them with a hydrogen-containing gas, Catalysts 2 and 3 at 250°C and Catalyst Mixture I first at 200°C and next at 250°C. Further information on the conditions used to carry out the experiments and the results obtained are given below.

Experiment 1

Two-step experiment starting from Feed 1.

First step: reforming of Feed 1 in the presence of a quantity of steam corresponding with a H_2O/CH_4 molar ratio of 2.0. CH_4 conversion achieved: 85.4%. After removal of water 91 %vol. of the reaction product consisted of a H_2/CO mixture with a H_2/CO molar ratio of 4 1.

Second step: the reaction product of the first step which had been freed from water was contacted at a temperature of 220°C, a pressure of 21 bar and a space velocity of 600 N $(H_2+CO).1^{-1}.h^{-1}$ with Catalyst 2. The (H_2+CO) conversion achieved was 61 %vol., and the C_6^+ selectivity 63%.

Experiment 2

Single-step experiment starting from Feed 2. In this experiment, in which Feed 2 was reformed without addition of steam, the CH_4 conversion was 59%, and the H_2CO mixture obtained had a H_2/CO ratio of 0.58.

Experiment 3

Single-step experiment starting from Feed 3. This experiment, in which Feed 3 was reformed in the presence of a quantity of steam corresponding with a H_2O/CH_4 molar ratio of 0.35, had to be terminated prematurely on account of clogging of the reactor due to coke formation.

Experiment 4

Two-step experiment starting from Feed 4.

First step: reforming of Feed 4 in the presence of a quantity of steam corresponding with a H_2O/CH_4 molar ratio of 0.8. CH_4 conversion achieved: 69%. After removal of water 78 %vol. of the reaction product consisted of a H_2/CO mixture with a H_2/CO molar ratio of 2.

Second step: the reaction product of the first step which had been freed from water was contacted at a temperature of 220°C, a pressure of 21 bar and a space velocity of 600 N1 $(H_2+CO).1^{-1}.h^{-1}$ with Catalyst 2. The (H_2+CO) conversion achieved was 96 %vol., and the C_6+ selectivity 80%.

Experiment 5

Two-step experiment starting from Feed 2.

First step: reforming of Feed 2 in the presence of a quantity of steam corresponding with a H_2O/CH_4 molar ratio of 0.5 CH_4 conversion achieved: 96.7%. After removal of water 72 %vol. of the reaction product consisted of a H_2/CO mixture with a H_2/CO molar ratio of 0.55.

Second step: the reaction product of the first step which had been freed from water was contacted at a temperature of 250°C, a pressure of 21 bar and a space velocity of 400 N1 $(H_2+CO).1^{-1}.h^{-1}$ with Catalyst Mixture I. The (H_2+CO) conversion achieved was 83 %vol., and the C_5^+ selectivity 83%.

Experiment 6

Three-step experiment starting from Feed 5.

First step: reforming of Feed 5 in the presence of a quantity of steam corresponding with a H_2O/CH_4 molar ratio of 0.5. CH_4 conversion achieved: 82.3%. After removal of water 85.5 %vol. of the reaction product consisted of a H_2/CO mixture with a H_2/CO molar ratio of 1.0.

Second step: the reaction product of the first step which had been freed from water was contacted at a temperature of 230°C and a pressure of 21 bar with Catalyst 3. The reaction product from the second step was divided by cooling into a gaseous fraction substantially consisting of unconverted H_2 and CO and C_4^- hydrocarbons, and a liquid fraction substantially consisting of C_5^+ hydrocarbons and water. The gaseous fraction was used as feed for the third step.

Third step: the gaseous fraction from step 2 was contacted at a temperature of 260°C and a pressure of 21 bar with Catalyst Mixture I. Steps 2 and 3 were carried out at a total (H_2+CO) through-put rate of 600 $N1.1^{-1}.h^{-1}$ and by using Catalyst 3 (in the second step) and Catalyst Mixture I (in the third step) in a 1:2 volume ratio. In this experiment the total H_2+CO conversion was 89% and the total selectivity 83%. The total H_2+CO conversion and the total C_5^+ selectivity are defined as follows:

$$\text{Total } H_2+CO \text{ conversion} = \frac{\text{mol } H_2+CO \text{ in feed of second step} - \text{mol } H_2+CO \text{ in product of third step}}{\text{mol } H_2+CO \text{ in feed of second step}} \times 100$$

$$\text{total } C_5^+ \text{ selectivity} = \frac{\text{pbw of } C_5^+ \text{ hydrocarbons in product of second + third step}}{\text{pbw of hydrocarbons in product of second + third step}}$$

Of experiments 1-6 described hereinbefore Experiments 4-6 are experiments according to the invention. These experiments, in which the reforming was carried out in the presence of such quantities of carbon dioxide and steam as to satisfy the relation (2 × a + 3 × b) ≥ 3, and in which the synthesis gas formed in subsequently contacted with the special cobalt catalyst or a catalyst combination which comprises the special cobalt catalyst, yielded both a high conversion and a high C_5^+ selectivity. Experiments 1-3 fall outside the scope of the invention. They have been included in the patent application for comparison. In Experiment 1 the reforming was carried out in the presence of only steam, and a synthesis gas was obtained which had a high H_2/CO molar ratio. Further processing of this gas in the second step over the special cobalt catalyst led to a low conversion and a low C_5^+ selectivity. In Experiment 2 the reforming was carried out in the presence of only carbon dioxide, and a synthesis gas was obtained in low yield which had a low H_2O/CO molar ratio. Although further processing of this gas in a second step over the special cobalt catalyst can lead to a high C_5^+ selectivity, conversion will only be low. In Experiment 3 the reforming was carried out in the presence of carbon dioxide and steam, but the quantities of carbon dioxide and steam were such that the relation (2 × a + 3 × b) ≥ 3 was not satisfied. In experiment 3 there was clogging of the reactor due to coke formation.

CLAIMS

1. A process for the preparation of C_5^+ hydrocarbons from C_4^- hydrocarbons, characterized in that C_4^- hydrocarbons are converted at a pressure higher than 10 bar by reforming in the present of carbon dioxide and steam into a mixture of carbon monoxide and hydrogen having a H_2/CO molar ratio between 0.25 and 2.25 by using a carbon dioxide/hydrocarbon ratio (a) higher than 0.1 but lower than 10 g mol CO_2/g atom C, a steam/hydrocarbon ratio (b) higher than 0.1 but lower than 1 g mol H_2O/g atom C and such a carbon dioxide/ steam ratio that (2 × a + 3 × b) ≥ 3, that the mixture of carbon monoxide and hydrogen thus prepared is converted into a mixture of hydrocarbons substantially consisting of C_5^+ hydrocarbons by contacting it at an elevated temperature and a pressure substantially corresponding with that used in the reforming with a cobalt catalyst comprising 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, which catalyst has been prepared by kneading and/or impregnation, and that when the H_2/CO mixture has a H_2/CO molar ratio lower than 1.5, the cobalt catalyst is used in a catalyst combination which has CO-shift activity.

2. A process as claimed in claim 1, characterized in that it is applied to a feed in which the C_4^- hydrocarbons substantially consist of methane.

3. A process as claimed in claim 2, characterized in that it is applied to natural gas as feed.

4. A process as claimed in claim 3, characterized in that it is applied to a carbon dioxide contaminated natural gas.

5. A process as claimed in any one of claims 1-4, characterized in that the reforming is carried out at a temperature of 700-1000°C, a pressure of 10-75 bar and by using a nickel-containing catalyst.

6. A process as claimed in any one of claims 1-5, characterized in that at least part of the steam and/or carbon dioxide present in the reaction products is separated therefrom and is recycled to the reforming.

7. A process as claimed in any one of claims 1-6, characterized in that the reforming is carried out by using a carbon dioxide/hydrocarbon ratio higher than 0.3 and lower than 4 g mol CO_2/g atom C, and a steam/hydrocarbon ratio higher than 0.2 and lower than 0.8 g mol H_2O/g atom C.

8. A process as claimed in any one of claims 1-7, characterized in that the cobalt catalyst satisfies the relation:

$(3 + 4\,R) > L/S > (0.3 + 0.4\,R)$, 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.

9. A process as claimed in any one of claims 1-8, characterized in that the cobalt catalyst comprises zirconium as other metal and silica as carrier.

10. A process as claimed in any one of claims 1-9, characterized in that the hydrocarbon synthesis is carried out at a temperature of 125-350°C and a pressure of 10-100 bar.

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

12. Hydrocarbons prepared by a process as claimed in any one of claims 1-11.

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