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(19) THE PATENT OFFICE LONDON

(72) Inventors HENRICUS MICHAEL JOSEPH BIJWAARD and
SWAN TIONG SIE

(54) PROCESS FOR THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen.

The preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen by contacting this mixture with a catalyst at elevated temperature and pressure is known in the literature as hydrocarbon synthesis according to Fischer-Tropsch. Catalysts frequently employed for this purpose comprise one or more metals of the iron group together with one or more promoters to increase the activity and/or selectivity and sometimes a carrier material such as kieselguhr. The catalysts employed in practice for hydrocarbon synthesis according to Fischer-Tropsch are as a rule prepared by precipitation or by melting. Briefly, the preparation of the catalysts by precipitation is effected by making basic an aqueous solution of a salt of a metal of the iron group to which a salt of a promoter and a carrier material may be added, if required, as a result of which the catalyst is formed as a precipitate. To this precipitate a promoter and a carrier material may be added. Examples of suitable catalysts for the hydrocarbon synthesis prepared according to the precipitation route, are $Fe/Cu/Na/SiO_2$ catalysts comprising 4.5 parts by weight of copper, 4 parts by weight of sodium and 20 parts by weight of silicon oxide per 100 parts by weight of iron, as well as $Co/ThO_2/MgO$/kieselguhr catalysts comprising 5 parts by weight of thorium oxide, 8 parts by weight of magnesium oxide and 100—200 parts by weight of kieselguhr per 100 parts by weight of cobalt. The preparation of the catalysts by melting in the case of, for example, iron catalysts is effected by fusing iron oxide with one or more promoter oxides. Examples of suitable catalysts for hydrocarbon synthesis prepared according to the melting route, are $Fe/Al_2O_3/K_2O/CaO$ catalysts comprising 5 parts by weight of aluminium oxide, 1 part by weight of potassium oxide and 3 parts by weight of calcium oxide per 100 parts by weight of iron.

Both the precipitation route and the melting route are rather unattractive methods for the preparation of the present catalysts, because their reproducibility is low. Besides, the precipitation route is very time-consuming, while the melting route requires much energy.

With respect to the performance of the above-mentioned catalysts when used for hydrocarbon synthesis according to Fischer-Tropsch the following remarks can be made. The performance of catalysts for hydrocarbon synthesis according to Fischer-Tropsch is assessed in the light of their activity and selectivity which have been defined as follows. The activity of the catalyst is the number of grammes of hydrocarbons produced per litre of catalyst per hour. The selectivity of the catalyst is the weight of C_{3+} hydrocarbons produced, calculated as a percentage of the total quantity of hydrocarbons produced. For a catalyst for hydrocarbon synthesis according to Fischer-Tropsch both a high activity and a high selectivity are desirable. Of these two parameters the selectivity is considered the more important one. Apart from the above-mentioned disadvantages of the catalysts prepared by precipitation or melting, their catalytic performance is not very satisfactory either. A characteristic of the catalysts prepared by melting is that in the temperature range of about 300—350°C, considered optimal for these catalysts, they exhibit a high activity, but only a moderate selectivity. Attempts to increase the selectivity of the catalysts prepared by melting to the level of the catalysts obtained by precipitation, by applying lower temperatures, as well as attempts to increase the activity of the catalysts prepared by precipitation to the level of the catalysts obtained by melting, by applying higher temperatures, have remained unsuccessful. It is true that these measures can bring about an improvement of the property in question, but this is accompanied by such a deterioration of the other major property of the catalyst that this other property has fallen below the minimum allowable level for this property long before the first property has reached the desired high level.

In view of the increasing interest in hydrocarbon synthesis according to Fischer-Tropsch there is an urgent need of catalysts for this purpose which possess an activity comparable with that of catalysts obtained by melting as well as a selectivity comparable with that of catalysts prepared by precipitation. Further it is desirable for preparation of these catalysts to be effected in a way that does not have the drawbacks of the above-mentioned precipitation or melting route.

An extensive investigation has been carried out by Applicant into the use for hydrocarbon synthesis according to Fischer-Tropsch of catalysts comprising 10—75 parts by weight of one or more metals of the iron group per 100 parts by weight of carrier, together with one or more promoters in a quantity of 1—50% of the metals of the iron group present on the catalyst and which catalysts have been prepared by impregnation of a porous carrier with one or more aqueous solutions of salts of the metals in question of the iron group and of the promoters in question followed by drying and calcining of the composition. It has been found that the selectivity of these catalysts, which can be prepared with good reproducibility in a simple way, is highly dependent on the quotient of the specific average pore diameter (p) and the specific average particle diameter (d) of the catalysts. For further information concerning p and d as well as the way in which these are determined, see British patent specification No. 1,408,759, in which these catalyst data were discussed in detail. The investigation concerning the above-mentioned catalysts prepared by impregnation has revealed that these catalysts with a p of at most 10,000 nm and a d of at most 5 mm, display both an excellent activity and an excellent selectivity when used for hydrocarbon synthesis according to Fischer-Tropsch, if the quotient p/d is larger than 2.0 (p in nm and d in mm).

The present patent application therefore relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, using a catalyst prepared by impregnation having the above-mentioned properties.

Comparison of the selectivity of the present catalysts prepared by impregnation with that of the afore-mentioned catalysts prepared by melting, reveals that the latter generally display such a low selectivity that for a hydrocarbon synthesis in which the selectivity is of major importance—as in the present patent application—these catalysts are of no interest and need not be further discussed. Comparison of the activity of the present catalysts prepared by impregnation with that of the afore-mentioned catalysts prepared by precipitation, reveals that the former show a considerably larger increase in activity per degree of rise of the reaction temperature and moreover that the maximum temperature at which these catalysts can still be employed bearing in mind the selectivity is considerably higher. The possibility of employing the present catalysts prepared by impregnation at a higher temperature than those prepared by precipitation, offers, in addition to the gain in activity, the advantage that the waste heat of the process can be utilised more effectively, for example for the production of steam with a higher pressure and higher temperature than is possible with the catalysts prepared by precipitation.

In the process according to the invention the starting material has to be a mixture of hydrogen and carbon monoxide. Such a mixture can very suitably be prepared by the partial combustion of a material containing carbon and hydrogen. Examples of such materials are lignite, anthracite, coke, crude petroleum and fractions thereof, as well as oils produced from tar sand and from bituminous shale. During the partial combustion the feed, in a finely dispersed form, is converted with the aid of oxygen or air enriched with oxygen, if desired, into a gas mixture comprising inter alia, hydrogen, carbon monoxide, carbon dioxide, nitrogen and water. In the partial combustion steam is preferably employed as temperature moderator. The partial combustion is preferably carried out at a temperature between 900 and 1500°C and a pressure between 10 and 50 bar. In order to be able to remove impurities such as ash, carbonaceous material and hydrogen sulphide from the gas obtained in the partial combustion, which gas has a temperature of more than 1000°C, this gas must first be cooled down to a temperature between 100 and 200°C. This cooling may be very suitably effected in a boiler in which steam is generated by means of the waste heat. The cooled gas may be freed from practically all solid matter by washing with water. After this wash, in which the temperature of the gas has fallen to 20—80°C, the gas is further purified by removal of hydrogen sulphide and carbon dioxide. This may be very suitably effected by means of the ADIP process or the SULFINOL process.

In the process according to the invention the starting material is a mixture of hydrogen and carbon monoxide having preferably a molar ratio between 0.5 and 3. If the process is carried out using an iron catalyst, special preference is given to the use of a mixture of hydrogen and carbon monoxide with a molar ratio between 0.5 and 1.5, and in the case of a cobalt or nickel catalyst to the use of a mixture of hydrogen and carbon monoxide with a molar ratio between 1.2 and 2.5. If the available mixture of hydrogen and carbon monoxide does not have the required molar ratio, this may be adjusted by adding hydrogen or carbon monoxide. An increase of the hydrogen content of the mixture with respect to the carbon monoxide content may also be very suitably effected by submitting the mixture to the well-known water gas shift reaction.

The process according to the invention is preferably carried out at a temperature of 200—350°C, a pressure of 10—70 bar and a space velocity of 500—5000 and in particular of 500—2500 Nl gas/litre of catalyst/hour. If the process is carried out using an iron catalyst special preference is given to a reaction temperature of 250—325°C and a reaction pressure of 20—50 bar and, when a cobalt or nickel catalyst is employed, to a reaction temperature of 220—300°C and a reaction pressure of 10—35 bar.

Catalysts employed in the process according to the invention comprise 10—75 parts by weight of one or more metals of the iron group, per 100 parts by weight of carrier, together with one or more promoters in a quantity of 1—50% of the quantity of metals of the iron group present on the catalyst. With respect to metals of the iron group, preference is given to the use of catalysts comprising 15—50 and in particular 20—40 parts by weight of one or more of these metals per 100 parts by weight of carrier. With respect to the promoters, preference is given to the use of catalysts comprising one or more promoters in a quantity of 5—40 and in particular 10—20% of the metals of the iron group present on the catalyst.

As promoters for the catalysts according to the invention a large number of elements is eligible. As examples the following may be mentioned: alkali metals, alkaline-earth metals, metals of Group VIB, Ti, Al, Si, As, V, Mn, Cu, Ag, Zn, Cd, Bi, Pb, Sn, Ce, Th and U. Very suitable combinations of promoters for iron catalysts according to the invention consist of an alkali metal such as K, a readily reducible metal such as Cu or Ag and, if desired, a metal that can only be reduced with difficulty such as Al or Zn. An example of a very suitable iron catalyst according to the invention is a catalyst comprising iron, potassium and copper on silica as the carrier. If in the process according to the invention use is made of an iron catalyst comprising K as selectivity promoter, preference is given to the use of a catalyst comprising not more than 0.15 g of K per g of Fe, because it has been found that, when higher K concentrations are used, the selectivity does not increase any farther, whereas, owing to coke deposition on the catalyst the stability decreases sharply. Very suitable promoter combinations for cobalt catalysts according to the invention consist of an alkaline-earth metal and Th, U or Ce. An example of a very suitable cobalt catalyst according to the invention is a catalyst comprising cobalt, magnesium and thorium on silica as the carrier. Other very suitable cobalt catalysts according to the invention are catalysts comprising Co/Cr, Co/Zr, Co/Zn or Co/Mg on silica as the carrier. Very suitable promoters for nickel catalysts according to the invention are Al, Mn, Th, W and U.

In the process according to the invention catalysts are employed which have been prepared by impregnation of a porous carrier with one or more aqueous solutions of salts of metals of the iron group and salts of promoters followed by drying and calcining of the composition. The carrier used to prepare the catalysts according to the invention may be amorphous or crystalline. Examples of suitable carriers are silica, alumina, zirconia, thoria, magnesia, boron oxide as well as combinations thereof such as silica-alumina and silica-magnesia. Other suitable carriers are zeolites such as mordenite, faujasite and zeolite-omega. Zinc oxide has also proved to be a suitable carrier for the present catalysts. In the preparation of the catalysts the salts can be incorporated into the carrier in one or more steps. The material is dried between the individual impregnation steps. Application of a multi-step impregnation technique may be necessary for the preparation of catalysts with a high metal content. The salts of the metals of the iron group and the salts of the promoters may be incorporated into the carrier separately or together starting from one solution. An attractive manner of incorporating the metals of the iron group and the promoters into the carrier is the dry impregnation technique, according to which the carrier is contacted with an aqueous solution of the salts concerned, which aqueous solution has a volume substantially equal to the pore volume of the carrier. Absorption of the aqueous solution may be facilitated by heating the mixture gently. If this method of preparation 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 dry the material between the individual impregnation steps.

The catalyst employed in the process according to the invention should have a specific average pore diameter (p) of at most 10,000 nm and a specific average particle diameter (d) of at most 5 mm. As regards p preference is given to catalysts with a p of at most 1000 nm and in particular with a p of at most 500 nm. The choice of d is determined by the way in which the process is carried out. A very suitable embodiment of the process according to the invention is that in which the feed is passed upwards or downwards through a vertically disposed reactor containing a fixed or moving bed of the catalyst particles concerned. The hydrocarbon synthesis may, for example, be effected by passing the feed upwards through a vertically disposed catalyst bed, the gas being made to flow at such a rate as to cause expansion of the catalyst bed. If desired, the hydrocarbon synthesis may also be effected using a suspension of the catalyst in hydrocarbon oil. According as the hydrocarbon synthesis is effected using a fixed catalyst bed, an expanded catalyst bed or a catalyst suspension, preference is given to the use of catalyst particles with a d between 1 and 5 mm, 0.5 and 2.5 mm and 20 and 150 μ, respectively. When the hydrocarbon synthesis is carried out using a fixed catalyst bed, waxy hydrocarbons will be deposited on the catalyst, as a result of which the activity decreases. To get round this difficulty the catalyst may be washed periodically, for example for some hours per 1000 run hours, with a solvent for the above-mentioned heavy hydrocarbons. A suitable solvent for this purpose is for example a mixture of methyl ethyl ketone and toluene. The above-mentioned deactivation of the catalyst is preferably counteracted by continuously washing the catalyst with a fraction of the product prepared in the hydrocarbon synthesis. For this purpose preference is given to a fraction with an initial boiling point above 200°C and a final boiling point below 550°C. An additional advantage of the above-mentioned continuous wash of the catalyst is that temperature control during the highly exothermic hydrocarbon synthesis reaction is simplified.

The reaction product which in the process according to the invention leaves the reactor contains in addition to hydrocarbons and oxygen-containing hydrocarbons whose molecular weight extends over a wide range, inter alia water, nitrogen, carbon dioxide and unconverted carbon monoxide and hydrogen. If the process according to the invention is carried out in what is known as "once-through" operation, the C_{3+} fraction is separated from the reaction product as end product. If the process according to the invention is carried out in what is known as "recycle" operation, the C_{3+} fraction is likewise separated from the reaction product as end product, but now the rest of the reaction product after reduction of the carbon dioxide content, if necessary, is recycled to the reactor, applying a bleed stream to avoid the build-up of nitrogen, inter alia.

The invention is now elucidated by means of the following example.

EXAMPLE

23 catalyst (catalysts A—D and 1—19) were tested for the hydrocarbon synthesis according to Fischer-Tropsch. The preparation of the catalysts was carried out as follows.

Catalyst A

A boiling solution of 2886 g of $Fe(NO_3)_3 . 9\,aq$ and 76 g of $Cu(NO_3)_2 . 3\,aq$ in 10 l of water was added with stirring to a boiling solution of 1000 g of anhydrous Na_2CO_3 in 10.5 l of water. To the mixture thus obtained were added in succession 130 g of anhydrous Na_2CO_3 and 14.4 g of clay. After filtration of the mixture the filter cake was washed with hot water until the filtrate was free of sodium and then washed with 10 l of an aqueous solution which contained 10 g of NH_4NO_3 per litre. The filter cake was kneaded with 240 g of soda water glass, dried for 24 hours at 110°C and ground. The catalyst A thus prepared by precipitation comprised 3.6 parts by weight of Cu, 4.1 parts by weight of Na and 23 parts by weight of SiO_2 per 100 parts by weight of Fe.

Catalyst B

In a similar way as described hereinbefore for catalyst A, a catalyst B was prepared by precipitation which comprised 4.43 parts by weight of Cu, 3.95 parts by weight of Na and 20.5 parts by weight of SiO_2 per 100 parts by weight of Fe.

Catalyst C

An aqueous solution of 225 g of $Fe(NO_3)_3 . 9$ aq, an aqueous solution of 5.9 g of $Cu(NO_3)_2 . 3$ aq and an aqueous solution of 3.2 g of KNO_3, were combined and the volume of the combined solution was made up with water to 150 ml. The solution was incorporated into 125 g of SiO_2 with a total pore volume of 150 ml. After some time the composition was dried at 120°C, calcined for 1 hour at 500°C, ground and sieved. The catalyst C thus prepared by impregnation comprised 25 parts by weight of Fe, 1.25 parts by weight of Cu and 1 part by weight of K per 100 parts by weight of SiO_2.

Catalyst D and 1—19

In a similar way as described hereinbefore for catalyst C, catalysts D and 1—19 were prepared by impregnation. In the preparation of the catalysts containing Th, Mg, Co, Al, Cr and/or Zn as promoters, use was made of aqueous solutions of nitrates of the elements concerned. In the preparation of the catalyst which container Zr as promoter use was made of an aqueous solution of zirconyl chloride.

The compositions of the catalysts as well as their specific average pore diameters and specific average particle diameters are given in Table A. The values given in the table for p and d were determined by means of nitrogen adsorption/desorption, mercury penetration and sieve analysis as described in British patent specification No. 1,408,759.

TABLE A

Catalyst No.	Composition expressed in parts by weight	p, nm	d, mm
C	25 Fe/1.25 Cu/1 K/100 SiO_2	2.4	2.2
D	25 Co/1.04 Th/1.18 Mg/100 SiO_2	2.4	2.2
1	25 Fe/1.25 Cu/1 K/100 SiO_2	20	2.2
2	ditto	220	2.2
3	ditto	220	0.6
4	ditto	70	2.2
5	ditto	320	2.2
6	25 Fe/1.25 Cu/2 K/100 SiO_2	220	2.2
7	25 Fe/1.25 Cu/5 K/100 SiO_2	220	2.2
8	25 Fe/0.5 Al/1 K/100 SiO_2	70	0.22
9	25 Fe/1.25 Cu/2 K/100 ZnO	20	0.22
10	25 Fe/1.25 Cu/2 K/100 (MgO—Al_2O_3)	14	0.22
11	25 Co/1.04 Th/1.18 Mg/100 SiO_2	70	2.2
12	25 Co/1.0 Cr/100 SiO_2	35	0.22
13	25 Co/1.8 Zr/100 SiO_2	35	0.22
14	25 Co/1.3 Zn/100 SiO_2	35	0.22
15	25 Co/0.5 Mg/100 SiO_2	35	0.22
16	25 Co/1.04 Th/100 SiO_2	35	0.22
17	25 Fe/1.16 Co/1 K/100 SiO_2	400	2.2
18	25 Co/1.04 Th/1.18 Mg/100 SiO_2	35	0.22
19	25 Co/1.04 Th/1.18 Mg/100 Al_2O_3	12	0.22

Catalysts A—D and 1—19 were tested for hydrocarbon synthesis according to Fischer-Tropsch in a 250-ml reactor containing a fixed catalyst bed of the catalyst in question, with a volume varying between 25 and 75 ml. Before being used for the hydrocarbon synthesis all the catalysts were first reduced for 2 hours with a mixture of hydrogen and nitrogen (molar ratio (3:1), at atmospheric pressure, 280°C and a superficial gas velocity of 1.6 m/sec.

For the preparation of hydrocarbons a mixture of carbon monoxide and hydrogen was passed over the catalysts at elevated temperature and pressure. The reaction product was worked up by cooling it down at the reaction pressure in two steps first to 150°C which caused separation of a heavy liquid phase and then to 15°C which caused separation of a light liquid phase and a gas phase. The composition of the reaction product was determined by means of TBP-GLC analysis.

The reaction conditions used in the experiments as well as the results obtained are given in Table B.

With the exception of the experiments mentioned under 19 and 19A all other experiments were carried out in once-through operation. The activities and selectivities listed relate to the situation at run hour 500, with the exception of those mentioned under 18, 18A, 18B, 19 and 19A.

The results mentioned under 19 and 19A were obtained in an experiment carried out in recycle operation. In this experiment the catalyst was continuously washed at a space velocity of 0.6 $l.l.^{-1}.hour^{-1}$ with part of the heavy liquid phase which had separated from it when cooling the reaction product to 150°C. The results mentioned under 19 and 19A relate to the situation at run hours 150 and 700, respectively. The results mentioned under 18, 18A and 18B were obtained in an experiment in which during the experiment the catalyst was washed for some hours per 1000 run hours with a 1:1 (v/v) mixture of methyl ethyl ketone and toluene. The results mentioned under 18, 18A and 18B relate to the situation at run hours 400, 800 and 900, respectively. Washing of the catalyst took place between run hours 800 and 900.

TABLE B

Experiment No.	Catalyst No.	Temperature, °C	Pressure, bar	Space velocity, l gas/l cat/ hour	H_2/CO ratio v/v	Activity, g C_{1+}/ l cat/hour	Selectivity, %w C_{3+} on C_{1+}
1	A	220	30	1000	2	65	90
2	A	280	30	1000	2	130	66
3	B	220	30	1000	2	105	83
4	B	280	30	1000	2	120	72
5	C	250	30	1000	1	75	69
6	C	280	30	1000	0.5	105	71
7	D	250	30	1000	1	100	75
8	D	280	30	1000	0.5	75	72
9	1	250	30	1000	1	75	78
10	1	220	30	1000	2	35	84
11	2	250	30	1000	1	80	82
12	2	250	30	2000	1	115	86
13	2	250	50	2000	1	160	87
14	2	250	90	2000	1	145	85
15	3	250	30	1000	1	105	86
16	4	250	30	1000	1	85	81
17	5	280	30	1000	1	100	73
18	5	250	30	1000	1	90	86
18A	5	250	30	1000	1	40	82
18B	5	250	30	1000	1	90	86
19	5	250	30	1000	1	80	86
19A	5	250	30	1000	1	65	86
20	6	220	30	1000	2	30	86
21	6	250	30	1000	1	80	87
22	6	280	30	1000	1	115	82
23	7	250	30	1000	1	60	88
24	7	280	30	1000	1	95	84
25	7	280	30	1000	0.5	80	89
26	8	250	30	1000	1	70	79
27	8	280	30	1000	0.5	115	85
28	9	220	30	1000	2	45	87
29	9	250	30	1000	1	140	88
30	9	280	30	1000	0.5	185	90
31	10	220	30	1000	2	45	83
32	11	220	30	1000	2	120	89
33	11	250	30	1000	1	140	91
34	11	280	30	1000	1	140	70
35	12	250	30	2000	1	295	96

TABLE B (cont.)

Experiment No.	Catalyst No.	Temperature, °C	Pressure, bar	Space velocity; 1 gas/1 cat/hour	H_2/CO ratio v/v	Activity, g C_{1+}/1 cat/hour	Selectivity, %w C_{3+} on C_{1+}
36	13	250	30	2000	1	280	97
37	14	250	30	2000	1	190	76
38	15	250	30	2000	1	230	89
39	16	250	30	2000	1	285	92
40	17	280	30	1000	1	110	87
41	18	250	30	2000	1	230	87
42	19	250	30	2000	1	270	89

Of the 42 experiments given in Table B only experiments 9—42 are experiments according to the invention. In these experiments catalysts were used which had been prepared by impregnation and which satisfied the conditions: $p<10,000$ nm, $d<5$ mm and $p/d>2$. Experiments 1—8 are outside the scope of the invention and have been included for comparison. Experiments 1—4 were carried out using catalysts prepared by precipitation. Experiments 5—8 were carried out using catalysts which, although prepared by impregnation, did not satisfy the condition $p/d>2$.

The experimental results presented in Table B give rise to the following remarks:

1. Comparison of exp. 1 with exp. 2 and comparison of exp. 3 with exp. 4 reveals that with the catalysts prepared by precipitation, an increase in activity due to the use of a higher temperature, is accompanied by a sharp decrease in selectivity. The activity and selectivity observed in exp. 1 are substantially in line with what may be expected of a good catalyst. The activity and selectivity found are comparable with those attained by Sasol in commercial application of the process of Lurgi Chemie.
2. Comparison of exp. 5 with exp. 9, 11, 16 and 18 and comparison of exp. 7 with exp. 33 reveals that the catalysts prepared by impregnation satisfying the condition $p/d>2$ have a higher activity and selectivity than catalysts prepared by impregnation which do not satisfy this condition.
3. It is generally assumed that the maximum temperature and pressure at which Co-catalysts prepared by precipitation may be used are about 215°C and 15 bar, respectively. The use of higher temperatures and/or pressures leads to very rapid deactivation of the catalyst. The experimental work has proved that the Co-catalysts according to the invention may be used at considerably higher temperatures and pressures.
4. Comparison of exp. 12, 13 and 14 with each other reveals that the activity of the catalysts according to the invention at first increases with increasing pressure until a maximum value has been reached. Upon a further increase in pressure a decrease in activity occurs.
5. Comparison of exp. 21 with 22 and comparison of exp. 23 with 24 reveals that with the catalysts according to the invention, an increase in activity due to the use of a higher temperature, is accompanied by only a slight decrease in selectivity.
6. Comparison of exp. 24 with 25 reveals that with the catalysts according to the invention, the use of a lower H_2/CO ratio leads to an increase in selectivity and a decrease in activity.
7. Comparison of exp. 17 with 40 reveals that with the Fe-catalysts according to the invention, replacement of Cu by Co leads to an increase in both activity and selectivity.
8. Comparison of exp. 11, 21 and 23 with each other reveals that with the Fe-catalysts according to the invention, an increase in K-content leads to an increase in selectivity, A very high K-content, however, has a detrimental effect on the activity. The experimental work has further shown that an increase in the K-content of the Fe-catalysts according to the invention leads to a sharp increase of oxygen-containing compounds in the reaction product. Thus, when using an Fe-catalyst according to the invention comprising 5 parts by weight of K per 25 parts by weight of Fe, about 80 per cent by weight of oxygen-containing compounds was found in the reaction product.
9. Comparison exp. 35, 36, 37, 38, 39 and 41 with each other reveals that in addition to the promoter combination Th/Mg frequently used in the Co-

catalysts prepared by precipitation, each of these elements individually, as well as the elements Cr, Zn and Zr, are likewise very suitable for use as promoters for the Co-catalysts according to the invention. The promoters may be ranked as follows in order of increasing attractiveness for this application: Zn, Th/Mg, Mg, Th, Cr and Zr.

10. Comparison of exp. 11 with 15 reveals that with the catalysts according to the invention a reduction in particle size leads to an increase in activity.
11. Comparison of exp. 18 and 18A with 19 and 19A reveals that the activity of the catalysts according to the invention is better maintained when a heavy fraction of the reaction product is continuously passed over the catalyst.
12. Comparison of exp. 18 with 18B reveals that a discontinuous wash of the reactivated catalyst with a solvent leads to a complete recovery of the activity and selectivity. Comparison of exp. 18 with 18A gives an impression of the deactivation that tends to occur. Comparison of exp. 18A with 18B gives an impression of the effect of washing.
13. Comparison of exp. 21 with 29, 20 with 31 and 41 with 42 reveals that for the catalysts according to the invention not only SiO_2 but also ZnO, $MgO—Al_2O_3$ and Al_2O_3 are very suitable carriers.

WHAT WE CLAIM IS:—

1. A process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, characterized in that a catalyst is used comprising 10—75 parts by weight of one or more metals of the iron group per 100 parts by weight of carrier, together with one or more promoters in a quantity of 1—50% of the quantity of metals of the iron group present on the catalyst, which catalyst is prepared by impregnation of a porous carrier with one or more aqueous solutions of salts of the metals in question of the iron group and the promoters in question followed by drying and calcining of the composition, which catalyst has such a specific average pore diameter (p) of at most 10,000 nm and such a specific average particle diameter (d) of at most 5 mm that the quotient p/d is larger than 2 (p in nm and d in mm).

2. A process as claimed in claim 1, characterized in that the molar ratio between hydrogen and carbon monoxide in the feed lies between 0.5 and 3.

3. A process as claimed in claim 1 or 2, characterized in that this process is carried out at a temperature of 200—350°C, a pressure of 10—70 bar, and a space velocity of 500—5000 and preferably of 500—2500 Nl gas/litre of catalyst/hour.

4. A process as claimed in any one of claims 1—3, characterized in that a catalyst is used comprising 15—50 and preferably 20—40 parts by weight of one or more metals of the iron group per 100 parts by weight of carrier.

5. A process as claimed in any one of claims 1—4, characterized in that a catalyst is used comprising one or more promoters in a quantity of 5—40.

6. A process as claimed in any one of claims 1—5 characterized in that a catalyst is used prepared according to the dry impregnation technique.

7. A process as claimed in any one of claims 1—6, characterized in that a catalyst is used with a p of at most 1000 nm.

8. A process as claimed in any one of claims 1—7, characterized in that this process is carried out using a fixed catalyst bed, an expanded catalyst bed or a catalyst suspension and using catalyst particles with a d between 1 and 5 mm, 0.5 and 2.5 mm and 20 and 150 μ, respectively.

9. A process as claimed in any one of claims 1—8, characterized in that this process is carried out using a fixed catalyst bed and in that the catalyst is washed periodically or continuously with a solvent for heavy hydrocarbons.

10. A process as claimed in claim 9, characterized in that the catalyst is washed continuously with a fraction of the product prepared in the hydrocarbon synthesis.

11. A process as claimed in any one of claims 1—10, characterized in that the molar ratio between hydrogen and carbon monoxide in the feed lies between 0.5 and 1.5 and in that an iron catalyst is used.

12. A process as claimed in any one of claims 1—11, characterized in that this process is carried out at a temperature of 250—325°C and a pressure of 20—50 bar and in that an iron catalyst is used.

13. A process as claimed in any one of claims 1—12, characterized in that an iron catalyst is used comprising an alkali metal, a readily reducible metal and, if desired, a metal that can only be reduced with difficulty as promoters.

14. A process as claimed in claim 13, characterized in that a catalyst is used comprising iron, potassium and copper on silica as the carrier.

15. A process as claimed in claim 13 or 14, characterized in that an iron catalyst is used comprising potassium in a concentration of at most 0.15 g of potassium per gram of iron.

16. A process as claimed in any one of claims 1—10, characterized in that the molar ratio between hydrogen and carbon monoxide in the feed lies between 1.2 and 2.5 and in that a cobalt or nickel catalyst is used.

17. A process as claimed in any one of claims 1—10 and 16, characterized in that this process is carried out at a temperature of 220—300°C and a pressure of 10—35 bar and in that a cobalt or nickel catalyst is used.

18. A process as claimed in any one of claims 1—10, 16 and 17, characterized in that a cobalt catalyst is used comprising an alkaline-earth metal and Th, U or Ce as promoters.

19. A process as claimed in claim 18, characterized in that a catalyst is used comprising cobalt, magnesium and thorium on silica as the carrier.

20. A process as claimed in any one of claims 1—10, 16 and 17, characterized in that a cobalt catalyst is used comprising one of the following elements: Zn, Mg, Th, Zr and Cr as the promoter.

21. A process as claimed in any one of claims 1—10, 16 and 17, characterized in that a nickel catalyst is used comprising Al, Mn, Th, W or U as the promoter.

22. A process for the preparation of hydrocarbons, substantially as described hereinbefore and particularly with reference to exp. 9—42 of the Example.

23. Hydrocarbons which are prepared using the process as claimed in any one or more of claims 1—22.

R. C. ROGERS,
Chartered Patent Agent.
Shell Centre,
London, SE1 7NA
Agent for the Applicants.

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