(12) UK Patent Application (19) GB (11) 2 053 713 A

(21) Application No **8022790**
(22) Date of filing **11 Jul 1980**
(30) Priority data
(31) **7905480**
(32) **13 Jul 1979**
(33) **Netherlands (NL)**
(43) Application published
11 Feb 1981
(51) **INT CL^3**
B01J 23/78 //
C97C 1/04
(52) Domestic classification
B1E 1162 1180 1208 1298
1315 1323 1331 1342 1461
1513 1514 1701 1712 1714
1719 1720 1724 1738 AD
(56) Documents cited
GB 1548468
GB 833976
(58) Field of search
B1E

(71) Applicants
Shell Internationale
Research Maatschappij
B.V.,
Carel Van Bylandtlaan 30,
The Hague,
The Netherlands.
(72) Inventors
Michael Adriaan
Maria Boersma
(74) Agents
R.C. Rogers

(54) A process for the preparation of fischer-tropsch catalysts

(57) A process for the preparation of Fischer-Tropsch catalysts, containing 30-75 pbw iron and 5-40 pbw magnesium per 100 pbw alumina by impregnating an alumina carrier with one or more aqueous solutions of salts of iron and of magnesium, followed by drying the composite, calcining it at a temperature of from 700 to 1200°C and reducing it.

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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 often 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 for 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 treatment 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 30-75 pbw iron and 5-40 pbw magnesium per 100 pbw alumina and have been calcined at a temperature of from 700 to 1200°C. These are novel catalysts.

The present patent application therefore relates to a process for the preparation of novel catalysts, in which catalysts containing 30-75 pbw iron and 5-40 pbw magnesium per 100 pbw alumina are prepared by impregnating an alumina carrier with one or more aqueous solutions of salts of iron and of magnesium, followed by drying the composite, calcining it at a temperature of from 700 to 1200°C and reducing it. 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 40-60 pbw iron and 7.5-30 pbw magnesium per 100 pbw alumina. Further, preference is given to catalysts which contain, in addition to iron and magnesium, a reduction promotor and a selectivity promoter. A suitable reduction promoter is copper. suitable selectivity promoters are the alkali metals, in particular potassium. In addition to iron and magnesium it is preferred in the catalyst preparation according to the invention to incorporate 0.5-5 pbw copper and 1-5 pbw potassium per 100 pbw alumina 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 separate impregnation steps and, optionally, to calcine it. The requirement of using a calcination temperature of

700-1200°C only applies to the calcination immediately preceding the reduction. If more calcinations are carried out in the catalyst preparation, e.g. between several impregnation steps, these calcinations may, if desired, be carried out at a lower temperature. The calcination immediately preceding the reduction is preferably carried out at a temperature of 750-850°C. The catalyst preparation is finished with a reduction. This reduction is carried out at elevated temperature with a hydrogenous gas, e.g. a mixture of hydrogen and nitrogen. The reduction is preferably carried out at a temperature of 250-350°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 contacting 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

Eleven catalysts (A-H and 1-3) were prepared and tested for the hydrocarbon synthesis according to Fischer-Tropsch. The preparation of the catalysts was effected by impregnating an alumina or silica carrier with aqueous solutions containing one or more of the following salts: iron nitrate, magnesium nitrate, copper 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 an alumina carrier first with a solution of $Mg(NO_3)_2$, followed by drying at 120°C and calcining for two hours at 400°C, and then impregnating with a solution of $Fe(NO_3)_3$, $Cu(NO_3)_2$ and KNO_3, followed by drying at 120°C, calcining for two hours at 400°C and reduction at 280°C.

Catalyst B

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst A, the difference being that after the second calcination at 400°C another calcination was carried out at 800°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 with higher concentrations of Fe, Cu and K and that the second calcination was carried out for 16 hours at 650°C.

Catalyst D

This catalyst was prepared by impregnating an alumina carrier with a solution of $Mg(NO_3)_2$, $Fe(NO_3)_3$, $Cu(NO_3)_2$ and KNO_3, followed by drying at 120°C, calcining for two hours at 400°C and reduction at 280°C.

Catalyst E

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst D, the differences being that a solution with higher concentrations of Fe, Cu and K and not containing Mg was used, and that the calcination was carried out for fourteen hours at 800°C.

Catalyst F

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst D, the differences being that silica was used as the carrier, that a solution was used with higher concentrations of Fe, Cu and K, and that the calcination was carried out for fourteen hours at 800°C.

Catalyst G

The preparation of this catalyst was performed in substantially the same way as the preparation of catalyst D, the differences being that a solution with higher concentrations of Mg, Fe, Cu and K was used, and that the calcination was carried out for fourteen hours at 800°C.

Catalyst H

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 1

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 with higher concentrations of Fe, Cu and K was used, that the second calcination was carried out for sixteen hours at 300°C, and that the reduction was carried out at 325°C.

Catalyst 2

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 Mg was used, that in the second impregnation a solution with higher concentrations of Fe, Cu and K was used, that the second calcination was carried out for sixteen hours at 800°C, and that the reduction was carried out at 300°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 calcination after the first impregnation step was omitted, that in the second impregnation a solution with higher concentrations of Fe, Cu and K was used, that the calcination after the second impregnation was carried out for sixteen hours at 800°C, and that the reduction was carried out at 325°C.

The composition of the catalysts is shown in Table A.

TABLE A

Cat. No.		Composition expressed in pbw				
	Fe	Mg	Cu	K	Al_2O_3	SiO_2
A	25	20	1.25	2	100	---
B	25	20	1.25	2	100	---
C	50	20	2.5	4	100	---
D	25	20	1.25	2	100	---
E	50	--	2.5	4	100	---
F	50	20	2.5	4	---	100
G	50	50	2.5	4	100	---
H	25	20	1.25	2	100	---
1	50	20	2.5	4	100	---
2	50	10	2.5	4	100	---
3	60	20	3	4	100	---

The testing of the catalysts A-H and 2 and 3 for the hydrocarbon synthesis according to Fischer-Tropsch from 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 1000 $Nl.l^{-1}.h^{-1}$.

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	75	-
2	B	28	-
3	C	87	37
4	D	64	-
5	E	71	-
6	F	74	-
7	G	69	-
8	H	76	-
9	2	91	89
10	3	92	89

Catalyst 1 was tested for 3150 h for the hydrocarbon synthesis according to Fischer-Tropsch from a synthesis gas with an H_2/CO molar ratio of 0.6 as the starting material. The experiment (exp. 11) was carried out in subsktantially the same way as the experiments 1-10, the difference being that the experiment was continued over a longer period, during which temperature and space velocity were varied. The results of experiment 11 and the reaction conditions used are shown in Table C.

TABLE C

Conditions during the experiment			Result	
Period in run hours	Temp., °C	Space velocity $Nl.l^{-1}.h^{-1}$	At run hour	Conversion of the synthesis gas, %
0- 25	280	1000	25	93
25- 500	280	1000	500	90
500- 900	280	1000	900	85
900-1350	270	500	1350	80
1350-1850	280	500	1850	80
1850-2300	295	500	2300	85
2300-2800	305	500	2800	81
2800-3150	305	350	3150	80

Of the experiments mentioned in Tables B and C only experiments 9-11 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 1-8 were carried out with catalysts which are outside the scope of the invention. They have been included in the patent application for comparison.

The iron content of the catalysts A, D and H was too low and the temperature at which these catalysts had been calcined was too low. The results of experiments 1, 4 and 8 show that these catalysts had a low activity.

The catalysts B, E, F and G contained too little iron, no magnesium, no alumina and too much magnesium respectively. The results of experiments 2, 5, 6 and 7 show that these catalysts had a low activity.

The temperature at which catalyst C had been calcined was too low. The results of experiment 3 show that this catalyst indeed had a high activity, but a very low stability.

CLAIMS

1. A process for the preparation of Fischer-Tropsch catalysts, characterized in that catalysts containing 30-75 pbw iron and 5-40 pbw magnesium per 100 pbw alumina are prepared by impregnating an alumina carrier with one or more aqueous solutions of salts of iron and of magnesium, followed by drying the composite, calcining it at a temperature of from 700 to 1200°C and reducing it.

2. A process according to claim 1, characterizedin that a catalyst is prepared containing 40-60 pbw iron per 100 pbw alumina and 7.5-30 pbw magnesium per 100 pbw alumina.

3. A process according to claim 1 or 2, characterized in that a catalyst is prepared containing 0.5-5 pbw copper per 100 pbw alumina.

4. A process according to any one of claims 1-3, characterized in that a catalyst is prepared containing 1-5 pbw potassium per 100 pbw alumina.

5. A process for the preparation of Fischer-Tropsch 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 to 350°C, a pressure of from 10 to 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 9-11 in the example.

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

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.