PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : **C07C 1/04, B01J 29/24, 29/26** **B01J 29/34, 29/36, 23/76** **B01J 23/78, 23/84**	**A1**	**(11) International Publication Number:** **WO 93/05000** **(43) International Publication Date:** 18 March 1993 (18.03.93)

(21) International Application Number: PCT/AU92/00457

(22) International Filing Date: 28 August 1992 (28.08.92)

(30) Priority data:
PK 7995 28 August 1991 (28.08.91) AU

(71) Applicant *(for all designated States except US):* THE BROKEN HILL PROPRIETARY COMPANY LIMITED [AU/AU]; 600 Bourke Street, Melbourne, VIC 3000 (AU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : BESSELL, Sandra [AU/AU]; 20 Glenwood Drive, Springvale South, VIC 3172 (AU). CHAFFEE, Alan, Loyd [AU/AU]; 25 Hamilton Road, Warrandyte, VIC 3113 (AU).

(74) Agent: GRIFFITH HACK & CO.; 3rd Floor, 509 St. Kilda Road, Melbourne, VIC 3004 (AU).

(81) Designated States: AU, CA, GB, US.

Published
With international search report.

(54) Title: FISCHER TROPSCH CATALYST COMPRISING COBALT AND SCANDIUM

(57) Abstract

The specification describes a Fischer-Tropsch catalyst which comprises cobalt, scandium and a suitable support. The specification also describes a process for producing hydrocarbons by contacting synthesis gas with the Fischer-Tropsch catalyst. Suitable supports include silica, alumina, silica-alumina and kieselguhr if the product required is a wax or distillate. Alternatively the support may be an acidic molecular sieve material such as a zeolite if gasoline or distillate and gasoline is/are required.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SK	Slovak Republic
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
UA	Ukraine
US	United States of America

FISCHER TROPSCH CATALYST COMPRISING COBALT AND SCANDIUM

TECHNICAL FIELD

The invention relates to catalyst compositions for use in the Fischer-Tropsch process for the conversion of synthesis gas into hydrocarbons, and an improved process using these catalyst compositions. It is particularly aimed at Fischer-Tropsch processes which produce higher hydrocarbons including waxes and hydrocarbons suitable for use as liquid fuels from a natural gas derived synthesis gas.

BACKGROUND

The Fischer-Tropsch process for hydrocarbon production is well known and described in various texts such as "The Fischer-Tropsch and Related Synthesis" by H.H. Stroch, N. Golumbic and R.B. Anderson (John Wiley and Sons, New York, 1951). Generally this process takes place over metals such as iron, cobalt, nickel and ruthenium, which may be supported on carriers such as kieselguhr or silica.

Nickel, although one of the most active metals for carbon monoxide hydrogenation, is not preferred for hydrocarbon production because of its high methane (rather than higher hydrocarbon)selectivity.

Ruthenium could not be used in any great capacity because of its high cost and limited availability.

The choice between iron and cobalt is dependent upon the following factors:

(i) Activity - Cobalt catalysts are more active than iron catalysts and thus require lower temperatures to reach similar levels of conversion.

(ii) Selectivity - Cobalt catalysts have a greater selectivity to higher hydrocarbons than iron catalysts.

(iii) Product Composition - Cobalt generally produces a product consisting of predominantly n-alkanes, whilst the product from iron catalysts contains more oxygenates and olefins.

(iv) Carbon Dioxide Selectivity - Iron catalysts are more active for the water gas shift reaction

$$CO + H_2O \quad CO_2 + H_2$$

This is desirable when hydrogen deficient synthesis gases are used (such as obtained from coal gasification) as the extra hydrogen required for the Fischer-Tropsch stoichiometry is generated. However, when hydrogen-rich synthesis gas (such as derived from natural gas) is used, this extra hydrogen is not required, and the water gas shift only leads to an overall loss in carbon efficiency.

(v) Methane Selectivity - In this regard iron catalysts are superior over cobalt catalysts. However the methane make of cobalt catalysts can be somewhat reduced by the addition of certain promoters including thoria.

Thus, if liquid fuels or wax production is being targeted from a natural gas derived synthesis gas, in light of points (i) to (iv) above, cobalt catalysts would be preferred.

The overall hydrocarbon distribution of a Fischer-Tropsch product generally follows the Schulz-Flory distribution, which may be represented by the following equation:

$$W_n = n\alpha^{n-1}(1-\alpha)^2$$

where W_n is the weight fraction of the product with a carbon number n, and (commonly known as the alpha value) is the probability of chain growth, and is assumed to be independent of chain length.

There is some deviation from this equation, especially at lower carbon numbers where independence of chain growth is less likely. Methane makes are generally "higher than expected", and lower low carbon fractions are generally "lower than expected". This is believed to be caused by methane being formed by additional mechanisms such as cracking and direct methanation (especially for nickel catalysts), and the greater reactivity of lower olefins (especially ethylene) towards chain growth.

The type of hydrocarbon product produced by cobalt catalysts is somewhat dependent on the nature of their support materials, and to a lesser extent operating conditions. The "classic" cobalt catalysts as described in Storch et al., which are supported on kieselguhr, produce predominantly n-alkanes. Similar products result from silica, alumina and silica-alumina supported cobalt catalysts. This high n-alkane content is desirable for wax and distillate production, but not gasoline production as linear hydrocarbons have poor octane ratings.

When gasoline production is targeted, zeolite supports such as Zeolite Y and ZSM-5, are used to produce a product which has enhanced levels of aromatics and/or branched hydrocarbons, and thus a high octane rating.

US Patent 4086262 (Mobil Oil Corporation) describes the use of zeolites such as ZSM-5 as supports for Fischer-Tropsch metals including iron, cobalt, nickel, ruthenium, thorium and osmium, to produce an aromatic rich product from synthesis gas.

Australian Patent Application AU 34883/84 (Union Carbide Corp.) describes the use of catalyst compositions consisting of steam-stabilized Zeolite Y as a catalyst support for conventional Fischer-Tropsch metals such as iron or cobalt. These compositions enhanced branching and aromatisation in the products, as well as the amount of product boiling in the liquid fuel range.

Australian Patent Application AU 88929/82 (U.S. Department of Energy) describes a catalyst composition of cobalt, promoted with thoria, on a ZSM-5 type zeolite support to produce high octane liquid hydrocarbon products that are in the gasoline boiling range, but contains branched aliphatic hydrocarbons rather than aromatics to impart high octane numbers.

When production of both gasoline and distillate is targeted zeolite supported cobalt catalysts can be operated under conditions which produce a naphtha fraction with enhanced branching over that of the corresponding distillate fraction, as described in our Australian Patent Application AU 26671/88.

As previously mentioned promoter(s) are often used in cobalt catalyst formulations to increase catalyst activity and to reduce methane selectivity (and subsequently increase higher hydrocarbon selectivity). The use of thoria, magnesia and manganese as such promoters for cobalt Fischer-Tropsch catalysts is well known, and has been described in Storch et al.

Shell Internationale have a series of Australian patent Applications including AU 28815/84, 39160/85, 41617/85, 44575/85 and 52402/86, describing improved cobalt Fischer-Tropsch catalysts, supported on silica, alumina, or silica-alumina, promoted by at least one of the group consisting of zirconium, titanium and chromium.

Exxon have described the promotion of titania supported cobalt Fischer-Tropsch catalysts by thorium in US Patent 4595703, by rhenium in Australian Patent Application

AU 33316/89, and by rhenium and thorium in Australian Patent Application AU 47014/85.

Rhenium has also been found to improve the activity of alumina supported cobalt Fischer-Tropsch catalysts by Den Norske Stats Oljeselskap in International Patent Application WO 89/03725. They have also described the use of platinum, iridium and rhodium to have a similar effect on alumina supported cobalt catalysts in International Patent Application WO 90/07377.

For any true commercial operation, activity and selectivity must be maximised. A high selectivity to desired products minimises unwanted by-products, whilst increasing catalyst activity will minimise the amount of unconverted gas either wasted in a once through operation, or the amount of gas recycled in a more complex plant.

As most of the world's natural gas supplies are in remote locations, for natural gas based Fischer-Tropsch processes, it is even more important to try to minimise the complexity and capital cost of a plant by alleviating the need for recycling or reducing the amount of unconverted gas which needs to be recycled.

Thus there is a considerable incentive to increase the activity of cobalt based Fischer-Tropsch catalysts, whilst maintaining a low selectivity to unwanted by-products in order to maximise the production of higher hydrocarbons. It is therefore the object of the invention to provide an improved Fischer-Tropsch process for the production of hydrocarbons from synthesis gas by providing a cobalt based Fischer-Tropsch catalyst of enhanced activity which increases the overall production of higher hydrocarbons.

It has now been found that addition of scandium to supported cobalt catalyst compositions, promoted or unpromoted, produces catalysts of increased Fischer-Tropsch activity, which give an overall increase in the production of higher hydrocarbons.

SUMMARY OF THE INVENTION

Accordingly in a first aspect the present invention provides a Fischer-Tropsch catalyst comprising cobalt scandium and a suitable support. In a second aspect the invention provides a process for converting synthesis gas into hydrocarbons which process comprises contacting synthesis gas with a catalyst comprising cobalt, scandium and a suitable support.

DETAILED DESCRIPTION OF THE INVENTION

The synthesis gas for conversion comprises substantial proportions of carbon monoxide and hydrogen, but may also contain carbon dioxide, water, methane and nitrogen. It may be obtained from carbonaceous sources such as natural gas, coal, oil shale and petroleum hydrocarbons by known processes such as partial oxidation, gasification and steam reforming. The relative concentrations of the gaseous components depend on the source of the synthesis gas and the process by which it is obtained. Hydrogen to carbon monoxide molar ratios of these synthesis gases for conversion are in the range of 0.2 to 6.

We are particularly interested in natural gas derived synthesis gas as a means of utilising Australia's abundant natural gas reserves, and thus preferable synthesis gases have hydrogen to carbon monoxide molar ratios of 1 to 3.

The invention is concerned with increasing the activity and higher hydrocarbon production of supported cobalt Fischer-Tropsch catalysts. Thus cobalt is an essential part of the catalyst composition, and is present in an amount of 1 to 50 weight percent based on the total weight of the catalyst composition.

The choice of the support is dependent upon the type of product targeted. When distillate or wax production is targeted, supports such as kieselguhr, silica, alumina, and silica-alumina can be used. When gasoline or gasoline and distillate is to be produced, acidic molecular sieve materials such as zeolites should be used as supports. The support preferably comprises from 10 to 98 weight percent of the total weight of catalyst.

It is known to those skilled in the art that thoria and/or other materials such as magnesia and manganese can be used as promoters for cobalt Fischer-Tropsch catalysts in order to improve catalyst activity and selectivity. As scandium addition was found to be beneficial to both these promoted and unpromoted catalysts, the presence of these promoter materials is optional, but preferred. Thoria and/or other promoters can be present in an amount of from 0.01 to 25 weight percent, more preferably between 0.05 and 5 weight percent.

Scandium is used as an additive to the above described catalyst formulation to achieve the enhanced catalyst activity and higher hydrocarbon production. For the purposes of the invention scandium is preferably present in an amount of from 0.01 to 25 weight percent based on the total weight of the catalyst composition, more preferably between 0.05 and 5 weight percent.

The cobalt, promoter and scandium may be loaded onto the support by any of the methods known to those skilled in the art. These methods include:

(i) mixture of the appropriate oxides and support;

(ii) precipitation of the metals from solution as carbonates, followed by drying, calcining and mixing the resulting oxides with the support;

(iii) precipitation of the metals as carbonates on the support, followed by drying and calcination;

(iv) impregnation of the support with appropriate metal carbonyl solutions and/or appropriate soluble metal salt solutions, followed by drying and calcination. Aqueous or organic solutions may be used as appropriate;

(v) combinations of the above methods.

Before using in synthesis gas conversion, the catalyst of the invention is normally reduced or activated. As is known by those skilled in the art, hydrogen, synthesis gas or another reductant may be used for this reduction step under conditions of elevated temperature and pressures of from atmospheric to the pressures used in the synthesis. Typical reduction temperatures are of the order of 250-300°C, with typical pressures of from atmospheric to 3.5 MPa.

The Fischer-Tropsch process can be performed over a wide range of temperatures, pressures and space velocities. The temperature used is dependent upon the required product. Large proportions of waxes are produced at low temperatures (150-230°C), distillates at moderate temperatures (200-260°C), and gasolines at high temperatures (230-300°C). Typical pressures used in the synthesis are of the order of from 0 to 5 MPa, usually from 1 to 3.5 MPa, whilst typical space velocities are at GHSV's of the order of from 10 to 10000 hr^{-1}, usually from 50 to 5000 hr^{-1}.

If distillate and gasoline are required then an acidic molecular sieve material may be used as support and the preferred process temperature lies in the range from 200 to 300°C.

The following examples illustrate the preparation of suitable supports, the preparation of catalysts according to the invention and the process of the invention.

Example 1: Preparation of Zeolite MA21 (ZSM-5)

A solution of 16.74 kg of Ludox[R] HS40 (40% silica) in 6 1 of water was stirred while adding a solution of 1000 g tetrapropylammonium bromide (Fluka) in 3 1 water.

A solution of 225 g sodium aluminate in 600 ml water was added to 900 g sodium hydroxide in 2 1 water.

The above two resulting solutions were mixed, well stirred and made up to 45 1 with water. The mixture was then charged to an autoclave and maintained at 100°C for 6 days, then 170°C for 2 days. The resulting product was filtered, washed and dried.

Example 2: Preparation of Zeolite MA4 (ZSM-11)

A mixture of 19.0 g of aluminium turnings and 137 g of sodium hydroxide in 2250 ml of water was stirred for 12 hours. Another 25 g of sodium hydroxide was then added with stirring.

Solutions of 1971 g of Cabosil[R] silica in 10,000 ml water and 1003.2 g of tetrabutylammonium bromide (Fluka) in 2000 ml of water were then added to the first solution and stirred until homogeneous. 140 ml of a 20% sodium hydroxide solution was added to raise the pH of the solution to 11.7, and the solution made up to 45 1 with water. The mixture was then charged to an autoclave and maintained at 100°C for 6 days and 170°C for two days. The resulting product was then filtered, washed and dried.

Example 3: Preparation of Zeolite MA26 (ZSM-12)

Two solutions were prepared. The first consisted of 59.88 g of a 40% tetraethylammonium hydroxide solution, 9300 g of Ludox[R] HS40 (40% silica) and 4550 g of water. The second consisted of 193 g of $Al(NO_3)_3.9H_2O$ in 4950 g of water. These two solutions were mixed, and 20 g of a seed ZSM-12 was added (preparation given in Example 4 below), and the solution made up to 45 l with water. The mixture was then sealed in an autoclave and maintained at 170°C for 6 days. The resulting product was then filtered, washed and dried.

Example 4: Preparation of seed ZSM-12

A solution of 199 g of 40% tetraethylammonium hydroxide and 186 g of Ludox^R HS40 (40% silica) in 91 g of water was mixed with a solution of 3.85 g $Al(NO_3)_3.9H_2O$ in 99 g of water, and placed in an autoclave maintained at 170°C for 6 days. The resulting product was filtered, washed and dried.

The zeolites of Examples 1 to 3 were examined by X-ray diffraction and were found to display the typical X-ray diffraction patterns of ZSM-5, ZSM-11 and ZSM-12, respectively.

Prior to use in the preparations of Examples 5 to 12, the zeolites of Examples 1-3 were calcined at 550°C, washed twice with 1M ammonium nitrate, dried, calcined at 550°C, washed a further two times with the ammonium nitrate solution, dried, calcined at 550°C, washed twice with 0.5M hydrochloric acid, dried and calcined at 550°C.

Examples 5 to 8: Preparation of Catalysts FT672, FT674, FT675 and FT678

The ZSM-5 zeolite MA21 was impregnated with appropriate amounts of cobalt carbonyl and scandium and/or thorium nitrates (where appropriate) dissolved in dimethyl ether, so as to make the desired catalyst formulations. The solvent was evaporated from the catalyst in a rotary evaporator, and the catalyst calcined at 500°C for approximately four hours. The resulting catalysts, identified by their "FT" code names, and their desired compositions in parts by weight were as follows:

5. FT672 75 Co:1000 MA21
6. FT674 75Co:5Sc:1000 MA21
7. FT675 75Co:5Th:1000 MA21
8. FT678 75Co:5Th:5Sc:1000 MA21

Examples 9 to 12: Preparation of Catalysts FT601, FT605, FT575 and FT604

The ZSM-11 zeolite MA4 and the ZSM-12 zeolite MA26, mixed with the appropriate amounts of scandium oxide (when necessary), were impregnated with the appropriate amounts of aqueous solutions of cobaltous nitrate. The impregnated zeolites were stirred under vacuum for 30 minutes, dried in a microwave oven, and then calcined at 500°C for approximately 4 hours. The resulting catalysts, identified by their "FT" code names, and their desired compositions in parts by weights were as follows:

9. FT601 75Co:1000 MA26
10. FT605 75Co:5Sc:1000 MA26
11. FT575 75Co:1000 MA4
12. FT604 75Co:5Sc:1000 MA4

Examples 13 to 18: Preparation of Catalysts FT662, FT663, FT666, FT667, FT668 and FT669

Commercially obtained mordenite (Norton Z-900H), kieselguhr (Ajax Labchem) and silica (Matrex 84160) were impregnated with appropriate amounts of aqueous solutions of cobaltous nitrate, and scandium nitrate (when necessary). The impregnated supports were stirred under vacuum for 30 minutes, dried in a microwave oven, and then calcined at 500°C for approximately 4 hours. The resulting catalysts, identified by their "FT" code names, and their desired compositions in parts by weight were as follows:

13. FT662 75Co:1000 mordenite
14. FT663 75Co:5Sc:1000 mordenite
15. FT666 75Co:1000 kieselguhr
16. FT667 75Co:5Sc:1000 kieselguhr

17. FT668 75Co:1000 silica
18. FT669 75Co:5Sc:1000 silica

The catalysts Example Nos. 5 to 18 were then pressed, ground and sieved, and size fractions between 1mm-2mm were charged to a microreactor for testing. Prior to use, the catalysts were reduced in a stream of hydrogen at atmospheric pressure at 250°C with a GHSV of 5000 hr^{-1} for 16 hours.

Each catalyst was used to convert a synthesis gas with a 2:1 hydrogen to carbon monoxide molar ratio. Reaction conditions were a temperature of 240°C, a pressure of 2 MPa and a GHSV of 1000 hr^{-1}.

The catalysts were run under these conditions for five days, and Table 1 summarises the average carbon monoxide conversion levels (averaged after 30 hours on line), the product selectivities obtained, and the higher hydrocarbon production rates for each. The carbon selectivities quoted represent the weight percentages of carbon from the carbon monoxide feed which have been converted into methane, carbon dioxide, and hydrocarbons containing more than two carbons. The C_2+ production represents the mg of carbon from the carbon monoxide feed which ends up as hydrocarbons with two or more carbon per g of catalyst per hour of running time (averaged over the whole run). It is assumed that of the carbon converted, that which is not converted to methane or carbon dioxide is converted to higher hydrocarbons, i.e. no carbon is deposited on the catalyst, etc.

TABLE 1: Carbon Monoxide Conversion, Product Selectivities and Higher Hydrocarbon Production for Various Cobalt Fischer-TropschCatalysts With and Without Scandium in Their Formulations (2:1 H_2:CO Synthesis Gas, 240°C, 2MPa, GHSV = 1000 hr^{-1}

Catalyst (Example No.)	Catalyst Compositions	% CO Conversion (Averaged after 30 hours on stream)	% C Selectivity (wt%)			C_2+ Production on mg/g/hr
			CH_4	CO_2	C_2+	
5.	75Co:1000 MA21 (ZSM-5)	50	10	0	90	157
6.	75Co:5SC:1000 MA21 (ZSM-5)	71	9	1	91	202
7.	75Co:5Th:1000 MA21 (ZSM-5)	70	8	1	91	190
8.	75Co:5Th:5Sc:1000 MA21 (ZSM-5)	72	8	1	91	213
9.	75Co:1000 MA26 (ZSM-12)	75	16	1	83	190
10.	75Co:5Sc:1000 MA26 (ZSM-12)	84	14	2	84	196
11.	75Co:1000 MA4 (ZSM-11)	32	22	0	77	86
12.	75Co:5Sc:1000 MA4 (ZSM-11)	58	18	1	81	141
13.	75Co:1000 mordenite	22	25	3	73	40

14.	75CO:5SC:1000 mordenite	52	40	1	58	76
15.	75Co:1000 kieselguhr	15	26	3	69	34
16.	75Co:5Sc:1000 kieselguhr	64	33	3	65	127
17.	75Co:1000 silica	19	13	5	82	68
18.	75Co:5Sc:1000 silica	68	35	5	60	153

These results clearly illustrate the invention, with the addition of scandium increasing the activity of the catalyst as measured by the % carbon monoxide conversion and the rate of C_2+ production over the corresponding unpromoted catalyst in all instances. It can also be seen that scandium addition has the same effect on a catalyst already promoted with thoria.

For the highly acidic ZSM-5, ZSM-11 and ZSM-12 zeolite supports, this increase in activity also results in an improvement in selectivity (except for the thoria-promoted case where the selectivity stays the same). These are the supports that would be used when gasoline or gasoline and distillate production is targeted. The operating temperature of 240°C as used in these examples is typical of a temperature which will be used if these types of products were to be made.

For the less acidic zeolite, mordenite, and the kieselguhr and silica supports, the more dramatic increase in activity has been accompanied by a deterioration in selectivity. However, because the increase in activity is so great there is still an overall increase in the higher hydrocarbon production rate, in spite of selectivity losses. Also, these supports would be used when distillate and wax production was targeted rather than gasoline. Thus a lower operating temperature than 240°C, as used in the examples, would be used. This would be possible in light of the very much enhanced activity of the scandium-promoted catalysts, and would much improve the selectivity to C_2+ hydrocarbons, with the possibility of even further improving the production rate of these higher hydrocarbons.

CLAIMS:

1. A Fischer-Tropsch catalyst comprising cobalt and scandium and a suitable support.

2. A Fischer-Tropsch catalyst according to claim 1 wherein the cobalt is present in an amount in a range from 1 to 50 weight percent based on the total weight of the catalyst.

3. A Fischer-Tropsch catalyst according to claim 1 or claim 2 wherein the scandium is present in an amount in a range from 0.01 to 25 weight percent of the total weight of the catalyst.

4. A Fischer-Tropsch catalyst according to claim 1 or claim 2 wherein the scandium is present in an amount in a range from 0.05 to 5 weight percent of the total weight of the catalyst.

5. A Fischer-Tropsch catalyst according to any one of the preceding claims wherein the support comprises from 10 to 98 weight percent of the total weight of the catalyst.

6. A Fischer-Tropsch catalyst according to any one of the preceding claims wherein the catalyst includes a promoter, the promoter comprising from .01 to 25 weight percent of the total weight of the catalyst.

7. A Fischer-Tropsch catalyst according to claim 6 wherein the promoter comprises from 0.05 to 5 weight percent of the total weight of the catalyst.

8. A Fischer-Tropsch catalyst according to claim 6 wherein the promoter is selected from the group consisting of thoria, magnesia and manganese.

9. A process for converting synthesis gas into hydrocarbons which process comprises contacting synthesis gas with a Fischer-Tropsch catalyst according to any one of the preceding claims.

10. A process according to claim 9 wherein the support is selected from the group consisting of kieselguhr, silica, alumina and silica-alumina and the synthesis gas is passed over the catalyst at a temperature in a range from 150°C to 260°C.

11. A process according to claim 9 wherein the support comprises an acidic molecular sieve material and the synthesis gas is passed over the catalyst at a temperature in a range from 200 to 300°C.

12. A process according to claim 11 wherein the acidic molecular sieve material is a zeolite.

13. A process according to claim 10 wherein the temperature lies in a range from 200 to 260°C.

14. A hydrocarbon product produced by the process of any one of claims 9 to 13.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU92/00457

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} C07C 1/04, B01J 29/24, 29/26, 29/34, 29/36, 23/76, 23/78, 23/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C07C 1/04, B01J 28/24, 29/26, 29/34, 29/36, 23/76, 23/78, 23/84

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
Derwent (WPAT and CAS): IPC as above and (Sc or Scandi: or rare earth:)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	DE,A, 3935112 (BASF AG) 25 April 1991 (25.04.91) See also US,A, 5132427, Column 2 lines 3-50.	1-8
X	WO,A, 90/07377 (DEN NORSKE STATS OLJESELSKAP A.S.) 12 July 1990 (12.07.90) See page 7 line 33 - page 8 line 21.	1-10,13-14
X	US,A, 4880763 (ERI et al) 14 November 1989 (14.11.89) See column 4 lines 10-38.	1-10,13-14

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 21 October 1992 (21.10.92)	Date of mailing of the international search report 6 NOV 1992 (06. 11. 92)
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer G Carter **G. CARTER** Telephone No. (06) 2832154

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	AU,B, 43793/85 (592057) (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ BV) 6 February 1986 (06.02.86) See page 7 line 28 - page 8 line 30.	1-10,13-14
A	AU,A, 89651/91 (TOSOH CORPORATION) 25 June 1992 (25.06.92) See claim 1.	11
A	AU,A, 36377/84 (COMPAGNIE FRANCAIS DE RAFFINAGE) 12 June 1986 (12.06.86) See claims 1-10.	1-14
A	US,A, 4338089 (SCHAPER et al) 6 July 1982 (06.07.82) See column 3 line 9 - column 6 line 58.	1-14
A	US,A, 3888792 (HUGHES) 10 June 1975 (10.06.75) See claim 1.	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family memb.

International application No.

PCT/AU92/00457

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	9007377	AU	47464/90	BR	8907286	CN	1045710
		DK	2047/90	EP	404902	FI	904240
		NO	903684	NZ	231998	US	5102851
		US	5116879				
DE	3935112	EP	424738	JP	3151351	US	5132427
US	4880763	AU	25446/88	BR	8807760	CN	1033755
		DK	5864/88	EP	313375	FI	902043
		JP	3502067	NO	884684	US	4801573
		WO	8903725	US	4857559	CA	2007143
AU	43793/85	ZA	8505317				
US	3888792	AU	30492/71	BE	768944	CA	976536
		DE	2131746	FR	2099890	GB	1350242
		JP	52003355	NL	7108637	ZA	7004407
AU	89651/91	CA	2057510	EP	491360	JP	4219149
		JP	4219148	JP	4219147	JP	4219143
AU	36377/84	EP	148048	FR	2556237	JP	60139342
		ZA	8409560				
US	4338089	AT	4033/80	AU	60995/80	BE	884471
		BR	8004880	CA	1140157	DE	3029547
		ES	493986	ES	8104162	FR	2463111
		GB	2055893	IN	153718	IT	1132312
		JP	56026822	NL	7906003	NZ	194559
		US	4338089	ZA	8004734		

END OF ANNEX