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(54) Title: FISCHER-TROPSCH CATALYSTS

(57) Abstract

A supported Fischer-Tropsch catalyst contains a minor amount of an element of Groups VI and/or VII of the Periodic Table. Production of CO_2 is reduced.

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FISCHER-TROPSCH CATALYSTS

The present invention relates to catalysts suitable for use in the Fischer-Tropsch process, and to a Fischer-Tropsch process carried out using the catalysts.

In the well-known Fischer-Tropsch reaction a mixture of carbon monoxide and hydrogen (usually referred to as "syngas") is reacted to give relatively low molecular weight hydrocarbons, a substantial proportion of which are liquid at normal temperature and pressure.

The Fischer-Tropsch process is disclosed in numerous references for example US 4 088 671. This discloses that the catalysts are usually supported Co and Fe catalysts. US 4 088 671 is concerned with a Co catalyst modified by the addition of Ru. Various catalysts supports are mentioned including activated carbon, coke, and charcoal. The supports exemplified however are all oxides, and there is nothing to suggest that the use of carbon supports would give any marked advantage over the oxide supports shown in the Examples.

The specification of US 4 688 671 states that the Co may be deposited on the support using chloride salts. The examples however show the addition of the Co as nitrate. The examples show the deposition of Ru as the chloride. This is because the only commonly available Ru salt is the halide. There is nothing to suggest that the presence of chloride would give any advantage in the catalyst.

We have found that when we attempted to make supported Fischer-Tropsch catalysts that satisfactory catalysts were not obtained when ferric chloride or cobaltous chloride was used to deposit iron or

cobalt on the catalyst.

In the operation of any catalytic process it is always a desirable objective to obtain a high conversion of feedstock to the desired product. In the Fischer-Tropsch reaction it is necessary to consider not only the conversion of feedstock to desired product but also the nature of the by-products, in particular CO_2. Feedstock converted to CO_2 is lost to the process, while feedstock which is unreacted can be recycled. We have now found a method of modifying a supported Fischer-Tropsch catalyst so as to reduce the amount of CO_2 produced.

According to the present invention a supported Fischer-Tropsch catalyst containing a catalyst metal is characterised in that the catalyst contains a minor amount of an element of Groups VI and VII of the Periodic Table.

The Periodic Table referred to is that published by United Kingdom Patent Office in the Classification Manual for Section C2 of the Patent Office Classification dated 1980.

The element is preferably in the form of an anion. The element or anion must be one which is adequately stable to hydrogenation under the conditions used. The anion is preferably an anion of the element itself, not linked to other elements. Preferred anions are the halides eg chloride.

The quantity of element of Group VI or VII of the Periodic Table introduced is preferably such that the conversion of CO by the catalyst is not less than 20%, preferably not less than 40% of the conversion (under the same conditions) obtained with a catalyst prepared in the same way but without the presence of the Group VI or VII element.

The catalyst of the present invention preferably has an activity such that at a temperature of 300°C, an H_2:CO ratio of 2:1, a pressure of 0.7 MPa absolute, and a GHSV of 500 h^{-1} the CO conversion is at least 50%, preferably at least 70%.

The quantity of the element may for example be in the range 0.001 to 3%, preferably 0.1% to 2%, based on weight of the catalyst including support.

The Fischer-Tropsch catalytic metals are active in the metallic form. The element of Group VI-VII must therefore be introduced without affecting the ability to reduce the metallic catalyst, and must not be removed by the procedures used to prepare and activate the catalyst. Thus although it is possible to deposit metals which normally have catalytic activity in the Fischer-Tropsch reaction on a support from aqueous solutions of their halides, this is not a desirable procedure where the metal halide can be reduced some or all of the halide will be removed as the hydrogen halide. Where the halide cannot be reduced or when the halide is retained by the reduced catalyst an active catalyst will not be obtained.

It is very difficult to obtain the very carefully controlled amounts of halide in relation to the active catalytic metal required to provide the minor amount of Group VII or VIII element required for the present invention. When we attempted to make Fischer-Tropsch catalysts from ferric chloride or cobaltous chloride the resulting products had such low activities (due to insufficient active metal and/or excessive Group VII element) that they were not useful Fischer-Tropsch catalysts.

The introduction of the Group VI or VII element is therefore preferably a separate operation from the deposition of the catalytic metal.

The element of Group VI or VII may conveniently be introduced by using a non-metallic compound, either an inorganic compound for example an ammonium compound e.g. ammonium chloride, or an organic compound e.g. a chlorohydrocarbon which decomposes to give chlorine under the conditions under which it is introduced or under the reaction conditions.

Supported Fischer-Tropsch catalysts and methods of making them are well-known. Examples of catalytic metals which may be used are Co, Fe and Ni but Ru may also be used.

The quantity of catalytic metal (e.g. iron or cobalt) deposited on the catalyst may be in the range 5 to 100% wt based on weight of support.

The catalyst may be prepared by impregnation with an aqueous

solution of a salt of the catalytic metal. Examples of suitable salts are nitrates.

Various supports have been proposed for Fischer-Tropsch catalysts, e.g. inorganic metal oxides e.g. alumina, silica, thoria, zirconia, and molecular sieves.

The present invention is particularly useful when applied to catalysts according to our copending patent application ..... (Case 5869) comprising cobalt or iron on a support characterised in that the support is a carbon having a BET surface area of at least 100 m^2/g, a ratio of BET to basal plane surface area not greater than 4:1, and a ratio of basal plane surface area to edge surface area of at least 10:1.

Carbons may be characterised by their BET, basal plane, and edge surface areas. The BET surface area is the surface area determined by nitrogen adsorption using the method of Brunauer Emmett and Teller J. Am Chem. Soc. 60,309 (1938). The basal plane surface area is the surface area determined from the heat of adsorption on the carbon of n-dotriacontane from n-heptane by the method described in Proc.Roy.Soc. A314 pages 473-498, with particular reference to page 489. The edge surface area is the surface area determined from the heat of adsorption on the carbon of n-butanol from n-heptane as disclosed in the Proc.Roy.Soc. article mentioned above with particular reference to page 495.

The carbon supports are known, for example from GB 1 565 074. However the catalysts of the present invention behave in a completely different manner from the catalysts of GB 1 565 074. Thus the catalysts of GB 1 565 074 have their activity increased by the presence of alkali metals, and the presence of chloride ion is stated to be undesirable.

The preferred carbons for use in the present invention have a BET surface area of at least 200 m^2/g,most preferable at least 300 m^2/g. The BET surface area is preferably not greater than 1000 m^2/g, more preferably not greater than 750 m^2/g.

The ratio of BET to basal plane surface area is preferably not greater than 2.5:1. It is particularly preferred to use carbons

with ratios of BET to basal plane surface area of not greater than 1.5:1.

It is preferred to use carbons with ratios of basal plane surface area to edge surface area of at least 100:1. It is not believed that there is an upper limit on the ratio, although in practice it will not usually exceed 200:1.

The preferred carbon support may be prepared by heat treating a carbon-containing starting material. The starting material may be an oleophilic graphite e.g. prepared as disclosed in GB 1 168 785 or may be a carbon black.

However oleophilic graphites contain carbon in the form of very fine particles in flake form and are therefore not very suitable materials for use as catalyst supports. We prefer to avoid their use. Similar considerations apply to carbon blacks which also have a very fine particle size.

The preferred materials are activated carbons derived from vegetable materials e.g. coconut charcoal, or from peat or coal or from carbonizable polymers. The materials subjected to the heat treatment preferably have particle sizes not less than these indicated above as being preferred for the carbon support.

The preferred starting materials have the following characteristics: BET surface area of at least 100, more preferably at least 500 m^2/g.

The preferred heat treatment procedure for preparing carbon supports having the defined characteristics, comprise successively (1) heating the carbon in an inert atmosphere at a temperature of from 900°C to 3300°C, (2) oxidizing the carbon at a temperature between 300°C and 1200°C, (3) heating in an inert atmosphere at a temperature of between 900°C and 3000°C.

The oxidation step is preferably carried out at temperatures between 300° and 600°C when oxygen (eg as air) is used as the oxidising agent.

The duration of the heating in inert gas is not critical. The time needed to heat the carbon to the required maximum temperature is sufficient to produce the required changes in the carbon.

The oxidation step must clearly not be carried out under conditions such that the carbon combusts completely. It is preferably carried out using a gaseous oxidizing agent fed at a controlled rate to avoid over oxidation. Examples of gaseous oxidising agents are steam, carbon dioxide, and gases containing molecular oxygen eg air. The oxidation is preferably carried out to give a carbon weight loss of at least 10% wt based on weight of carbon subjected to the oxidation step, more preferably at least 15% wt.

The weight loss is preferably not greater than 40 % wt of the carbon subjected to the oxidation step, more preferably not greater than 25 % wt of the carbon.

The rate of supply of oxidizing agent is preferably such that the desired weight loss takes place over at least 2 hours, more preferably at least 4 hours.

Where an inert atmosphere is required it may be supplied by nitrogen or an inert (Group 0) gas.

The catalysts of the present invention may be used for the Fischer-Tropsch conversion of synthesis gas to hydrocarbons which are liquid at normal temperatures and pressures.

The temperature may for example be in the range 150° to 300°C, preferably 200 to 250°C. The pressure may for example be in the range 1 to 50 bar. The molar ratio of hydrogen to carbon monoxide may for example be in the range 3:1 to 1:1, more preferably about 2:1. The gas hourly space velocity may be 100 to 10000, preferably 500 to 3000.

The invention will now be illustrated by reference to the following experiments, some of which are Examples of the invention and some of which are Comparative Tests, not according to the invention.

Comparative Test A

This Experiment shows the preparation of a cobalt Fischer-Tropsch catalyst supported on a graphitised carbon.

The carbon used as support was prepared from a commercially available extrudate activated carbon sold by Degussa under the

designation Katepon BKIV. The carbon was in the form of extrudates of 4mm diameter and had typical BET, basal plane, and edge surface areas of 939,182 and 32 m^2/g respectively. The activated carbon was heat treated as follows. The carbon was heated from room temperature in a stream of helium to 1700°C over a period of about 1 hour. When the temperature reached 1700°C the carbon was allowed to cool in the stream of helium to 25°C. The carbon was then heated in air in a muffle furnace at approximately 520°C for a time known from experience to give a weight loss of 20 %wt. The carbon was then heated in helium to between 1800°C and 1850°C as in the helium heating step mentioned above. The carbon was allowed to cool to room temperature in a helium atmosphere.

Typical values found for carbon treated in this manner were:

BET surface area	710-749 m^2/g
Basal plane surface area	416-666 m^2/g
Edge surface area	3.6-3.8 m^2/g

The support was ground and sieved to 16-30 mesh (0.5-1.0 mm) and washed by refluxing in (1) dilute (10% w/w) hydrochloric acid and (2) distilled water to remove sulphur and impurity transition metals before use.

The carbon was then impregnated with an aqueous solution of cobalt nitrate (analytical reagent grade). The quantity of cobalt nitrate used was such that 10g of carbon support were treated with 2g of cobalt (giving a nominal metal loading of 16.7% w/w based on weight of catalyst). The quantity of water used was the minimum used necessary to ensure even wetting of the carbon support (a few drops of methanol may be added to assist in wetting of the support).

The impregnation of the carbon was conducted in a rotary evaporator at 50-80°C under a vacuum of 200-800 m bar (20 kPa-80 kPa). The impregnated carbon was dried overnight in a vacuum oven at 120°C, 200-300 m bar (20 kPa-30 kPa).

The catalyst was tested (using a 2.2 ml sample) in a once-through microreactor equipped with an on-line gas chromatography apparatus to analyse for CO, CO_2, and C_1-C_{10} organic products. The catalyst was reduced before use by treating for

2-8 hours with a stream of hydrogen (25-100 ml/min) at 400-450°C and 8 bar (0.8 MPa) gauge. Synthesis gas at a molar ratio of CO-H_2 of 2:1 was then admitted. The conditions used and the results obtained are given in Table 1.

Definition of Terms used in the Results

The CO conversion is defined as the percentage of the carbon monoxide fed to the reactor that was converted to analysed products. It may be represented as:

$$100-\left[\frac{\text{molar \% CO in product}}{\text{SUM(molar \% carbon-containing material x carbon no.)}} \times 100\right]\%$$

The selectivity to organic products is defined as the percentage of the total carbon monoxide converted to C_1-C_{10} organic products rather than to CO_2. It may be represented as:

$$\frac{\text{SUM(molar \% organic products x carbon number)} \times 100\%}{\text{SUM(molar \% organic products + carbon number)} \times \text{molar \% } CO_2}$$

The alpha factor represents the relative quantities of the organic products and is defined by P. Biloen and W.M.H. Sachtler in "Advances in Catalysis", Volume 30, pp 165 et seq, published by the Academic Press Inc 1981. In the present application the factor is calculated for products with carbon numbers from C_3-C_{10}.

The gas hourly space velocity (GHSV) is defined as the ml/hour of CO/H2 feedstock (at NTP) per ml of catalyst.

Example 1

The Example shows the effect of chlorine on the catalysts of the present invention.

After a sample of the catalyst used in Test A had been reduced with hydrogen it was impregnated with ammonium chloride so as to add 0.1% w/w chlorine. The catalyst was then tested as in Test A and the results given in Table 1. A reduction in activity (from 99% to 67% at about 270°C) was accompanied by an increase in the selectivity towards organic products (from 65% to 75% at about 270°C).

Test B

A further batch of catalyst was prepared and tested as in

Test A. The results are given in Table 2.

Example 2

Test B was repeated except that chlorine was introduced on to the catalyst by treatment with chloroethane. A quantity of chloroethane calculated to introduce 0.3% w/w of catalyst of chlorine was passed in a stream of hydrogen (1% v/v in hydrogen) over another sample of the catalyst prepared for in Test B. A gas flow of 3 ml/min (total flow) was used at 225°C and atmospheric pressure. For the purposes of calculating the amount to be used it was assumed that all chlorine fed was retained by the catalyst. The results are given in Table 2.

Comparative Test C

A carbon supported catalyst containing 16.7% w/w of iron on graphitised carbon was prepared from ferric nitrate using the technique described in Test A. The results are shown in Table 3.

Example 3

Example 6 was repeated except that 0.05% w/w of chlorine was introduced by re-impregnation of a sample of the reduced catalyst with ammonium chloride. The results are shown in Table 3.

Test D

A further sample of iron on graphitised carbon containing 16.7% w/w Fe was prepared and tested as in Example 6.

Example 4

The catalyst used in Test D was retained in the test reactor and the pressure was then reduced to atmospheric pressure and 1% v/v chloroethane in hydrogen was then passed over the catalyst (as described in Example 2) until a theoretical chlorine loading of 0.05% w/w had been achieved. The activity and selectivity of the resulting catalyst was then measured as previously. The cycle of pressure reduction and chloroethane treatment was subsequently repeated to give cumulative chlorine loadings of 0.15, 0.25 and 0.50% w/w. The effect of increase in chlorine content is clearly indicated in Table 4.

Table 1

Experiment		A		1	
Chlorine (% w/w) - Doped as NH_4Cl		0		0.1	
Temperature	(°C)	245	267	247	272
CO Conversion	(%)	70	99	34	67
Selectivity to Organic Products	(%)	83	65	94	75
" " Carbon Dioxide	(%)	17	35	6	25
Alpha Factor		0.69	0.45	0.60	0.41

Base catalyst nominal composition:- 16.7% w/w Co/carbon
GHSV:- 500 h^{-1}
H_2:CO 2:1
Pressure:- 6 Bar Gauge (0.7 MPa absolute)

Table 2

Experiment		B	2
Chlorine (% w/w) - C_2H_5Cl Pretreatment		0	0.3
Temperature	(°C)	246	254
CO conversion	(%)	99	74
Selectivity to Organic Products	(%)	79	90
" " Carbon Dioxide	(%)	21	10
Alpha Factor		0.62	0.62

Base catalyst nominal composition:- 16.7% w/w Co/carbon
GHSV:- 500 h^{-1}
H_2:CO 2:1
Pressure:- 6 Bar Gauge (0.7 MPa absolute)

Table 3

Experiment		C	3
Chlorine (% w/w) - Doped as NH_4Cl		0	0.05
Temperature	(°C)	240	242
CO Conversion	(%)	38	17
Selectivity to Organic Products	(%)	67	90
" " Carbon Dioxide	(%)	33	10
Alpha Factor		0.57	0.63

Base catalyst nominal composition:- 16.7% w/w Fe/carbon
GHSV:- 500 h^{-1}
H_2:CO 2:1
Pressure:- 6 Bar Gauge (0.7 MPa absolute)

Table 4

Experiment		D	4			
Chromine (% w/w) - C_2H_5Cl Pretreatment		0	0.05	0.15	0.25	0.50
Temperature	(°C)	249	247	247	247	247
CO conversion	(%)	40	32	25	17	11
Selectivity to Organic Products	(%)	65	67	74	78	77
" " Carbon Dioxide	(%)	35	33	26	22	23
Alpha Factor		0.58	0.64	0.64	0.64	0.63

Base catalyst nominal composition:- 16.7% w/w Fe/carbon
GHSV:- 500 h^{-1}
H_2:CO 2:1
Pressure:- 6 Bar Gauge (0.7 MPa absolute)

Comparative Test E

A carbon support was prepared using a method similar to that described in Test A. The starting material however was a commercially available activated carbon sold by Degussa as BK 16.

The heat-treated carbon used as support had the following surface area values:-

BET surface area	300 m^2/g
Basal plane surface area	121 m^2/g
Edge surface area	1.42

The particle size was 16-30 BSS (0.5-1 mm).

A carbon-supported catalyst containing 16.7% w/w of iron as graphitised carbon was prepared from ferric chloride using the technique described in Test A. The results are shown in the Table 5 and show very low catalyst activity.

Comparative Test F

The above experiment was repeated using cobaltous chloride to produce a catalyst containing 16.7% w/w of cobalt. The results are also shown in Table 5, this catalyst also being of low activity.

Table 5

Catalyst Nominal Composition	16.7% w/w Fe/carbon	16.7% w/w CO/carbon	
Temperature (°C)	292	220	293
CO conversion	5	0	6
Selectivity to organic products (%)	86	-	73
Selectivity to carbon dioxide (%)	14	-	27
Alpha factor	0.55	-	0.69

The conditions used for the test were the same as in the previous examples.

Claims:

1. A supported Fischer-Tropsch catalyst containing a metal characterised in that the catalyst contains a minor amount of an element of Groups VI and/or VII of the Periodic Table.

2. A catalyst according to claim 1 wherein the element of Groups VI and/or VII is in the form of an anion.

3. A catalyst according to claims 1 or 2 wherein the anion is a chloride.

4. A catalyst according to any one of the preceding claims wherein the quantity of elements of Groups VI or VII in the catalyst is such that the conversion of CO by the catalyst is not less than 20% of the conversion under the same conditions obtained with a catalyst prepared in the same way but without the Group VI and/or VII element.

5. A catalyst according to any one of the preceding claims wherein the catalyst has an activity of such that at a temperature of 300°C, an H_2:CO ratio of 2:1, a pressure of 0.7 MPa absolute and a GHSV of 500 h^{-1} the CO conversion is at least 50%.

6. A catalyst according to any one of the preceding claims wherein the quantity of the Group VI and/or Group VII element is in the range 0.001 to 3% by weight of the catalyst.

7. A catalyst according to claim 6 wherein the quantity of the element is in the range 0.1% to 2% by weight of the catalyst.

8. A catalyst according to any one of the preceding claims prepared by introducing the element of Group I and/or Group VII by a step separate from the deposition of the catalytic metal.

9. A catalyst according to any one of the preceding claims wherein the element of Group VI or VII is introduced in the form of a non-metallic compound.

10. A catalyst according to claim 9 wherein the non-metallic compound is an organic compound.

11. A catalyst according to claim 10 wherein the organic compound is a chloro-hydrocarbon which decomposes to give chlorine under the conditions under which it is introduced or under the reaction conditions.

12. A process according to claim 9 wherein the non-metallic compound is an ammonium compound.

13. A catalyst according to any one of the preceding claims wherein the catalytic metal is cobalt or iron.

14. A process according to any one of the preceding claims characterised in that the catalytic metal is supported on a carbon having a BET surface area of at least 100 m^2/g, a ratio of BET to basal plane surface area not greater than 4:1 and a ratio of basal plane to edge surface area of at least 10:1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00386

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

IPC[4]: C 07 C 1/04; B 01 J 23/74; B 01 J 35/10

II. FIELDS SEARCHED

Minimum Documentation Searched [7]	
Classification System	Classification Symbols
IPC[4]	C 07 C; B 01 J

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]
X	GB, A, 621902 (STANDARD OIL) 22 April 1949, see claims; page 1, lines 66 to 71	1-9,13
X	GB, A, 1565074 (BRITISH PETROLEUM) 16 April 1980, see claim 1	14
X	US, A, 4054644 (EXXON RESEARCH & ENGINEERING CO.) 18 October 1977, see claims 1,17	1-9,14
P,X	US, A, 4478954 (STANDARD OIL) 23 October 1984, see claim 1; column 2, lines 48 to 54	14

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
4th December 1985	20 DEC. 1985
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 85/00386 (SA 10506)

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 18/12/85

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A- 621902		None		
GB-A- 1565074	16/04/80	NL-A-	7712072	08/05/78
		BE-A-	860440	03/05/78
		FR-A,B	2369872	02/06/78
		DE-A-	2748972	11/05/78
		US-A-	4163775	07/08/79
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		AU-A-	3022577	10/05/79
		US-A-	4250057	10/02/81
		CA-A-	1097887	24/03/81
		AU-B-	515799	30/04/81
US-A- 4054644	18/10/77	US-A-	3974096	10/08/76
US-A- 4478954	23/10/84	US-A-	4513096	23/04/85