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(71) Applicant: THE BRITISH PETROLEUM COMPANY P.L.C. [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).

(72) Inventors: NAY, Barry ; 29 Greenham Walk, Woking, Surrey GU21 3HB (GB). SMITH, Mark, Royston ; 10 Camilla Close, Sunbury-on-Thames, Middlesex TW16 7PZ (GB). TELFORD, Clive, David ; 145 Cavendish Meads, Sunninghill, Berks, SL5 9TG (GB).

(74) Agent: WILSON, Michael, John; BP International Limited, Patents & Agreements Division, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN (GB).

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(54) Title: CATALYST TREATMENT

(57) Abstract

A cobalt catalyst for use in the Fischer Tropsch reaction of synthesis gas to form hydrocarbons is activated or regenerated by treatment of a cobalt containing catalyst with a gas containing carbon monoxide, said gas containing less than 30 % v hydrogen. The catalyst obtained has increased activity and greater selectivity towards producing C_5+ hydrocarbons.

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CATALYST TREATMENT

This invention relates to a catalyst treatment for a Fischer-Tropsch process.

The Fischer-Tropsch process for the conversion of synthesis gas into hydrocarbons over an iron or cobalt containing catalyst is very well known. Various different methods of either activating a fresh catalyst or regenerating a used catalyst have been proposed. Most preferred is the treatment of the catalyst with hydrogen especially alone, but the use of hydrogen mixed with a minor proportion of carbon monoxide has also been described (see e.g. USP 4626552). DE 977498 describes the pretreatment with a carbon monoxide containing gas of a catalyst of Group VIII of the Periodic Table, especially an iron one, for the hydrogenation of carbon monoxide.

We have now found a special treatment programme for cobalt-containing catalysts which can be incorporated into a Fischer-Tropsch reaction to increase the catalyst activity and/or increase the selectivity for producing C_5+ hydrocarbons.

Accordingly the present invention provides a treatment process for a cobalt-containing catalyst which comprises treating the catalyst at elevated temperature with a gas containing carbon monoxide, said gas containing less than 30%v of hydrogen.

The elevated temperature is usually in the range of from 100 to 500°C, preferably 200 to 350°C and in particular at a temperature above the mean temperature in the subsequent Fischer Tropsch process preferably at least 10°C above said temperature such as 10-60°C or especially 25-55°C above; most preferred elevated temperatures are 220-260°C especially around 250°C.

The gas used may be composed substantially entirely of carbon monoxide or of carbon monoxide containing only small amounts of other materials e.g. up to 10% v/v such as 1-10%, but the gas may if desired contain up to 95 %v, e.g. 10-95% for example up to 60 %v e.g. 20-50%v based on the total volume of the gas), of other components such as nitrogen or argon which are inert. These gases may act as inert carrier gases. The gas comprising carbon monoxide is preferably substantially free from hydrogen. If it does contain some hydrogen, it is essential that the hydrogen content of the gas is less than 30, especially less than 20, preferably less than 10 and most preferably less than 5, %v based on the volume of carbon monoxide; the gas may contain 1-30% or 5-20% v/v hydrogen (based on carbon monoxide). The treatment may be carried out at any desired pressure e.g. 50-1000kPa (0.5-10 bar) with, atmospheric pressure being preferred. The treatment time is not crucial, the optimum treatment time depending of course on the precise conditions such as the temperature and flow rate of the gas. Suitable treatment times are for example at least 10 minutes, preferably from 1 to 12 hours. The cobalt in the cobalt containing catalyst before said treatment is usally present at least partially in an oxidic form e.g. as free cobalt oxide or a mixed oxide with an oxidic support; the cobalt with catalyst before treatment may be in a major proportion in the oxide form with at most a minor proportion of cobalt metal; but especially, with a fresh catalyst may be substantially in the oxidic form. Under the preferred treatment conditions, the cobalt containing catalyst interacts with the carbon monoxide but avoids significant deposition, especially substantially any deposition of refractory carbon residues; thus conditions of 230-270°C for 10-1hr at atmospheric pressure may be used, higher temperatures requiring shorter times. The interaction is believed to be a reduction of the oxidic cobalt catalyst; in particular to reduce the cobalt to give a product in which a majority of the cobalt is present as cobalt metal e.g. 51-99% such as 80-90% (as determined by hydrogen analysis or carbon dioxide analysis on the gaseous effluent from the treatment), and a minority of the cobalt is present as a cobalt oxide e.g. 1-49% such as 10-20%.

This treatment can be used as an activation for a fresh cobalt-containing catalyst, or it can be used as part of a regeneration sequence for a cobalt containing catalyst which has already been used in a Fischer-Tropsch reaction. In either case, the treatment leads to improved performance in a subsequent Fischer-Tropsch reaction. This improvement is not seen with conventional activation or regeneration treatments such as treatment at elevated temperature with hydrogen. Thus in a further embodiment, the present invention provides a method of increasing the activity and/or selectivity of a cobalt containing Fischer Tropsch catalyst towards C_5 + hydrocarbons, in which the catalyst has been treated by the process of the invention, and also provides the use of said treated catalyst for said purpose.

Prior to treatment with carbon monoxide, the cobalt-containing catalyst may be given a pre-treatment by treating at elevated temperature with a gas containing molecular oxygen, such as air. This pretreatment is especially useful with used Fischer Tropsch catalysts which can be oxidized by it to produce the cobalt containing catalyst in an oxidic form. The elevated temperature for this pre-treatment is usually in the range of from 200 to 600°C, especially 300 to 500°C or 280-550°C. The treatment may be carried out at any desired pressure, atmospheric pressure being preferred. The optimum treatment time will depend upon the history of the catalyst, on the oxygen content of the gas used and on the treatment conditions. The treatment time should in general be of sufficient length to remove any carbonaceous residues present on the catalyst especially one for regeneration. Treatment times of at least 30 minutes, preferably from 1 to 48 hours, are preferred.

A well known problem with Fischer-Tropsch reactions is the start-up procedure. To obtain stable conditions, a very long start-up period may be required. Temperature instabilities can lead to major difficulties. US 4626552, describing these problems, states that it requires from 8 to 18 days to bring a Fischer-Tropsch reactor on stream, and discusses the problem of temperature runaway, caused by excessive heat and/or pressure during start-up. The present invention leads to a way of avoiding these problems. Thus, in a further embodiment, the present invention provides a process for the conversion of synthesis gas into hydrocarbons which comprises passing synthesis gas over a cobalt-containing catalyst under Fischer-Tropsch conditions; characterised in that the process comprises the following steps in succession: i) treating the cobalt-containing catalyst at elevated temperature with a gas containing carbon monoxide, said gas containing less than 30%v of hydrogen based on the volume of carbon monoxide; ii) passing synthesis gas over the cobalt-containing catalyst so treated at a temperature which is at least 10°C higher than the maximum temperature attained during the subsequent step carried out under said Fischer-Tropsch conditions; and iii) passing synthesis gas over the cobalt-containing catalyst under said Fischer-Tropsch conditions. Benefits of step (ii) can be shortened start-up time to uniform Fischer Tropsch operation, a higher activity catalyst and better selectivity to C_5+ hydrocarbons.

Following the treatment step i) of the process according to the invention, the cobalt-containing catalyst is subjected to a start-up procedure, step ii), which involves passing synthesis gas over the cobalt-containing catalyst at a temperature which is at least 10°C higher, preferably at least 20°C higher such as 10-150°C especially 50-110°C higher than the maximum temperature attained during the subsequent Fischer-Tropsch reaction, step iii). Suitable temperatures for step (ii) are in the range of from 220 to 330°C e.g. 230 to 300°C, especially 240 to 300°C. The pressure is preferably in the range of from 100 to 10,000 kPa (to 100 bar), more preferably 100 to 5,000 kPa (to 50 bar), especially 1,000 to 5,000 kPa (10 to 50 bar).

During step ii), it may be observed that an exotherm moves through the entire catalyst bed, especially with a fixed bed. The optimum period of time required for the step is that time required for the exotherm to move right through the bed. Once this has happened, it is desirable to end start-up step ii). The optimum duration of step ii) will depend on the flow ratio of carbon monoxide. Preferably the duration of step ii) is greater than 15 minutes, for example 0.5 to 12 hours.

The start-up step ii) is unusual in Fischer-Tropsch technology,where conventional wisdom is that high temperatures and pressures must be avoided during start-up in order to avoid temperature runaway and damage to the catalyst.

Following the start-up step ii), the desired Fischer-Tropsch reaction is carried out in step iii). Fischer-Tropsch conditions are well known to those skilled in the art. Preferably, the temperature is in the range of from 150 to 300°C, especially 180 to 240°C, most preferably 180 to 230°C with a mean temperature of 190-235°C especially 195-220°C, and the pressure is in the range of from 100 to 10,000 kPa (to 100 bar), more preferably 100 to 5000 kPa (to 50 bar), especially 1,000 to 5,000 kPa (10 to 50 bar). Preferably there is no interruption in the synthesis gas feed between steps ii) and iii), but if desired, the catalyst can be stored after step ii) is complete and used subsequently in step iii) when required. After step (ii), the temperature can be reduced to that required for the Fischer Tropsch process, but preferably the temperature is reduced to a temperature below 200°C especially to 150-190°C before being raised again to the mean Fischer Tropsch operating temperature.

Synthesis gas is a mixture of hydrogen and carbon monoxide. The relative quantities of the two components may vary, but the molar ratio of hydrogen to carbon monoxide is usually in the range of from 1:1 to 3:1. Preferably the molar ratio of hydrogen to carbon monoxide is in the range of from 1.8:1 to 2.2:1. The feedstock gas used in step ii) or step iii) may if desired contain other components, for example nitrogen, paraffins, olefins and/or carbon dioxide. Nitrogen may be present to act as a carrier gas or co-feed, and if so is preferably present in an amount of less than 40%v, for example from 10 to 40%v. Other components are preferably present in minor amounts, typically less than 20%, especially less than 15, %v.

The cobalt catalyst used in the present invention preferably comprises cobalt on a support. Very many suitable supports may be used, for example silica, alumina, titania, ceria, zirconia or zinc oxide. The support may itself have some catalytic activity. Preferably the catalyst contains from 2 to 35%w, especially from 5 to 25%w, of cobalt. Alternatively, the cobalt catalyst may be used without a support. In this case, the catalyst is often prepared in the form of cobalt oxide. Active metal catalytic components or promoters may be present as well as cobalt if desired.

The process of the invention may be performed in a fluid bed or a fixed bed or in a slurry in a liquid e.g. of liquid hydrocarbon product. The treatment process of the invention with carbon monoxide e.g. step (i) above may be performed in the same or a different reactor from that of the start-up or Fischer Tropsch step (e.g. (ii) or (iii) above).

The following Examples 1 and 3-5 illustrate the invention.

Example 1

Catalyst Preparation

A catalyst containing 10%wt cobalt on zinc oxide was prepared as follows.

Deionised water (3.35 kg) was added to ZnO (10.00 kg) with mixing. After 5 minutes $Co(NO_3)_2.6H_2O$ (5.55 kg) dissolved in deionised water (4.15 kg) was added with stirring using a Z-blade mixer. After mixing the water was removed by drying in air at 120°C for 15 hours to leave a product, which was then further heated to 500°C (at a rate of 50°C/h) and then maintained at 500°C for a further 5 hours. The calcined catalyst obtained (9.23 kg) was lubricated with 2 wt% stearic acid and formed into tablets 3.175mm (1/8" diameter x 2 mm) which were subsequently heated to 500°C (at a rate of 100°C/h) and then maintained at 500°C for 1 hour in air. The tablets were cooled to room temperature in air, ground and sieved to 250-500μm mesh size.

Example 2 (Comparative)

In situ H_2 Pretreatment

10 g (250-500µm) of the catalyst prepared in Example 1 were charged into a microreactor. Hydrogen was introduced at a GHSV (gas hourly space velocity) of 1000 h^{-1} and the temperature raised from 30°C to 320°C at 10°C min^{-1}. The temperature was held at 320°C for 10h, and then the reactor cooled at 10°C min^{-1} to room temperature.

Example 3

3h Carbon Monoxide in situ Reduction

10 g (250-500µm) of the catalyst prepared in Example 1 were charged into a microreactor. Nitrogen was introduced at GHSV=1000 h^{-1} and the temperature raised from 30°C to 250°C at 10°C min^{-1}. Then the nitrogen was switched off and carbon monoxide introduced at GHSV=900 h^{-1} for 3h. The reactor was then cooled at 10°C min^{-1} to 30°C.

Example 4

In situ Air Pretreatment Followed by 3h Carbon Monoxide Reduction

10 g (250-500µm) of the catalyst prepared in Example 1 were charged into a microreactor. Air was introduced at GHSV=6000 h^{-1} and the temperature raised from 30 to 500°C at 10°C min^{-1}. The temperature was held at 500°C for 44 h and then cooled to 250°C. Carbon monoxide was introduced at GHSV=900 h^{-1} and after 3 h at 250°C the reactor was cooled at 10°C min^{-1} to 30°C.

Catalysts from Examples 2, 3 and 4 were all tested using the following procedure.

Reaction Start-up and Fischer-Tropsch Reaction

Following on from Examples 2, 3 and 4 the microreactor at a temperature below 30°C, was purged with a gas mixture containing 20%v nitrogen, and also hydrogen and carbon monoxide in a molar ratio of 2.07:1. The pressure was then increased to 3000 KPa (30 bar) and the GHSV of the gas mixture passed adjusted to 1250 h^{-1}. The applied temperature was raised to 250°C at 2°C min^{-1}, and then held for 1 h at 250°C. The bed temperature was then decreased to 180°C and then slowly increased until about 80% carbon monoxide conversion was achieved. Conversion was measured from gas chromatography analysis of exit gas using N_2 marker. The results are shown in Tables 1 to 4. Productivity C_{5+} is the total number of grams of C_{5+} product formed per litre of catalyst per hour.

Because the tests were arranged to run at constant conversion, the bed temperature observed gives a measure of the activity of the catalyst being tested. Thus, a more active catalyst can achieve an 80% carbon monoxide conversion at a lower temperature than a less active catalyst.

Comparison of Tables 1 and 2 shows that the catalyst treated with carbon monoxide according to the invention shows higher initial activity than the catalyst given a conventional hydrogen treatment. In addition, production of undesired C_1 products is considerably lower and production of the desired C_{5+} products is considerably higher.

Table 3 shows the additional benefits of an air treatment followed by a carbon monoxide treatment: the productivity is considerably increased.

TABLE 1

Catalyst Treatment According to Example 2 (Comparative)

Hours on Stream	Mean Bed Temp (°C)	Conversion		% Carbon Molar Selectivity						Bed Prod C_{5+}
		CO	H_2	CH_4	CO_2	C_2	C_2+C_4	C_{5+}	C_{2+}	
54	214	73.9	82.8	8.0	0.5	1.7	9.0	80.9	91.5	125
149	216	74.2	80.1	7.8	1.4	1.3	6.9	82.6	90.8	128

TABLE 2

Catalyst Treated According to Example 3

Hours on Stream	Mean Bed Temp (°C)	Conversion		% Carbon Molar Selectivity						Productivity $C_{5\pm}$
		CO	H_2	CH_4	CO_2	C_2	C_2+C_4	C_{5+}	C_{2+}	
26	202	78.7	82.2	5.9	1.1	0.6	3.6	88.8	93.0	145
77	209	83.9	90.4	7.1	2.4	0.5	2.2	87.8	90.6	153
149	210	86.4	88.5	7.0	2.2	0.5	2.2	88.0	90.8	158

TABLE 3

Catalyst Treated According to Example 4

Hours on Stream	Mean Bed Temp (°C)	Conversion		% Carbon Molar Selectivity						Productivity C_{5+}
		CO	H_2	CH_4	CO_2	C_2	C_2+C_4	C_{5+}	C_{2+}	
26	204	90.4	92.5	7.6	1.5	0.7	3.4	86.8	90.9	163
94	205	84.2	87.1	5.5	0.8	0.5	2.6	90.6	93.7	159
144	205	79.8	80.6	6.2	0.8	0.6	3.4	89.0	93.0	148

Example 5

A 10% cobalt on zinc oxide catalyst was prepared by the general method of Example 1. One portion of the catalyst was treated with air for 6 hours at 500°C followed by hydrogen for 9 hours at 320°C, while a second portion was treated with air for 50 hours at 500°C followed by carbon monoxide for 3 hours at 250°C. Both catalysts were then tested by the method described above. The results are given in Table 4 below, and show the clear advantages of the treatment involving carbon monoxide.

TABLE 4

Catalyst Treatment	Hours on Stream	Mean Bed Temp (°C)	CO Conversion (%)	% Carbon Molar Selectivity		
				CH_4	CO_2	C_{5+}
Air/H_2 (Comparative)	214	214	87	7.5	2.5	76.8
Air/CO	213	212	87	4.6	1.9	91.0

Example 6

An Unsupported Catalyst

Preparation

Ammonium bicarbonate (1145 g) was dissolved in deionised water (10.4 dm^3) and 500 cm^3 of the solution added to a continuous precipitation cup. In a second vessel cobaltous nitrate (450.6 g) was dissolved in deionised water (2.8 dm^3). The two solutions were pumped simultaneously into the solution already in the precipitation cup at such a rate as to ensure complete precipitation of cobalt oxide (rapid agitation was required within the precipitation cup). The precipitate was constantly being removed *via* a weir and filtered on a Buchner funnel. The complete precipitation process was completed in 2 hours. The filter cake was dried overnight in air at

150°C and then in air at 350°C for 6hr to give 114.4 g of Co_3O_4.

Test

A portion of the above catalyst was treated with hydrogen as described in Example 2 and tested using the reaction start-up procedure described earlier. The results are shown in the first row of Table 5. The catalyst so tested was then treated with 1% O_2/99% N_2 at 500°C for 23 hours. The temperature was then reduced to 250°C and the catalyst treated with CO for 3 hours. The catalyst was again tested using the same reaction start-up procedure. The much improved results are shown in the second row of Table 5.

TABLE 5

Catalyst Treatment	Hours on Stream	Mean Bed Temp (°C)	CO Conversion (%)	% Carbon Molar Selectivity		
				CH_4	CO_2	C_{5+}
H_2 (Comparative)	25	257	33	37.4	1.3	28
1% O_2/CO	25	231	69	14.1	1.5	105

Claims:

1. A process for treating a cobalt containing catalyst characterized by contacting said catalyst at elevated temperature with a gas containing carbon monoxide, said gas containing less than 30% by volume of hydrogen, in order to produce a treated cobalt containing catalyst.

2. A process according to claim 1 characterized in that said oxide containing catalyst comprises cobalt on a support.

3. A process according to claim 1 or 2 characterized in that the catalyst is contacted with carbon monoxide substantially free of hydrogen.

4. A process according to any one of claims 1-3 characterized in that the catalyst contacts the gas at 200-350°C, preferably 230-260°C.

5. A process according to any one of the preceding claims characterized in that the cobalt containing catalyst is one obtained by contacting a catalyst containing cobalt at an elevated temperature, preferably 380-600°C, with a gas containing molecular oxygen.

6. A process for the conversion of synthesis gas into hydrocarbons over a treated cobalt containing catalyst under Fischer Tropsch conditions characterized in that said catalyst has been obtained by a process as claimed in any one of claims 1-5.

7. A process according to any one of claims 1 to 5 which is followed by passing synthesis gas over the treated cobalt containing catalyst under Fischer Tropsch conditions to form hydrocarbons.

8. A process according to claim 6 or 7 characterized by first passing synthesis gas over said treated catalyst at a temperature which is at least 10°C higher than the maximum attained during the subsequent contacting step under Fischer Tropsch conditions.

9. Method of increasing the activity and/or selectivity of a cobalt containing Fischer Tropsch catalyst towards C_5+ hydrocarbons, characterized in that said catalyst has been obtained by a process according to any one of claims 1-5.

10. Use of a catalyst obtained by a process according to any one of claims 1-5 for increasing the activity and/or selectivity of a cobalt containing Fischer Tropsch catalyst towards C_5+ hydrocarbons.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/01141

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01J37/16; B01J23/74; C07C1/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01J ; C07C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	DE,C,977 498 (H. KÖLBEL) 3 November 1966 cited in the application see page 1, line 33 - page 2, line 20 see page 4; examples 1,2 see claims	1-10
A	FR,A,1 108 326 (RHEINPREUSSEN AG) 11 January 1956 see the whole document	1-10
A	BE,A,502 597 (RUHRCHEMIE AG) 18 July 1952 see page 1, line 1 - line 11 see page 2, line 36 - line 48 see claims	1-10

° Special categories of cited documents : [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 11 SEPTEMBER 1992	Date of Mailing of this International Search Report 21 SEP 1992
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer LO CONTE C.

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9201141 SA 61298

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/09/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-C-977498		None	
FR-A-1108326		None	
BE-A-502597		None	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82