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(54) A process for the preparation of Fischer-Tropsch catalysts

(57) SiO_2-supported Cr-promoted Fe-catalysts are prepared by impregnation, calcination and reduction at 350–750°C. Hydrocarbons are prepared from H_2-poor syngas with the use of this catalyst.

SPECIFICATION

A process for the preparation of Fischer-Tropsch catalysts

The invention relates to a process for the preparation of Fischer-Tropsch catalysts.

The preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen by contacting this mixture at elevated temperature and pressure with a catalyst is referred to in the literature as the hydrocarbon synthesis according to Fischer-Tropsch. Catalysts which are often used for this purpose contain one or more metals from the iron group together with one or more promoters and sometimes a carrier material. The preparation of the Fischer-Tropsch catalysts can, in principle be carried out in three ways, viz. by precipitation, by melting or by impregnation. The preparation of the catalysts by precipitation briefly consists in an aqueous solution of a salt of a metal from the iron group, to which, if desired, a salt of a promoter and a carrier material may have been added, being rendered alkaline, resulting in the precipitation of the catalyst. One or more promoters and a carrier material may be added to this precipitate. The preparation of the catalysts by melting is effected, for instance, for iron catalysts by fusing iron oxide with one or more promoter oxides. Both the precipitation route and the melting route are not very attractive procedures for the preparation of the Fischer-Tropsch catalysts, since their reproducibility is small. The precipitation route has the additional disadvantage that it takes up a great deal of time, whilst the melting route requires much energy. Moreover, the catalytic properties of the catalysts prepared by melting and by precipitation, particularly the activity and stability are unsatisfactory. A much more attractive procedure for the preparation of the Fischer-Tropsch catalysts is the impregnation route. It is easy to carry out, gives well reproducible results and, as a rule, leads to catalysts with high activity and stability. The impregnation route briefly consists in a porous carrier being impregnated with one or more aqueous solutions of salts of one or more metals from the iron group and of one or more promoters, followed by drying, calcining and reducing of the composite. Many elements, such as alkali metals, alkaline-earth metals, metals from group VI B, Ti, Zr, Th, V, Mn and Cu, are eligible promoters for the catalysts prepared by impregnation. As the carrier materials for the catalysts prepared by impregnation amorphous as well as crystalline materials, may be used. Suitable carriers are, inter alia, silica, alumina, zirconia, thoria, boria and combinations thereof, such as silica-alumina and silica-magnesia and further zeolites, such as mordenite, faujasite and zeolite-omega.

The Applicant has carried out an extensive investigation concerning the preparation of hydrocarbons from H_2/CO mixtures with an H_2/CO molar ratio smaller than 1.0, using Fischer-Tropsch catalysts prepared by impregnation. In the above-mentioned conversion the behaviour of these catalysts was found to be greatly dependent on the following factors:

1. the nature of the metal from the iron group and the load used,
2. the nature of the promoter and the load used,
3. the nature of the carrier, and
4. the temperature used.

Catalysts prepared by impregnation were found to have a very high activity and a very high stability for the conversion of H_2/CO mixtures with an H_2/CO molar ratio smaller than 1.0, if they contain 10–40 pbw iron and 0.25–10 pbw chromium per 100 pbw silica and have been reduced at a temperature of 350–750°C. These are novel catalysts.

The present patent application therefore relates to a process for the preparation of novel catalysts, in which catalysts containing 10–40 pbw iron and 0.25–10 pbw chromium per 100 pbw silica are prepared by impregnating a silica carrier with one or more aqueous solutions of salts of iron and of chromium, followed by drying the composite, calcining it and reducing it at a temperature of 350–750°C. The patent application further relates to the use of these catalysts for the preparation of hydrocarbons with an H_2/CO mixture with an H_2/CO molar ratio smaller than 1.0 as the starting material.

When for the above-mentioned application use is made of catalysts prepared according to the invention, preferred catalysts are those containing 20–35 pbw iron and 0.5–5 pbw chromium per 100 pbw silica. Further, preference is given to catalysts which contain, in addition to iron and chromium a selectivity promoter. Suitable selectivity promoters are the alkali metals, in particular potassium. In addition to iron and chromium it is preferred in the catalyst preparation according to the invention to incorporate 1–5 pbw potassium per 100 pbw silica into the catalyst by impregnation.

In the preparation of the catalysts the metal salts can be deposited on the carrier in one or more steps. Between the impregnation steps the material is dried and optionally, calcined. Impregnation in more than one step may be necessary for the preparation of catalysts with a high metal load. The metal salts may be deposited on the carrier separately or together from one solution. An attractive method of depositing the metal salts on the carrier is the dry impregnation technique, according to which a carrier is contacted with an aqueous solution of the salts concerned, which aqueous solution has a volume which is substantially the same as the pore volume of the carrier. Sorption of the aqueous solution by the carrier can be facilitated by heating the mixture. If this method is chosen for the preparation of catalysts with a high metal load, it may be necessary to carry out more than one dry impregnation and to dry the material between the opposite impregnation steps and, optionally, to calcine it. The calcination is preferably carried out at a temperature of 350–700°C. The catalyst preparation is finished with a reduction. This reduction is carried out at a temperature of 350–700°C with a hydrogenous gas, e.g. a mixture of hydrogen and nitrogen. The reduction is preferably carried out at a temperature of 350–500°C.

The catalysts prepared according to the invention are pre-eminently suitable for the preparation of hydrocarbons from an H_2/CO mixture with an H_2/CO molar ratio smaller than 1.0. Such H_2/CO mixtures can very suitably be prepared by steam gasification of a carbon-containing material. Examples of such materials are brown coal, anthracite, coke, crude mineral oil and fractions thereof and oils produced from tar sand and bituminous shale. The steam gasification is preferably carried out at a temperature of from 900 to 1500°C and a pressure of from 10 to 50 bar.

The preparation of hydrocarbons from an H_2/CO mixture with an H_2/CO molar ratio smaller than 1.0, using a Fischer-Tropsch catalyst according to the invention is preferably carried out at a temperature of from 200 to 350°C and in particular of from 250 to 350°C, a pressure of from 10 to 70 bar and in particular of from 20 to 50 bar and a space velocity of from 500 to 5000 and in particular of from 500 to 2500 Nl gas/l catalyst/h. The hydrocarbon preparation according to the invention can very suitably be carried out by conducting the feed in upward or downward direction through a vertically mounted reactor in which a fixed or a moving bed of the catalyst concerned is present.

The invention will now be explained with reference to the following example.

Example

Six catalysts (A–C and 1–3) were prepared and tested for the hydrocarbon synthesis according to Fischer-Tropsch. The preparation of the catalysts was effected by impregnating a silica or alumina carrier with aqueous solutions containing one or more of the following salts: iron nitrate, chromium nitrate and potassium nitrate. In all impregnations the dry impregnation technique was used. The reduction of the catalysts was carried out at atmospheric pressure with an H_2/N_2 mixture in a volume ratio of 3:1 at a superficial gas rate of 1.6 m/s. Further details about the preparation of the individual catalysts are given below.

Catalyst A

This catalyst was prepared by impregnating a silica carrier first with a solution of KNO_3, followed by drying at 120°C and calcining for two hours at 400°C, and then impregnating with a solution of $Fe(NO_3)_3$ and $Cr(NO_3)_3$, followed by drying at 120°C, calcining for two hours at 500°C and reduction at 280°C.

Catalyst 1

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst A, the difference being that the reduction was carried out at 400°C.

Catalyst B

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst A, the differences being that alumina was used as the carrier and that the reduction was carried out at 400°C.

Catalyst C

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst A, the differences being that in the second impregnation a solution was used which did not contain chromium and that the reduction was carried out at 400°C.

Catalyst 2

This catalyst was prepared by impregnating a silica carrier with a solution of $Fe(NO_3)_3$, $Cr(NO_3)_3$ and KNO_3, followed by drying at 120°C, calcining for two hours at 500°C and reduction at 400°C.

Catalyst 3

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst A, the differences being that in the first impregnation a solution with a higher concentration of K was used, that in the second impregnation a solution with higher concentrations of Fe and Cr was used, and that the reduction was carried out at 400°C. The composition of the catalysts is shown in table A.

Table A

Cat. No.	Composition expressed in pbw, Fe	Cr	K	SiO_2	Al_2O_3
A	25	1	2	100	—
B	25	1	2	—	100
C	25	—	2	100	—
1	25	1	2	100	—
2	25	1	2	100	—
3	35	1.5	2.75	100	—

The testing of the catalysts A–C and 1–3 for the hydrocarbon synthesis according to Fischer-Tropsch with synthesis gas with an H_2/CO molar ratio of 0.5 as the starting material was performed in a 250-ml reactor which contained a catalyst bed with a volume of 50 ml. The experiments were carried out at a temperature of 280°C, a pressure of 30 bar and a space velocity of 10000 $Nl.1^{-1}.h^{-1}$.

The results of these experiments are shown in Table B.

Table B

Exp. No.	Cat. No.	Conversion of the synthesis gas, % after 25 h	after 500 h
1	A	79	
2	B	72	
3	C	69	
4	1	91	90
5	2	90	89
6	3	91	89

After run hour 500 experiment 4 was continued for another 500 hours with catalyst 1. By gradually increasing the reaction temperature the conversion of the synthesis gas was maintained at 90%. At run hour 1000 the temperature was 290°C.

Of the experiments mentioned in Table B only experiments 4–6 were carried out with catalysts prepared according to the invention. In these experiments the catalysts showed both a very high activity and a very high stability. The experiments 1–3 were carried out with catalysts which outside the scope of the invention. They have been included in the patent application for comparison.

Catalyst A had been reduced at too low a temperature. Catalyst B did not contain silica. Catalyst C did not contain chromium. The results of experiments 1–3 show that these catalysts had a low activity.

CLAIMS

1. A process for the preparation of Fischer-Tropsch catalysts, characterized in that catalysts containing 10–40 pbw iron and 0.25–10 pbw chromium per 100 pbw silica are prepared by impregnating a silica carrier with one or more aqueous solutions of salts of iron and of chromium, followed by drying the composite, calcining it and reducing it at a temperature of 350–750°C.

2. A process according to claim 1, characterized in that a catalyst is prepared containing 20–35 pbw iron per 100 pbw silica, and 0.5–5 pbw chromium per 100 pbw silica.

3. A process according to claim 1 or 2, characterized in that a catalyst is prepared containing 1–5 pbw potassium per 100 pbw silica.

4. A process according to any one of claims 1–3, characterized in that the calcination is carried out at a temperature of 350–700°C.

5. A process for the preparation of catalysts, substantially as described hereinbefore, and in particular with reference to the preparation of the catalysts 1–3 in the example.

6. Catalysts prepared according to a process as described in any one of claims 1–5.

7. A process for the preparation of hydrocarbons from an H_2/CO mixture, characterized in that an H_2/CO mixture with an H_2/CO molar ratio smaller than 1.0 is contacted at elevated temperature and pressure with a catalyst according to claim 6.

8. A process according to claim 7, characterized in that the preparation of the hydrocarbons

from the H_2/CO mixture is carried out at a temperature of from 200–350°C, a pressure of from 10–70 bar and a space velocity of from 500 to 5000 Nl gas/l catalyst/h.

9. A process for the preparation of hydrocarbons from an H_2/CO mixture with an H_2/CO molar ratio smaller than 1.0, substantially as described hereinbefore and in particular with reference to the experiments 4–6 in the example.

10. Hydrocarbons prepared according to a process as described in any one of claims 7–9.

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