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(54) Cobalt catalyst activation

(57) The activation of catalysts comprising cobalt and one or more of titanium, zirconium and chromium on a silica and/or alumina support which have been prepared by impregnation and/or kneading is carried out at a temperature between 200 and 350°C with a H_2-containing gas under such conditions that a specified relation is met between on the one hand the applied space velocity (D), total pressure (P_{tot}) and H_2 partial pressure (P_{H_2}) and on the other hand the surface area (S), the Co load (L) and the Zr load (Z) of the catalyst. This relation reads:

$$\frac{D}{10^4 \times (P_{H_2})^2 \times P_{Tot}} > \frac{10 \times S}{L \times (Z+1)},$$

In this way a catalyst with optimum stability is obtained.

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SPECIFICATION

Catalyst activation

The invention relates to a process for the activation of a catalyst which is to be used for the conversion of a mixture of carbon monoxide and hydrogen into hydrocarbons.

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 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 cruds mineral oil. The middle distillation 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 compounds occur and which consists 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 lies above the final boiling point of the heaviest middle distillate desired as end product. The hydrocraking, 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.

Preparatory of being eligible for use in the preparation of hydrocarbons from a H_2/CO mixture the cobalt catalysts should be activated. This activation may suitably be carried out by contacting the catalyst at a temperature between 200 and 350°C with hydrogen or a hydrogen-containing gas.

Further investigation into the activation and performance of the afore-mentioned cobalt catalysts has now shown that where stability is concerned, their performance is to a great extent dependent on the space velocity of the hydrogen-containing gas, the hydrogen partial pressure and overall pressure used during the activation as well as on the surface area, the cobalt load and the zirconium load of the catalyst to be activated.

It has been found that where their stability is concerned, the catalysts show optimum performance when the activation is carried out under such conditions as to satisfy the relation

$$\frac{D}{10^4 \times (P_{H_2})^2 \times P_{Tot}} > \frac{10 \times S}{L \times (Z + 1)}, \text{ wherein}$$

D = space velocity, expressed as $Nl.l^{-1}$.
P_{H_2} = hydrogen partial pressure, as bar,
P_{Tot} = overall pressure, as bar,
S = surface area of the catalyst, as m^2/ml,
L = cobalt load of the catalyst as mg Co/ml, and
Z = zirconium load of the catalyst as mg Zr/100 mg carrier.

The present patent application therefore relates to a process for the activation of a catalyst, in which a 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, is contacted at a temperature between 200 and 350°C with hydrogen or a hydrogen-containing gas under such conditions as to satisfy the afore-mentioned relation.

The process of the invention is preferably applied to the cobalt catalysts which form the subject matter of Netherlands patent application No. 8301922. They 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.

Further the process of the invention is preferably applied to cobalt catalysts which have been prepared 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.

Further the process according to the invention is preferably applied to 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.

The catalysts activated according to the process of the invention are excellently suitable for use in the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen. The present patent application therefore also relates to a process for the preparation of hydrocarbons from a H_2-and-CO-containing feed by using a catalyst which has been activated according to the invention. The conversion of the H_2-and-CO-containing feed into hydrocarbons is preferably carried out at a temperature of 125–350°C and in particular of 175–275°C and a pressure of 5–100 bar and in particular of 10–75 bar.

H_2-and-CO-containing feeds which are eligible to be converted into hydrocarbons by using a catalyst activated according to the invention may very suitably be obtained from light hydrocarbons, such as natural gas, by steam reforming or partial oxidation. Suitable H_2-and-CO-containing feeds may also be otained by separating a fraction containing unconverted hydrogen and carbon monoxide and other components, if desired, from the reaction product obtained by contacting a H_2/CO mixture with a catalyst containing 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.

The H_2-and-CO-containing feed which is converted into hydrocarbons by using a catalyst activated according to the invention preferably has a H_2/CO molar ratio higher than 1.5. If the feed has a H_2/CO molar ratio lower than 1.5, the latter is preferably raised to a value between 1.5 and 2.5 and in particular a value between 1.75 and 2.25 before it is contacted with the cobalt catalyst. The H_2/CO molar ratio of low-hydrogen feeds may be raised, for instance, by adding hydrogen, removing carbon monoxide, mixing with a hydrogen-rich H_2/CO mixture, or subjecting the low-hydrogen feed to the CO shift reaction.

The cobalt catalysts which have been activated according to the invention are very suitable for use in a process for the preparation of hydrocarbons containing at least five carbon atoms per molecule (hereinafter referred to as "C_{5+} hydrocarbons") from hydrocarbons containing at most four carbon atoms per molecule (hereinafter referred to as "C_{4-} hydrocarbons"), in which C_{4-} hydrocarbons are converted in the first step by steam reforming or partial oxidation into a H_2/CO mixture, which mixture is subsequently converted in a second step into a mixture of hydrocarbons substantially consisting of C_{5+} hydrocarbons by contacting it at elevated temperature and pressure with a cobalt catalyst activated according to the invention, in which the feed for the second step contains nitrogen and/or carbon dioxide as contaminants, which contaminants are found in said feed substantially because the feed for the first step contained more than 20 %v of nitrogen and/or carbon dioxide and/or because the first step was carried out by partial oxidation by using an oxygen-containing gas mixture containing more than 50 %v of nitrogen.

Further the cobalt catalysts which have been activated according to the invention are very suitable for use in the preparation of C_{5+} hydrocarbons from C_{4-} hydrocarbons, in which C_{4-} hydrocarbons are converted in the first step by steam reforming into a H_2/CO mixture, which mixture is subsequently converted in a second step into a mixture of hydrocarbons consisting substantially of C_{5+} hydrocarbons by contacting it at elevated temperature and pressure with a cobalt catalyst activated according to the invention, in which the reaction product of the second step is divided into a gaseous fraction substantially consisting of unconverted hydrogen and carbon monoxide, C_{4-} hydrocarbons formed as by-product and carbon dioxide formed as by-product, and a liquid fraction substantially consisting of C_{5+} hydrocarbons and water at least part of which has been formed as by-product in the second step, in which the gaseous fraction is recycled to the first step and in which the excess hydrogen formed as well as the partg of the steam added during the steam reforming which has remained unconverted are separated off during the process.

Finally the cobalt catalysts which have been activated according to the invention are very suitable for use in the preparation of C_{9+} hydrocarbons from C_4^- hydrocarbons, in which C_4^- hydrocarbons are converted in the first step by steam reforming into a H_2/CO mixture, which mixture is subsequently converted in a second step into a mixture of hydrocarbons consisting substantially of C_{9+} hydrocarbons by contacting it at elevated temperature and pressure with a cobalt catalyst activated according to the invention, in which the reaction product of the second step is divided into a gaseous fraction consisting substantially of unconverted hydrogen and carbon monoxide, C_{8-} hydrocarbons formed as by-product and steam which has remained unconverted during the steam reforming as well as steam formed as by-product in the second step, and a liquid fraction consisting substantially of C_{9+} hydrocarbons, in which the gaseous fraction is recycled to the first step and in which the excess hydrogen formed in separated of during the process.

The three two-step processes described hereinbefore are preferably applied to a feed in which the C_{4-} hydrocarbons consist substantially of methane. Special preference is given to natural gas as feed.

As already observed hereinbefore, the present cobalt catalysts when used for the conversion of a H_2-and-CO-containing feed 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. 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. 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, it is preferred to use for this purpose the total C_{5+} fraction of the product prepared over the cobalt catalyst, 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 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.

If the hydrocarbon synthesis carried out over the cobalt catalyst activated according to the invention is followed by a hydrocracking treatment for the preparation of middle distillates, the two steps can be carried out in 'series-flow', since the reaction product prepared over the cobalt catalyst will contain sufficient unconverted hydrogen for carrying out the hydrocracking. It is a matter of common knowledge that carrying out a multi-step process in 'series-flow' comprises using the total reaction reaction product—without any components being removed therefrom or added thereto—of a certain step as feed for the following step, which is carried out substantially at the same pressure as the preceding step.

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

EXAMPLE

Catalyst preparation

Eight $Co/Zr/SiO_2$ catalysts (Catalysts 1–8) were prepared by impregnation and/or kneading of silica carriers using solutions of cobalt and zirconium compounds. In each impregnation step the quantity of solution used had a volume which corresponded substantially with the pore volume of the carrier concerned. After each impregnation step the solvent was removed by heating and the material was calcined at 500°C. When a kneading step was used, the quantity of solution used has a volume which corresponded substantially with 150% of the pore volume of the carrier concerned. When a kneading step was used, the mixture was kneaded for three hours in a kneading machine. During the kneading a small portion of the solvent was removed by heating. After the kneading step the paste obtained was removed from the kneading machine, the remainder of the solvent was removed by heating and the material was ground and calcined at 500°C.

Catalysts 1–8 were prepared as follows.

Catalyst 1

Kneading 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 zirconyl chloride in water.

Catalyst 2

Single-step impregnation of a silica carrier with a solution of cobalt nitrate, followed by single-step impregnation of the cobalt-loaded carrier with a solution of zirconium nitrate in water.

Catalyst 3

Single-step co-impregnation of a silica carrier with a solution of cobalt nitrate and zirconyl chloride in water.

Catalysts 4–8

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.

Catalysts 5–7

Two-step impregnation of a silica carrier with a solution of zirconium tetra n-propoxide in a mixture of n-propanol and benzene, followed by a single-step impregnation of the zirconium-loaded carrier with a solution of cobalt nitrate in water.

Further information on Catalysts 1–8 is given in Table I.

Catalyst activation

19 Activation experiments (1–19) were carried out in which treatment with hydrogen or a mixture of hydrogen and nitrogen was used to prepare starting from Catalysts 1–8, the activated Catalysts 1A–1F, 2A and 2B, 3A, 4A and 4B, 5A and 5B, 6A and 6B, 7A and 7B and 8A and 8B, respectively. The condiftions used to carry out the activation experiments are given in Tables II and III.

Catalyst trial

The activated catalysts 1A to 8B were used in nineteen experiments (I–XIX) in the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen of a H_2/CO molar ratio of 2. The experiments were carried out in a reactor containing a fixed catalyst bed. The conditions used to carry out these experiments and the results of these experiments are given in Tables IV and V.

Of the activation experiments given in Tables II and III Experiments 3–6, 8, 11, 13–17 and 19 are experiments according to the invention. The catalysts obtained in these experiments, in which the relation which according to the invention should exist between catalyst properties and conditions used in the activation was satisfied, showed high stability, as is seen from the results given in Tables IV and V. Experiments 1, 2, 7, 9; 10, 12 and 18 fall outside the scope of the invention. They have been included in the patent application for comparison. The catalyst obtained in these experiments, in which the relation according to the invention between catalyst properties and conditions used during activation was not satisfied, showed low stability, as is seen from the results given in Tables IV and V.

TABLE I

Catalyst No.	1	2	3	4	5	6	7	8
Co-load, pbw/100 pbw SiO_2	25	25	25	25	25	25	25	10
Zr-load, pbw/100 pbw SiO_2 (Z)	0.9	0.9	0.9	18	12	11	10	18
L, mg Co/ml catalyst	110	98	121	97	102	82	87	40
S, m^2/ml catalyst	25	96	17	100	100	102	100	30

TABLE II

Catalyst to be activated No.	1						2		3
Activation experiment No.	1	2	3	4	5	6	7	8	9
Activated catalyst No.	1A	1B	1C	1D	1E	1F	2A	2B	3A
Activation conditions									
P_{Tot}, bar	1,1	2	1	1,3	1	1	1,3	2	1,1
P_{H_2}, bar	1,1	2	0,1	1	0,1	0,1	1	0,02	1,1
T, °C	250	250	250	250	240	280	250	250	250
D, $Nl.l^{-1}.h^{-1}$	6000	6000	6000	48000	6000	6000	48000	1200	6000

TABLE III

Catalyst to be activated No.	4		5		6		7		8	
Activation experiment No.	10	11	12	13	14	15	16	17	18	19
Activated catalyst No.	4A	4B	5A	5B	6A	6B	7A	7B	8A	8B
Activation conditions										
P_{Tot}, bar	1,1	1,3	1,8	1,3	1,3	2	2	2	1,1	1
P_{H_2}, bar	1,1	1	1,8	1	1	0,2	0,04	0,08	1,1	0,1
T, °C	250	250	250	250	250	250	260	260	250	250
D, $Nl.l^{-1}.h^{-1}$	2000	180000	10000	90000	90000	12500	1200	1200	2000	6000

TABLE IV

Experiment No.	I	II	III	IV	V	VI	VII	VIII	IX
Catalyst No.	1A	1B	1C	1D	1E	1F	2A	2B	3A
Conditions									
temperature, °C	220	220	220	220	230	230	220	220	220
pressure, bar	30	30	30	30	20	20	20	20	20
space velocity, Nl.l^{-1}.h^{-1}	800	800	600	600	900	900	1000	1000	600
Initial CO, conversion, %v	72	69	85	87	83	82	85	84	78
Loss of CO, conversion, %v/100 h	4	10	2	2	2	2	9	2	21

TABLE V

Experiment No.	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
Catalyst No.	4A	4B	5A	5B	6A	6B	7A	7B	8A	8B
Conditions										
temperature, °C	220	220	220	220	220	220	220	220	220	220
pressure, bar	20	20	20	20	20	20	20	20	20	20
space velocity, Nl.l^{-1}.h^{-1}	2000	2000	2000	2000	2000	2000	2000	2000	800	800
Initial CO, conversion, %v	75	74	60	72	69	61	60	67	72	70
Loss of CO, conversion, % v/100 h	7	3	15	3	3	2	2	2	7	3

CLAIMS

1. A process for the activation of a catalyst, characterized in that a 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, is contacted with hydrogen or a hydrogen-containing gas at a temperature in the range between 200 and 350°C under such conditions as to satisfy the relation:

$$\frac{D}{10^4 \times (P_{H_2})^2 \times P_{Tot}} > \frac{10 \times S}{L \times (Z + 1)}, \text{ wherein}$$

D = space velocity, as $Nl.l^{-1}.h^{-1}$,
P_{H_2} = hydrogen partial pressure, as bar,
P_{Tot} = overall pressure, as bar,
S = surface area of the catalyst, as m^2/ml,
L = cobalt load of the catalyst as mg Co/ml, and
Z = zirconium load of the catalyst as mg Zr/100 mg carrier.

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

5. 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 is contacted at elevated temperature and pressure with a catalyst as claimed in any one of claims 1–4.

6. A process as claimed in claim 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 for the activation of a catalyst as claimed in claim 1, substantially as described hereinbefore and in particular with reference to the example.

8. Catalysts activated according to a process as claimed in any one of claims 1–5.

9. A process for the preparation of hydocarbons as claimed in claim 5 or 6, substantially as described hereinbefore and in particular with reference to the example.

10. Hydrocarbons prepared by a process as claimed in claim 5, 6 or 9.

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